PHOTOGRAPHIC CHEMISTRY

Pierre Glafkidès

PHOTOGRAPHIC CHEMISTRY

VOLUME TWO

PIERRE GLAFKIDES
Chemical Engineer of the Institute of Chemistry of Paris

PHOTOGRAPHIC CHEMISTRY

VOLUME TWO

Translated from the French by
KEITH M. HORNSBY, F.R.P.S.

FOUNTAIN PRESS · LONDON

Volume Two
of the English language edition first published 1960

Translated into English in two volumes from the second French edition
with the authorization of the
Publications Photographiques et Cinematographiques Paul Montel, Paris

Printed in Great Britain by
J. W. Arrowsmith Ltd., Bristol

CONTENTS

(Figures in brackets refer to page numbers)

Part Three

COLOUR REPRODUCTION

Chapter XXXI

Chapter XXXII

Chapter XXXIII *Page*

Part Four

COLOUR SENSITIZATION

Chapter XXXV

Chapter XXXVI

Chapter XXXVII

Chapter XXXVIII *Page*

CARBOCYANINES 807

Chapter XXXIX

HEMICYANINES 838

Appendix

SUMMARY OF FUNDAMENTAL CHEMICAL LAWS

PART THREE

Colour Reproduction

Chapter XXVI

LIGHT SOURCES

449. Black body radiation

The term *black body* is applied to all bodies capable of absorbing all radiations which they receive, and transforming them integrally to heat. It can be represented very approximately by a thick layer of carbon black.

Conversely, when heated, the black body emits a *continuous light spectrum* whose characteristics depend on the *absolute temperature* T.(1) The absolute temperature is that measured from the absolute zero(2) at $-273°$C. That is $T = t + 273°$ where t is the centigrade temperature measured with reference to melting ice.

The energy at each wavelength emitted by the black source depends on the temperature to which the source is heated. The primary energy flux per cm^2 of the source, or *radiance* r is given by Planck's formula

$$r_{\lambda T} = \frac{C_1}{\lambda^5\left(\dfrac{C_2}{e^{\lambda T}}-1\right)}$$

where $C_1 = 3{\cdot}70 \times 10^{-5}$ erg/sec/cm^2 or $3{\cdot}70 \times 10^{-12}$ watt/cm^2 and C_2 is 14,320, λ being measured in μ. T is the absolute temperature and e is the Napierian logarithm base.

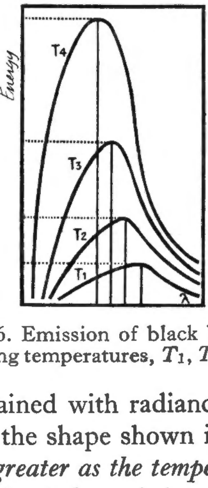


FIG. 56. Emission of black body at increasing temperatures, T_1, T_2, T_3, T_4

The *isothermal* curves obtained with radiance on the ordinates and wavelength on the abscissae have the shape shown in Fig. 56: they show that the *emitted energy becomes much greater as the temperature is raised.*

In addition, the *wavelength of the emission maximum is displaced towards the shorter wavelengths as the temperature increases,* the other wavelengths following in a similar way. This is a photographically important phenomenon whose practical result is that the more the temperature is raised the richer the radiation in violet rays, and conversely, at lower temperatures the more red radiated. The *colour of an incandescent* black body therefore varies with the temperature; as this increases, it passes from red to white.

The product of the maximum wavelength λ_m by the absolute temperature is a constant (Wien's law): $\lambda_m T = A = 2{,}884{,}000$, λ_m being measured in mμ.

It is therefore easy to calculate λ_m at various temperatures.

T	λ_m
1000°K	2884 mμ infra-red
2000°K	1442 mμ infra-red
3000°K	961 mμ infra-red
4000°K	721 mμ red
5000°K	577 mμ yellow
6000°K	360 mμ ultra-violet

If the ordinates at $\lambda = 590$ mμ are brought to the same value, the curves of Fig. 57 are obtained, which enables spectral composition of light emitted by a black body at various temperatures to be compared.

The *total emission* per cm^2 per second is measured by the area described by the isothermal curve, and is calculated by Stefan's formula $E = \sigma T^4$ where $\sigma = 5{\cdot}7 \times 10^{-12}$ watts/cm^2 or 1364×10^{-12} cal/cm^2/sec.

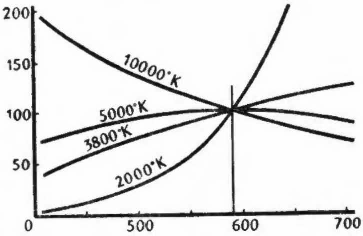


FIG. 57. Isotherms in the visible spectrum (ordinates brought together at 590 mμ).

449b. Actual sources

The emission of a black body represents an ideal case which is never realized with actual sources.

If B_T is the brightness[3] of an incandescent *non-black body*, and $\mathscr{B}_T$ the brightness of a black body at the same temperature T, then $B_T = \mathscr{B}_T \alpha$ where α is the *absorption coefficient* of the non-black body. As α is always < 1 the brightness B_T is lower than that of the black body. It follows that the spectral brightness of an actual source $b_{\lambda T}$ and the absorption factor $\alpha_{\lambda T}$ have at each individual wavelength, a constant relationship at the same temperature, equal to the spectral brightness $b_{\lambda T}{}^*$ of a black body (Kirchhoff's law):

$$b_{\lambda T}/\alpha_{\lambda T} = b_{\lambda T}{}^*.$$

$\alpha_{\lambda T}$ is also termed the *monochromatic emissive power*.

450. Colour temperatures

Within the visible spectrum, the emission of a non-black body is equal, or nearly so, to that of a black body at a temperature T_c. This is the *colour temperature* of the body and must not be confused with its *true temperature* T. The black-body at temperature T_c must have the same spectral distribution as the actual source at temperature T.

The colour temperatures of some light sources in increasing order are

Hefner amyl acetate lamp	1875°K
Vernon-Harcourt pentane lamp	1920°K
Paraffin candle	1925°K
English standard candle	1930°K
Melting platinum	2046°K
Paraffin lamp (flat wick)	2050°K
Carbon filament lamp	2080–2130°K
Acetylene lamp (cylindrical flame)	2360°K
Acetylene lamp 'Crescent Aero'	2450°K
Nernst lamp (rare earth oxides)	2400°K
Tungsten filament (vacuum) lamp	2400°K
Gas-filled tungsten lamps	
20·3 lumens/watt	2985°K
24·2 lumens/watt	3175°K
27·3 lumens/watt	3220°K
Electric arc	3780°K
H.I. arc (sun arc)	5500°K
Mean sunlight	5400°K
Sunlight before atmospheric absorption	6500°K
Clear north sky	about 22,000°K

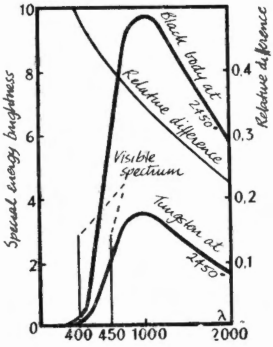


FIG. 58.

The curves in Fig. 58 show the differences existing between the spectral energy brightnesses of tungsten at 2450°K and a black-body at the same temperature. The relationship between the curves shows the variation of emissive power of tungsten with wavelength.

451. Measurement of colour temperature. Thermocolorimeters

The measurement of the colour temperature of the light emitted by a photographic source can be made rapidly using one of several available colour temperature meters.

In principle, the light is analysed by one or more photocells carrying colour filters. The produced current can be amplified, and the colour indicated by a spot on the screen of a cathode ray tube which is marked as a colour triangle. *Neale's apparatus*(4) is of this type and uses three photocells, each with a colour filter and placed in front of a rotating drum shutter.

Harding's apparatus(5) uses a comparison lamp. Others are based on the fact that the colour temperature is given approximately by the ratio of blue to red. One of these instruments, also due to *Harding*, has two selenium cells, carrying, respectively, a blue and a red filter, in opposition on a microammeter; the two cells are alternately covered. The apparatus of Dawson, Grant and Ott(6) passes the blue and red filters alternately in front of the cell. Before this, the light is received on an opal diffuser. We would also mention:

the *Rebikoff thermocolorimeter*;

the *three colour spectrometer* of the Photo Research Corp.,(7) a colour indicator in which the theoretical log relationships of the red/green on the abscissa and the blue/red on the ordinate are considered, the representative points (of a black body) are on a straight line;

the *EEL colour temperature meter* of Evans Electroselenium Ltd., which uses a microammeter, a selenium cell and red and blue filters.

452. Practical light sources

In current practice the light sources used are the incandescent lamp, the carbon arc, the mercury vapour lamp and the metal-filled flashbulb. They emit light of very different spectral composition.

Incandescnt lamp. The efficiency of an incandescent electric lamp, and therefore its emission spectrum, depends on the filament temperature, the filament type and the surrounding gaseous atmosphere.

The *efficiency* (lumens/watts) increases with temperature.

	Type of Lamp		*Colour temperature*	*Luminous efficiency*	*Brightness*
Vacuum:	Carbon filament	(50 W)	2130°K	2·5	55 c/cm^2
	Tantalum ,,	(50 W)	2260°K	4·9	53 c/cm^2
	Tungsten ,,	(10 W)	2390°K	7·7	128 c/cm^2
Gasfilled:	Tungsten filament	(75 W)	2705°K	11.8	560 c/cm^2
	,, ,,	(200 W)	2810°K	15·2	780 c/cm^2
	,, ,,	(500 W)	2880°K	17·5	1000 c/cm^2
	,, ,,	(2000 W)	3000°K	21·5	1350 c/cm^2
	,, ,,	(10,000 W)	3300°K	31	3050 c/cm^2
	Projector lamp	(1000 W)	3220°K	27·3	2660 c/cm^2

To obtain 10 lumens per watt, for example, the colour temperature of a vacuum lamp must be at least 2450°K; with an argon-filled lamp it must be increased to 2800°K whilst with nitrogen, a better conductor, 2900°K must be reached.

Incandescent lamps for studio lighting are obtainable in many different types working on 110–120 V.

200 W : 1·7 A
500 W : 4·4 A
1000 W : 8·7 A
2000 W : 17·4 A
5000 W : 43·5 A
10,000 W : 87 A

Incandescent lamps emit a *yellowish light rich in red rays*: consquently they benefit panchromatic emulsions. Their light becomes whiter as the colour temperature is raised. For colour photographs 3380°K lamps are used together with bluish glass filters.

For indoor pictures, and for some studio effects, *overrun* lamps are used which give a powerful light with a small bulb; Photoflood, Nitraphot, Photolita, Mazdastudia, etc. The colour temperature of these lamps is high, therefore the light is whiter, some of them are blue glass from 250–1000 W with a life of 3–10 hours. With a 500 W 100 hour lamp 11,000 lumens can be obtained. The life of the lamp does not exceed 2 hours if 16,000 lumens are reached by increasing the voltage.

Studio spot lamps have spherical or parabolic reflectors together with lenses. The mirror is silvered glass or chromium plated metal; the former reflects 82–95%, whilst the latter reflects only 62–70%. With steel, 59% is reflected.

453. Carbon arc

The carbon arc is used for studio lighting and for film projection. The light is normally centred on the crater of the positive carbon. Its colour temperature, which is at least 3780°K, depends on many factors: type of carbons, shape of crater, length of the arc, current density, gaseous atmosphere, etc. When the carbons contain metallic salts which change the colour of the light produced, this occurs primarily in the arc itself, between the two carbons.

The light of the arc is much whiter than that of an incandescent lamp because of the higher colour temperature; it is rich in violet rays. It does not affect photographic emulsions in the same way as ordinary electric light; as with daylight, the densities obtained with panchromatic emulsions are lower than when electric light is used.

The carbons containing mineral salts (of cerium or copper) give bluer light, approaching by this means daylight. In addition, at a pressure of 5 atm., a colour temperature of 4460°K can be reached, whilst at 25 atm. 6000°K can be achieved.

Studio spotlight arcs work at 38–150 A at 35–67 V. They are equipped with mirrors or combinations of mirrors and Fresnel lenses. The diameter of the carbons is from 6 to 16 mm depending on the intensity.

Stable arcs can have a power up to 200 kW if they are cooled by circulating water round the positive carbon.(8) The light is then emitted by a cloud of vapour from the positive crater.

High intensity arcs. Hundred amp arcs have an anode (+) of carbon whose core contains a high proportion of salts of rare earths, particularly cerium fluoride. The considerable heat produced when the carbons are separated, due to the small area of contact, gives rise to the volatilization of some carbon and the emission of electrons which produce the arc. A crater soon forms on the anode, where the cerium salt is volatilized.

The electrons ejected at the cathode strike the cerium atoms which pass into the excited state, with liberation of luminous energy. This is made up of the different radiations corresponding to the excitation state of the 58 electrons of the metal setting out again in their 14 orbits. The light produced in this way is white, but the action of the electrons from the negative pole on the gas molecules in the air produces a bluish light which is superimposed on the former.

454. Mercury vapour lamp

The light from the simple mercury vapour lamp is weak, with a discontinuous spectrum, very rich in ultra-violet and poor in red. It is therefore useless under conditions where emulsions sensitive to this colour are used.

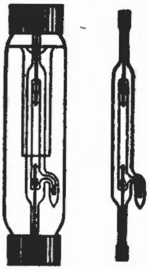


FIG. 59. High pressure water cooled mercury vapour lamp 1000 W, at a pressure of 75 atm., 840 V, 1·4 A, giving 65 lumens/watt. Luminosity 65,000 lumens. Brightness 30,000 candles/cm². Length of arc 25 mm. The illustration shows the luminous quartz tube, placed in its water jacket (E. B. Noël and R. E. Farnham in *J.S.M.P.T.E.*, 1938, **31**, 222).

The mercury vapour lamp is used for studio lighting (which avoids dazzling the subject); the rendering of colours however is abnormal. It is also used for printing chlorobromide and print-out papers. In industrial work it enables blue-prints of all types to be made quickly, and is also used for gelatin-dichromate and all photogravure methods. Dejardin and Jamin have made a tube 1·25 m in length filled with argon and mercury at 0·5 atm. Power 3 kW. Voltage 570, struck at 700 V.(9)

Cooled high-pressure mercury vapour lamps (Fig. 59) can provide high luminous intensities with brightness exceeding 50,000 candles/cm². Their emission spectrum improves with increased pressure (see Fig. 60). The low-power Philips *Philora* type need not be cooled.

455. Fluorescent lamps

The light given by these lamps comes from a fluorescent layer covering the interior of the glass tube, which is excited by the ultra-violet radiation of a mercury arc.

The composition of the light depends on the fluorescent substances used: blue with *magnesium tungstate*; green with *zinc silicate* (willemite); orange with *cadmium borate*.

A mixture of these substances gives a white light with several strong bands.

Very brilliant fluorescent layers are obtained with magnesium germanate or fluorogermanate whose emission maximum is at 635 and 666 mμ.⁽¹⁰⁾

The efficiency of fluorescent lamps is 30 to 40 lumens per watt and their brightness is as low as 0·3 candles per cm^2. They give off no heat. The Philips HP2 tubes of 80 and 125 W have an internal coating of magnesium arsenite in an atmosphere of carbon dioxide. An internal silica tube is filled with mercury vapour under pressure with a little argon. They operate on 220 V with a brightness of 5–8 candles per cm^2.⁽¹¹⁾

456. Metallic arc lamps

A stable and compact mercury lamp can be obtained by striking an arc between two tungsten or tantalum electrodes in a quartz bulb containing an inert gas under low pressure, to simplify striking, and high-pressure mercury. The inert gas can be a mixture of argon and neon whilst the mercury can be replaced advantageously with cadmium amalgam. The length of the arc is from 1·5 to 4 mm, according to the power, and has a brightness in the order

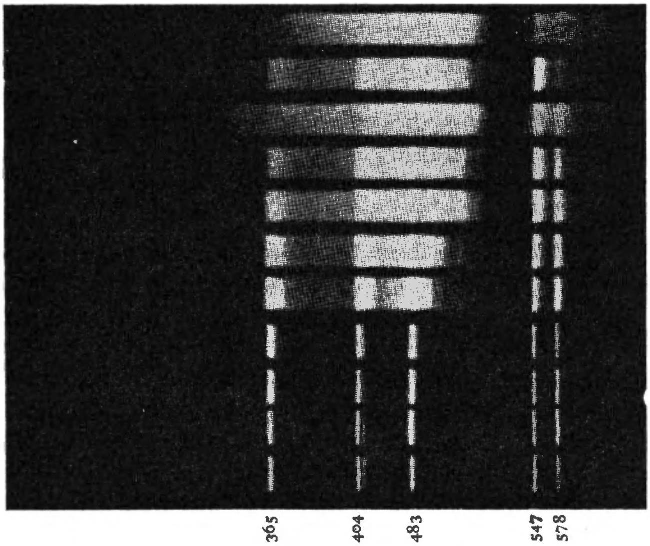


FIG. 60. Variations in the spectrum of a mercury vapour lamp as a function of the pressure. At low pressures the spectrum is discontinuous; it is composed of several lines, the most intense of which are shown in the spectrograms at the bottom of the figure. Starting at 25 atm. broad bands begin to appear, still dominated by the characteristic lines, but the ultra violet emission is suppressed more and more to the advantage of the green and red. At 250 atm. an almost continuous spectrum is formed. There is still a strong depression in the blue green around 500 mμ (E. B. Noël and R. E. Farnham, *J.S.M.P.T.E.*, 1938, 221).

of 18,000 candles/cm^2 (or stilbs). The working pressure inside the lamp is 10–40 atm. Power 250–10,000 W. Working voltage: 60–85 V. Current: 7–150 A or 450–17,000 W. The emission has a continuous background superimposed on the broadened bands of mercury and cadmium. These lamps can be used for projection, for printing (mercury only), and in the higher powers, for photography in black and white or colour. They have the advantage that they do not heat the subject as much as carbon arcs. For studio lighting see Bourne and Beeson.(12) Another type described by Cumming uses an arc in a xenon-filled tube.(13)

457. Compact source arcs

This new type of arc lamp is principally represented by the zirconium electrode lamp, being a bulb filled with inert gas (argon) which contains two metal electrodes. The anode is a flat ring in the centre of which is the cathode comprising a tantalum tube filled with zirconium oxide. Light at 3000°K is emitted from the thin film of zirconium which forms on the surface of the cathode when the arc is running; it has a line spectrum on a continuous background. Power: 2–1500 W. Corresponding arc lengths: 0·075–9 mm; Brightness: 10,000 stilbs. Lights almost instantaneously. Life: several hundred hours. The compact source arc is suitable for projection, enlarging and microscopy. It has the disadvantage of needing a high-tension transformer and vacuum rectifier for starting, and a low-tension transformer with a dry rectifier. One type works on alternating current, and avoids the use of a high-tension supply, by including a filament heater to produce the ionization necessary for striking. The current commercial types range from 2 to 1000 W and work on 37–17 V; they have brightnesses of 9600–5000 candles/cm^2. Life: 175–2000 hours. With the Telcoarc(14) which works in the open air, a brightness of 13,000 candles/cm^2 is achieved and 20,000 lumens at 55 V, 18 A. The electrodes are filled with a powder of zircon and nickel and are used at the rate of 1 mm per hour. Colour temperature 3600°K.

458. Discharge lamps

These lamps are composed of a quartz tube, straight or in spiral form, filled with low-pressure xenon, working from a 0·1–125 μF condenser charged at 2 kV. Striking, which necessitates ionization of the gas, is brought about by an impulse of 10 kV. The xenon can be replaced by argon, krypton or hydrogen. For high frequencies, a mixture of argon and hydrogen is used: the tube must then be cooled. The useful life of the tube is 10,000–100,000 flashes.

The spectrum of a discharge lamp is similar to that of a spark in the gas. It has a large number of broadened lines. The maximum emission is in the blue at about 475 mμ, the colour temperature exceeds 6500°K which represents the combination of sun and sky. It is, however, rich in infra-red from 720 to 900 mμ. For colour photography the excess blue is normally suppressed with a CC 13 filter. The total light by integration of successive flashes is measured by a cell connected to a condenser whose voltage can be found.

Discharge lamps are used for studio lighting (10 kW for tube 2 cm diam and 20 cm long) and for aerial photography in place of parachute flares. For the latter purpose the lamp uses 57 kW at 4 kV with 7200 μF. It provides 2,300,000 lumens per sec.; for 8 kW the complete installation weighs 1700 kg. (H. E. Edgerton: *P.S.A. Jl.*, 1947, 439.)

Exposures of 5 μ sec. can be obtained by coupling the discharge lamp to a stroboscopic apparatus (cf. H. E. Edgerton: *J.O.S.A.*, 1946, 390 and D. A. Senior: *Jl. Sci. Inst.*, April 1941, 81). Applications: photography of rapid movement(15) and photomicrography.

For ordinary photography, the microsecond is useless. By reducing the E.M.F. to less than 1000 V and increasing the discharge current the exposure can be increased to a millisecond, when considerable lightening can be effected by avoiding accumulators, rectifier, transformer and vibrator. The energy is then supplied by dry batteries of 450–900 V. Marsal and Potter have also used a 225 V battery.(16) D. Rebikoff used electronic flash for underwater photography.(17) The loss due to absorption by water is 86% at a depth of 10 m.

For motion picture projection, M. Laporte(18) investigated large section lamps whose electrodes formed part of the outer casing to permit cooling. The 500 W lamp made gave two flashes per frame, i.e. 48 flashes per second. The shutter could therefore be dispensed with.

459. Flashbulbs

Of aluminium foil or wire burning in an atmosphere of pure oxygen: the colour temperature of these lamps varies between 3400 and 4000°K comparable with that of Photoflood overrun lamps. The 'Kodak blue varnish' raises the T_c to 6500°K. Other types have a $T_c = 5000$°K.

The flash, of 30–60 milliseconds' duration, is due mainly to incandescent aluminium vapour (F. G. Brockman) and not the incandescence of aluminium oxide. The spectrum of the emitted light shows the metal lines broadened by the pressure. The aluminium oxide vapour provides 3% of the blue and green radiation. To this must be added the spectrum of the iron in the starter and those of potassium and sodium whilst the continuous background is due to the possible combinations of electrons and the different ions or neutral molecules. Some types of lamp have a sharply peaked combustion curve, others are flattened. Voltage: 3·5 V. Current: 0·4 A.

Flashpowders. Widely used at one time, they have now been practically abandoned in favour of more convenient and less hazardous lighting systems. The mixtures giving most light contain magnesium and sodium nitrate or ammonium perchlorate, or aluminium and strontium nitrate. To obtain a white light, sulphur or an organic substance such as starch must be added. P. Tavernier described a hundred mixtures in *Memorial des Poudres*, 1949, 429.

460. Daylight

The spectral composition of daylight varies constantly with the distance between earth and sun, and its position with regard to our atmosphere; that is, depending on the season, the day, the hour, the latitude and the elevation.

The atmospheric layer absorbs a large part of the sun's rays, the minimum absorption being at midday when the rays are almost perpendicular.

The spectrum of daylight, after absorption, has an energy maximum in the yellow at about 585 mμ (curve a, Fig. 61). Before absorption, the maximum is at about 490 mμ in the blue (curve b). Strong absorption bands are also present in the infra-red (Fig. 62). Daylight becomes even more red away from midday, when the elevation is lower, and the latitude further from the equator. The presence of clouds alters the distribution, increasing the red content.

The average colour temperature of sunlight at midday in June is 6500°K and 5400°K towards the end of the day in winter.⁽¹⁹⁾ Latitude differences give the following variations: 5200°K at 13°, 5400°K at 23°, 5800°K at 42°, 6200°K at 62°. The blue colour of the sky is due to the atmospheric diffusion of the blue-violet rays, which are the most refrangible in the spectrum (this effect is common to all turbid media which the red rays pass through most easily).

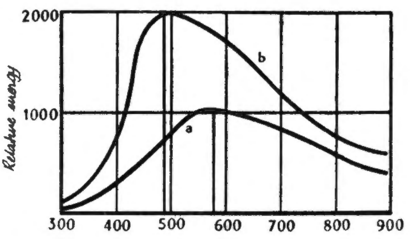


FIG. 61

(a) After atmospheric absorption.
(b) Before absorption.

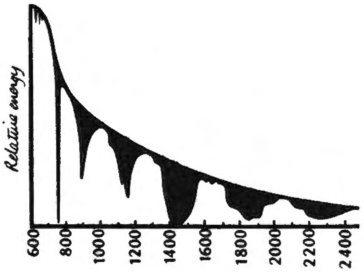


FIG. 62. Natural light spectrum in the infra-red after atmospheric absorption.

Moonlight. The reflection factor of the moon is twice as great for the red as for the violet; this explains the lower colour temperature: 4125°K. Following Purkinje's phenomenon, the low intensity moonlight appears bluer than it is. Moonlight is extremely variable; at full moon it is 150,000 times weaker than sunlight. Exposures must be doubled when the moon is at 45° elevation, and multiplied by ten, 7 days before and after full moon.⁽²⁰⁾

LIGHT FILTERS

461. Light standards

Two white lights of different spectral composition, but which produce the same visual sensation, will affect the photographic emulsion differently. That is, the *luminous intensity* which depends on the visual sensation, and therefore on the spectral composition, must not be confused with the *energy intensity*. It is possible to go from one to the other using *coefficients of visibility*.

The unit of luminous intensity is the *new candle* represented by an incandescent filament at 2360°K. The new candle is of the same order as the *decimal candle* which is one-twentieth of the *Violle standard*, a source of one square cm of the surface of a bath of platinum at its solidifying temperature. An ordinary candle is slightly greater than a new candle.

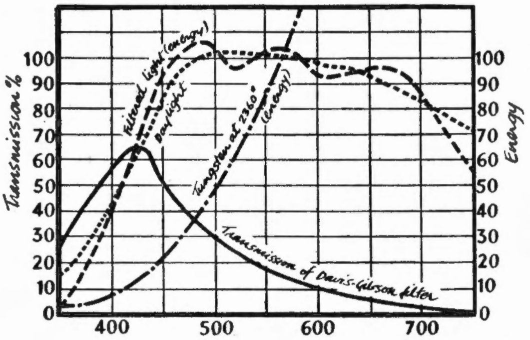


FIG. 63. Transmission of Davis-Gibson filter.

To obtain a source with the same spectral composition as *daylight*, a 2360°K lamp is used in conjunction with a filter consisting of two cells with parallel faces, preferably in crown or borosilicate glass, giving a layer 1 cm thick and containing the two following solutions[20b] (Fig. 63). The resulting light is at 5235°K.

A.	Copper sulphate, $5H_2O$	3·707 g
	Mannitol	3·707 g
	Pyridine	30 cc
	Distilled water to	1000 cc
B.	Cobalt ammonium sulphate, $CoSO_4 . (NH_4)_2SO_4 . 6H_2O$	26·827 g
	Copper sulphate, $5H_2O$	27·180 g
	Sulphuric acid, S.G. 1·835	10 cc
	Distilled water to	1000 cc

462. Compensating filters

Wratten filters[21] specially prepared for this are very convenient.

Bluish: No. 78 *increases* C.T. from 2360°K to 5500°K
No. 78A *increases* C.T. from 2360°K to 4400°K
No. 78B *increases* C.T. from 2360°K to 3200°K
No. 78C *increases* C.T. from 2360°K to 2800°K.

For studio lighting, the colour temperature of an incandescent lamp can be increased from 3350°K to 6300°K and 7100°K with Macbeth Whiterlite filters, in Corning blue glass 5900 No. 165 and 145.

Yellowish: No. 86 *reduces* the C.T. from 5500°K to 2360°K
No. 86A *reduces* the C.T. from 3200°K to 2360°K
No. 86B *reduces* the C.T. from 2700°K to 2360°K
No. 86C *reduces* the C.T. from 2500°K to 2360°K.

For precise measurements all of these filters should first be standardized.

We would recall that light intensity is measured in *lumens*. The lumen is the luminous flux on a surface 1 m^2 cut from a sphere 1 m radius at whose centre is a new candle. The complete sphere receives 4π lumens. As the distance is increased, the illumination decreases as the square of the distance.

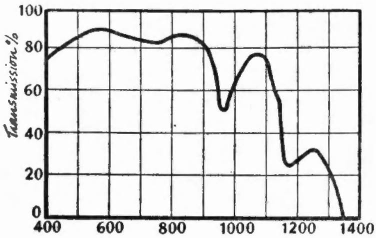


FIG. 64. Transmission of water
(Thickness 1 cm).

The intensity of illumination I, that is, the flux per square metre, is measured in lux or candle metres. The mean intensity of the sun at midday is about 100,000 lux.

463. Liquid filters

The absorption of light by *water* becomes appreciable when the thickness reaches 1 cm. This happens on one hand in the violet and ultra-violet and on the other in the infra-red (Fig. 64); at 77°C an absorption band at about 740 mμ appears.

A large number of inorganic compounds can be used in aqueous solution to absorb certain radiations: *potassium dichromate*, *copper sulphate*, *nickel sulphate*, *cupric chloride*, etc. Thus 60 g.p.L ammoniacal copper sulphate transmits the blue between 435 and 480 mμ, and 50 g.p.L potassium chromate transmits the yellow from 530 mμ.

The following table by J. Bowen enables restricted spectral regions to be isolated from the ultra-violet to 580 mμ. The wavelengths shown are those emitted by a mercury vapour lamp.

Liquid filters are also prepared by dissolving *dyes* in alcohol or water.

464. Glass filters

The glass is 'dyed' in the mass by adding various substances:

Yellow glasses: cadmium sulphide, silver oxide, cerium oxide.
Orange glasses: selenium together with cadmium sulphide, molybdenum oxide.

λ Mercury lines (mμ)	First Filter	Second Filter		
248 254	Nickel sulphate 145 g $NiSO_4 . 7H_2O$ Cobalt sulphate 41·5 Water 1 L th = 10 cm	Chlorine gas at 1 atm. th = 3 cm	Iodine 0·108 Pot. Iodide 0·155 Water 1 litre	th = 1 cm (1)
265 270			Mercuric chloride 45 g Water 1 litre	th = 1 cm (2)
275 280·5				
289·5 303		Copper sulphate 15g Water 1 L		th = 1 cm
313·5		Pot. acid phthalate 5 g Water 1 L	th = 1 cm	
334		Uric acid satd. soln. th = 1 cm		
366	Copper sulphate 4·4 $CuSO_4 . 5H_2O$ Water 1 L Ammonia 150 cc th = 10 cm	Black glass 'Chance UV' th. 2–3 cm		
405		Iodine 7·5 g + Carbon tetrachloride CCl_4 1 L Quinine HCl 10 g + Water 1 L		th = 1 cm +th = 2 cm
436		Sodium nitrite 75 g +Water 100 cc		th = 1 cm (2)
546	Copper sulphate 13 g $CuSO_4 . 5H_2O$ Pot. dichromate 0·44 H_2SO_4 conc. 50 cc Water 1 L th = 10 cm	Corning glass 512		th = 5 cm
577 579		Corning glass 344		th = 3·4 cm

(1) renew frequently (2) renew from time to time

Red glasses:	selenium, cuprous oxide.
Pink glasses:	Cassius' purple, manganese and titanium oxides.
Violet glasses:	manganese oxide, nickel oxide.
Blue glasses:	cobalt oxide, cupric oxide, tungsten oxide.
Green glasses:	cupric oxide (lead glass), ferrosoferric oxide, chromium oxide.

Figures 65–67 show the transmission curves of some coloured glasses—green, blue, red and yellow.

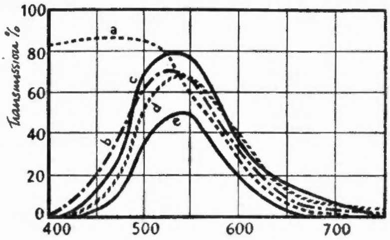


FIG. 65. Transmission of green glasses.

(a) Corning blue green 428 (3 mm);
(b) Corning sextant green (1 mm);
(c) Corning yellow green or Cuo (3·5 mm);
(d) Jena 4930 (1 mm);
(e) Corning sextant green (1·65 mm).

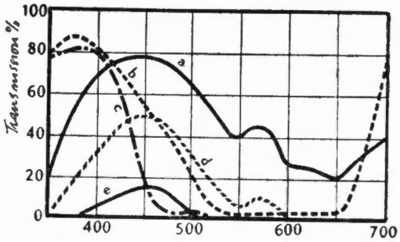


FIG. 66. Transmission of blue glasses.

(a) Jena 8780 (0·3 mm);
(b) Corning 503 (2 mm);
(c) Corning signal blue 556 (5 mm);
(d) Jena 8780 (1 mm);
(e) Jena 8780 (3 mm).

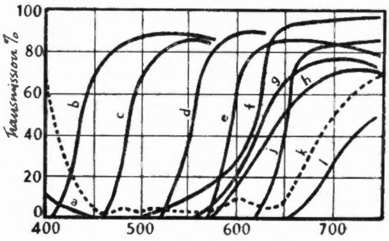


FIG. 67. Transmission of yellow and red glasses.

(a) Corning deep red 584;
(b) Corning Noviol A;
(c) Corning Noviol C 338;
(d) Corning 248 Y4;
(e) Corning 246 RM;
(f) Jena 4512 (1 mm);
(g) Corning G24 (6 mm);
(h) Jena 2745 (1 mm);
(j) Corning G 20 (7 mm);
(k) Corning deep purple-red (1 mm);
(l) Corning deep red 584 (1 mm).

465. Coloured gelatin filters

When the highest precision is not required, dyed gelatin filters can easily be obtained by bathing fixed and washed photographic plates, for a few moments, in the dye solution. The dyed plates are then rinsed quickly in water for a few seconds, drained and dried.

To prepare uniform transparent filters the solution of dye is added to 12% gelatin which is then filtered. The dyed gelatin is then coated on to lukewarm perfect plate glass whose surface has been previously polished with a wad of cotton dipped in a dilute solution of a vegetable oil in benzene or other solvent. After the gelatin has set, it is dried in a dust-free place. The dry gelatin film is carefully removed from its support, cut between two sheets of paper and cemented between two glasses, optically worked if possible, using a solution of Canada balsam in xylene. The amount of gelatin solution used is 50–100 cc per sq. ft.(22) The amount of dye used is 150–300 mg per sq. ft., or less. The most widely used are *tartrazine*, *rose Bengal*, *rhodamine S*, *carmine blue* and *naphthol green*, but there are thousands of others having more adequate transmission. It is easy to use them together, but mixing acid and basic dyes must be avoided. The transmission spectrum must be examined after the filter has been prepared.

Gelatin filters have the disadvantage of needing two glasses which can influence the definition of the image. These glasses are cemented with Canada Balsam, or better, with Piccolyte, a terpene polymer made by the Pennsylvania Industrial Chem. Corp.(23) The resin is dissolved in xylene and does not become yellow with age.

465b. Cellulose ester filters

Filters can also be made from collodion and other plastic materials. Cellulose acetate filters have been made by Zelster and Kriukova.(24) The dyes are first converted to their leuco derivatives. In basic solution, the latter readily penetrate cellulose acetate films and become insoluble again by oxidation. Acetate films can be dyed also, on one or two faces, by means of a roller dipping in an organic solution of dye. Printing filters can thus be made.(24b)

466. Correction filters absorbing violet and ultra-violet

Ordinary glass itself absorbs all the ultra-violet below 300 mμ (Fig. 68).(25) Gelatin absorbs a further 30% of the radiations between 300 and 350 mμ. Cellulose films also have an appreciable absorption (Fig. 69).

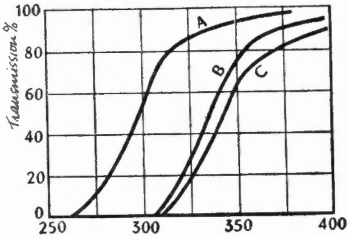


FIG. 68. Transmission of white glasses.

(A) New Helioglass;
(B) New window glass;
(C) Window glass exposed to the sun.

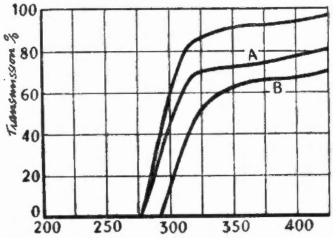


FIG. 69. Transmission of cellulose ester films.

(A) Cellulose acetate; (B) Celluloid.

β-naphtholdisulphonic acid absorbs in the ultra-violet up to 360 mμ. *Aesculine* absorbs completely to 380 mμ, 65% up to 400 mμ and 25% of the violet. *β-methylaesculetine* and *β-methylumbelliferone* are preferred.

Among the yellow dyes, *tartrazine*, *thioflavine T*, *acridine yellow*, *quinoline yellow* and *kiton yellow S* only partially absorb in the ultra-violet.

Auramine O has an absorption band from 350 to 380 mμ. *Rhoduline yellow* 6*G* (Bayer) absorbs between 380 and 400 mμ. The absorption of *flavinduline O* is between 310 and 330 mμ, *primuline* between 320 and 360 mμ and *salicine yellow* between 330 and 380 mμ.

The following dyes absorb the near ultra-violet more strongly:(26) *flavazine LL* from 325 to 400 mμ with slight transmission at 390; *baumwold gelb GX*(*B*) strong absorption from 350 to 410 mμ; *beizen gelb GT*(*B*) maximum absorption at 375 mμ with transmission in the violet; *echt gelb* (*B*) absorption maximum at 390 mμ extending to 420 mμ.

The absorption maxima are in the violet with the following:

thioflavine T, 408 mμ;
pyramine yellow G(*B*), 408 mμ
aurophenine O, 408 mμ
metanil yellow, 410 mμ
brilliant yellow S(*B*), 411 mμ
methylene yellow H, 412 mμ
acridine yellow T (*L*), 417 mμ
curcumine S, 420 mμ
oxyphenine A, 423 mμ
kiton yellow R, 424 mμ
xylene yellow 3*G*(*S*), 425 mμ
mikado yellow (*By*), 428 mμ
auramine O, 433 mμ
naphthol yellow, 435 mμ
chrysoidine, 434 mμ
tartrazine O, 432 mμ

We would also mention *sodium glucose-phenylhydrazone-p-carboxylate* which is a good ultra-violet absorber.

New ultra-violet-absorbing substances have been prepared from derivatives of *indole* and *pyrrole*, by reacting with a compound having one of the following groups:(27)

Barbituric and thiobarbituric acids: rhodanines; benzoylacetonitrile; pyruvic acid; maleic acid, etc., all of which contain a reactive methylene group and a neighbouring CO or CS.

Good ultra-violet filters can also be obtained with *colourless cyanines*(28) having their absorption bands in this region (oxacyanines), or with *acetophenones* such as *benzalacetophenone* (2 g.p.L), 3-*sulphoanisalacetophenone* (3 g.p.L) *cinnamalacetophenone*, etc. The acetophenones are used in slightly alkaline gelatin solutions.

The light yellow compensating filters are *correction filters*, for their absorption in the blue and violet increases progressively. Deep yellow and orange play the part of *contrast filters*: they absorb most of the violet and blue. *Tartrazine* and *metanil yellow* for example have less sharp absorptions than *naphthol yellow*, which itself is less acute than *picric acid* or *quinoline yellow*.

467. Green correction filters

Green filters increase the relative strength of the green light received by the emulsion, which is often less sensitive to this colour. Green foliage is rendered lighter and clouds appear darker. The general effect is of more contrast.

For the preparation of green correction filters a green dye can be used with a yellow ultraviolet absorber. Among the green dyes are: ***naphthol green*** (maximum transmission at 558 mμ) and ***lumière green SF—yellowish*** (transmission maximum at 490 mμ, minima at 425 and 625 mμ).

468. Interference filters

The interference technique offers an excellent method of obtaining filters with very sharp absorption bands, practically monochromatic.

Interference filters comprise very thin layers of alternate high and low refractive index materials deposited on glass (for example sodium fluoride and zinc sulphide). The films are deposited by vacuum evaporation.(29) The transmission depends on the refractive indices, the layer thickness and the number of layers. Thus two layers, with refractive index 2·10 and thickness $\lambda/2$ separated by a layer of index 1·25 and thickness $\lambda/4$ deposited on glass with an average index of 1·54 give a filter which transmits totally at 440 mμ and reflects 80% of light at the neighbouring wavelength of 434 mμ.

Interference filters are *dichroic* systems: the part of the light which is not transmitted is reflected. They can therefore be used as partial reflectors for colour separation. Used in the R.C.A. colour television system,(30) where two perpendicularly mounted filters transmit the green and reflect laterally, one the red and the other the blue; the green is reflected in phase by each reflector whilst the red and the blue are out of phase. With 4–11 layers of ZnS or TiO_2 (high index) and MgF_2 (low index) an element is obtained which transmits only the ultra-violet and the infra-red but reflects the whole visible spectrum.(31) Another infra-red eliminating system consists of superimposed alternate layers of germanium and of magnesium fluoride and zinc sulphide.

Among commercial interference filters, the best known are the Swiss G.A.B. filters (Balzers) with which the required wavelength can be obtained to almost ± 2 mμ.

A second class of interference filters is made from Lippman grainless plates exposed in contact with a layer of mercury (para. 493). After developing, fixing and intensifying with mercury, strata of transparent layers are formed in the gelatin which reflect the same light which was used for the exposure.(32)

468b. Other filters

Lyot polarization filters: birefringent layers of increasing thickness are placed between film polarizers. *Dichroic cellopolar filters:* obtained by stretching cellulose impregnated with grey dye;(33) they polarize only a fraction of the incident light varying with the wavelength.

Electro-optical cells using monoammonium orthophosphate:(34) a thin layer of this crystal placed between two transparent electrodes (across which a potential difference of several thousand volts is applied) is interposed between two pola screens. The spectral transmission depends both on the thickness of the layer and the applied potential.

Dispersion monochromatic filters: invented by Christiansen in 1884, consists of powdered glass (0·1–2 mm) immersed in an organic liquid. The system glass-liquid only transmits the wavelength corresponding to the intersection of the refractive spectral curves of the two elements. A study of these filters has been made by Korolev and Klementeva:(34b) with two cells, they obtained a 22 mμ band.

469. Filters transmitting ultra-violet

Two 'Schott Uviol blue' filters 2 mm thick are each covered with a layer of gelatin coloured with *p-nitrosodimethylaniline.* Transmission 278–383 mμ (see also chapter XXII on 'Ultra-violet Photography'). Black nickel glass transmits ultra-violet. In general the glasses with low refractive index and high dispersion are very transparent to ultra-violet. They are made by fusing the fluorides of glucinium, aluminium and rare earths.(35)

470. Filters transmitting infra-red

Yellow, red and violet *glasses* generally transmit infra-red. Blue and green glasses often show absorption bands between 700 and 1500 mμ. Infra-red filters are made of deep red glass whose density is such that objects can only just be seen in sunlight, and the filament of a 100 W lamp can hardly be seen. Such a glass is Schott R.G.S. For a filter which is more opaque to visible light, a red filter and an infra-red transmitting blue filter are combined. The same result is achieved with black glasses (see para. 464).

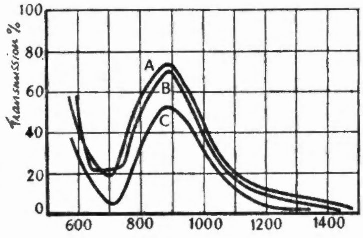


FIG. 70. Transmission of nickel salt solutions.
(A) Sulphate; (B) Nitrate; (C) Acetate.

For the most part, *dyestuffs* transmit infra-red; they give a simple method of preparing filters; for example, a mixture of *methyl violet, malachite green* and *chrysoidine* or two combined layers dyed respectively with *malachite green* and *Congo red. Chlorophyll* can also be used (2 mg per cm^2).(36)

Two transmission bands, in the green and infra-red (maximum at 900 mμ) are obtained with a solution of *nickel acetate* or *sulphate.* Useful concentration: layer 1 cm thick of 100 g.p.L solution (Fig. 70).

471. Infra-red absorbing filters

Safelights for developing infra-red sensitive materials are made in several ways:

(*a*) Liquid screen, made from a saturated solution of *copper sulphate* containing 10% of 6% *potassium dichromate*; thickness 7 cm for a 25 W lamp. A good green light is obtained. The copper sulphate can be replaced by cupric chloride.

(*b*) Brown neodymium glass with 2% cerium oxide, 2% ferric oxide and 0·1% nickel oxide.(37)

(*c*) For projectors, Chance ON19 colourless glass transmits only 8·5% of the infra-red.

(*d*) Calflex G.A.B. interference filter which passes all the visible light and reflects the infra-red.

(*e*) Combination of a yellow filter with a very dense photographic plate toned with *ferro cyanide*.

(*f*) *Fluorescent lamps* in which the short wavelength radiations excite uranium or praseodymium fluorescent glass.

(*g*) *Sodium lamps*, whose emission is practically limited to the D line 589 $m\mu$. They are used with a colour filter. With a mercury vapour lamp whose principal lines are at 516, 517. 518 $m\mu$, the filter consists of 1 mm of Schott OG1 glass and 3 cm of a 6% copper sulphate solution. This filter absorbs the 1014 $m\mu$ mercury line and also the 818 and 819 $m\mu$ lines of sodium. The *thallium vapour* lamp gives similar results. In this case two glasses 1 mm thick are used—Schott OG1 and Schott BG7.

472. Neutral grey filters

Perfectly neutral filters are obtained by evaporating the alloy *inconel* on a glass plate.(38) Inconel contains 80% Ni, 3% Cr and 6% Fe. Rhodium also gives good results;(39) the metal to be evaporated is carried on a tungsten filament. A pressure of 10^{-4} mm Hg is used.(40)

Almost neutral filters can be prepared with gelatin and graphite of average diameter 5 μ, or gelatin containing developed silver 1·5 μ diameter.

SPECTROSENSITOMETRIC MEASUREMENTS

473. Spectrosensitometry

Consists of exposing a photographic layer to a known spectrum then measuring the variations in the resulting deposit, to determine the relative sensitivity to different radiations.

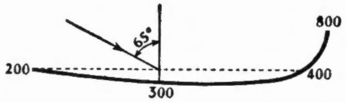


FIG. 71. Dispersion of the spectrum with a prism.

The colour sensitivity of an emulsion can be measured in two ways:

(*a*) Exposure in a spectograph.

(*b*) Exposure under colour filters.

In each case, the choice of the light source is of great importance.

Spectrographs. The sensitive layer being tested is exposed in a prism, or preferably, a grating spectrograph, the latter having the advantage of providing a regularly dispersed spectrum.

We know that the dispersion of two neighbouring radiations by a prism depends on their difference of refractivity. Now the variations in refractivity are a function, as a first approximation, of $1/\lambda^3$; this results in two neighbouring wavelengths being dispersed unequally, the greatest dispersion being in the short wavelengths—that is, in the violet and ultra-violet. The latter in particular occupies a scale 5 times as great as that of the visible region. The prism spectrograph gives a spectrum having the form of a 'caustic' curve shown in Fig. 71.

A glass prism is used in a spectrograph for the examination of the visible and infra-red spectrum, whilst a quartz or fluorite prism is used for ultra-violet work. The light emitted by a source is condensed on to a narrow slit, and the light is collimated with a positive lens; it is then received by a prism which disperses it. The dispersed beam is finally focused on the photographic plate with a further lens (Fig. 72).

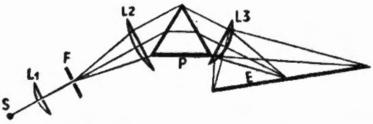


FIG. 72. Principle of the prism spectograph.

The spectrograph is then standardized with reference to the lines of certain metals, and hydrogen:

Element	*Colour*	*Wavelength in mμ*
Lithium	Red	670·7
Hydrogen	Red	656
Sodium	Yellow-orange	589·2
Mercury	Yellow	579
Mercury	Yellow-green	576
Mercury	Green	546
Mercury	Violet	435·8
Mercury	Violet	404·6

Grating spectrographs. The gratings are obtained by engraving, on a mirror or a transparent material, a large number of equidistant and very fine parallel lines (Fig. 73); they give, by diffraction, regularly dispersed spectra.

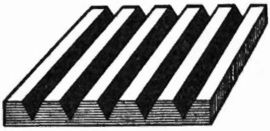


FIG. 73. Diffraction grating on a mirror.

The grating spectrographs have either a concave mirror forming the grating (Fig. 74) or a transparent grating, generally moulded (Fig. 75). The grating has 500–600 lines per cm; this gives a dispersion of 5 mμ per millimetre. Only the first order spectrum is recorded by the photographic layer.

For spectrosensitometry of colour images, see para. 527.

474. Operating methods

First method. A series of exposures is made with decreasing time by uncovering successively different parts of the same plate; this results in a series of graded spectra, the last showing the maximum colour sensitivity. By superimposing a mercury spectrum it becomes easy to establish the wavelengths. This method is most suitable for prism spectrographs whose dispersion is not uniform. Instead of using a single plate, several small plates can be used and subsequently assembled.

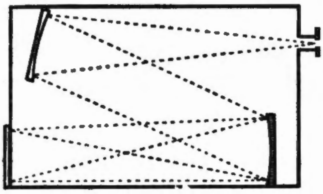


FIG. 74. Spectrograph with mirror grating.

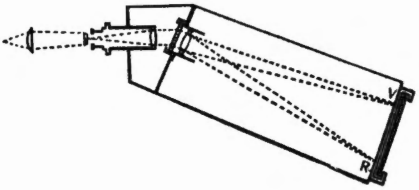


FIG. 75. Moulded grating spectrograph.

Second method. The images obtained at different exposures in a grating spectrograph are passed through a microphotometer. The density curves are then similar to those in Fig. 76.

Third method. This gives an automatic indication of the colour sensitivity, by using a *neutral wedge*, or a *rotating disc*, cut to a suitable shape (Fig. 77). In each case the variations are logarithmic.

The lack of neutrality of wedges reduces the precision below 460 mμ; but on the other hand the discs are difficult to make and the exposure is intermittent.

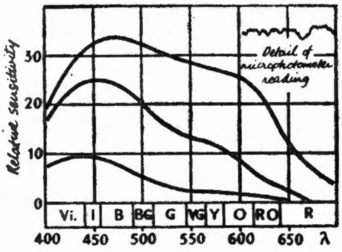


FIG. 76.

Whichever method is used, it is essential to specify the nature of the light source. A low colour temperature is advantageous to the red and gives an indication of sensitivity which is much higher than the true sensitivity. It is possible to interpose compensating filters to raise the colour temperature and bring it up to 5400°K (para. 462). At this temperature, the energy distribution of a black body is the nearest to a straight line representing the ideal white (Fig. 78). In order to make measurements which are independent of the colour sensitivity of the emulsion an equal energy source must be used.

FIG. 77.

475. Absolute colour sensitivity

Visibility curve. When each wavelength which constitutes white light is considered, it can be stated that the *visual effect* depends on the wavelength: with *equal energy* the blue and the red are much less visible than the yellow-green. The maximum luminosity is at 555 mμ. Taking 1 as the *coefficient of visibility* at 555 mμ, the relative coefficients at other wavelengths vary from 0·0003 to 1. The average of many observations, calculated by Gibson and Tyndall is given by the curve in Fig. 79. Therefore to produce a *sensation* of one lumen, a much greater quantity of blue or red light is required compared with yellow-green.

If L is the mechanical equivalent of light for $\lambda = 555$ mμ (energy necessary to produce 1 lumen) the energy flux ϕ is given by the equation $\phi_{555} = LF_{555}$ where F_{555} is the luminous flux for $\lambda = 555$ mμ.

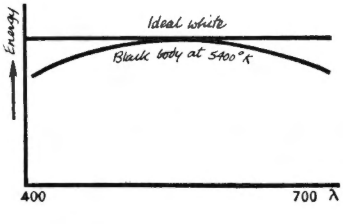


FIG. 78. The equal energy 'ideal white' appears purplish.

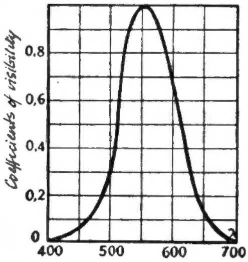


FIG. 79. Gibson-Tyndall visibility curve.

L is equal to 0·00161 watt-lumens. For all other radiations L_λ is obtained by dividing L by the coefficient of visibility.

$$L\lambda = \frac{L}{V_\lambda} \text{ and } \phi_\lambda = \frac{LF_\lambda}{V_\lambda}$$

Normal equal energy standard. An imaginary source whose energy is uniformly distributed following a straight line and producing an intensity of 1 candle metre from L_0 watts can be used as a 'normal standard' to calculate the *absolute colour sensitivity* of an emulsion. Let us first consider the value L_0: it is found without complicated mathematics in the following way:

On the abscissa (Fig. 80) have the wavelengths, and on the ordinates the energies corresponding to each interval of the radiations d_λ: taking ϵ as the unit of energy (sufficiently small) and d_λ equal to 1, the rectangle of surface $\epsilon \times d_\lambda = \epsilon$ measures the same unit of energy. The energy distribution follows a straight line (curve A), and the spectral energy is found from the area of the rectangle abcd.

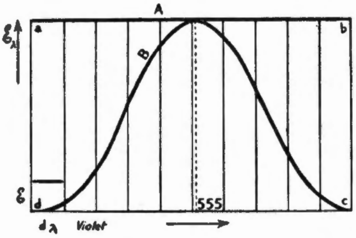


FIG. 80

By multiplying the ordinates ϵ_λ by those of the visibility curve, curve B is obtained: the area bounded by this curve is a measure of the total *luminous* energy of our imaginary normal equienergy scale.

If L watts produce 1 lumen for a spectral band d_λ of mean λ555 mμ, L watts give for the following bands V_2, V_3, V_4, lumens. For n bands d_λ, nL watts give $1+V_2$, $+V_3+V_4+\ldots V_n$ lumens. Supposing that the total luminosity (area bounded by B) is reduced to 1 lumen, the corresponding energy will be $L_0 = \dfrac{nL}{\text{sum of } V_n}$ watts.

If $d_\lambda = 1$ mμ between 400 and 700 mμ, then n = 300.

To measure the sum of the visibility coefficients, the Gibson-Tyndall area is divided into 300 vertical bands 1 mμ wide (Fig. 81). Knowing that a is the graphical representation in cm of 1 mμ, b the representation in cm of the area limited by the curve, one has:

$$\text{Sum } V_n = \frac{S}{ab}$$

S can easily be measured with a planimeter. Finally it can be found that the energy corresponding to 1 lumen for the equienergy scale is 0·00438 watts.

Knowing the colour temperature of the *actual source* used, it is, on the other hand, easy to calculate the energy coefficients of the actual and hypothetical sources for each wavelength. The equienergy light, having an excess of blue and red compared with white light, appears purplish.

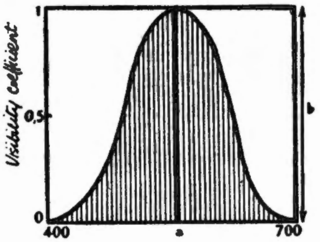


FIG. 81.

Measurement of the absolute chromatic sensitivity. The sensitive layer is exposed in a grating spectrograph. The spectral energy is first checked using a *thermopile* which is passed along the spectrum. To obtain a direct spectrogram of a normal source with uniform energy distribution, one can: filter the light to give a constant thermopile reading from violet to red (purplish light) which is a difficult operation, or use a compensating shutter unevenly cut away in a vertical direction. This shutter can be a rotating disc (Schmieschek apparatus)(41) or a roller-blind shutter. The total sensitivity is therefore equal to the sum of the partial sensitivities of each spectral region.

Once the spectrum has been made uniform, the exposure time to give an exposure of 1 c.m.s. in the different colour areas is determined, then for the complete spectrum (white light). It is then possible with a series of exposures of different times, and after microdensitometric measurements, to draw the characteristic curves corresponding to each wavelength, at least to each relatively narrow band. The results can be presented as a family of curves, or as a three-dimensioned solid (log It, λ, D).

Note. It is better to use log ϵ (energies), λ and D, for the idea of exposure leads to confusion; in fact, for an exposure of 1 lumen in white light, the yellow-green y comprises one-third on its own. Measured under these conditions, the characteristics of a non-colour sensitive emulsion, or a red-sensitive one related to the same candle metre seconds become nonsensical.

476. Colour filter method

A photographic material is exposed to white light under a wedge, then to light filtered by a blue, green, red or yellow screen. Each time the exposed area becomes smaller as the sensitivity to the colour considered is lower. If 1_0 is the length in cm of the dark area obtained with white light, 1_f the corresponding length with the colour filter, and k the constant of the wedge, then $(1_0 - 1_f)k$ represents the log of the *filter coefficient* F. To obtain the latter, it is only necessary to find the antilog of $(1_0 - 1_f)k$.

The sensitivity is the reciprocal of the filter coefficient. For example, if for the red filter transmitting from 600 to 700 mμ $F = 5$, the emulsion sensitivity to red is one-fifth of the total sensitivity for the particular light.

It is immaterial whether the filter is placed over the light source or in front of the wedge. With a lamphouse having an opening 4 cm diameter and containing a 40 W lamp, at a distance of 1·5 m from a wedge with a constant of 0·5, the exposure time is about 5 secs. for a high-speed pan emulsion.

For each measurement it is necessary to consider: (*a*) the type of light source; (*b*) the quantitative transmission of the filter; (*c*) the more or less perfect spectral transmission of the filter. The results are usually only a guide as they have not the precision of spectrographic measurements.(42)

The *spectral absorption* of the filter is found with a spectrophotometer.

To obtain the *characteristic curve of an emulsion in monochromatic light*, it is sufficient to expose the material using both filter and wedge, and to develop and measure the sensitometric strip in the usual way.

RESULTS: INFLUENCE OF WAVELENGTH ON THE PHOTOGRAPHIC EMULSION

477. Apparent spectral sensitivity

The colour (or spectral) sensitivity of a photographic layer closely follows its spectral absorption. The silver halides absorb the ultra-violet completely, and part of the blue-violet. In fact silver chloride has a whitish appearance whilst silver bromide is yellowish; as for silver iodide – it is definitely yellow.

Silver chloride whose absorption hardly exceeds 400 mμ is mainly sensitive between 280 and 400 mμ in the ultraviolet with a maximum at about 340 mμ. A second zone of low sensitivity extends from 250 to 450 mμ. A third zone starting at 250 mμ extends to the short wavelengths but is limited by the absorption of the gelatin. The spectral sensitivity of silver chloride varies somewhat with the nature of the soluble chloride used in precipitation, the crystal structure being influenced by the cations present in the solution.

The spectral absorption and sensitivity of *silver bromide* in emulsions is to a great extent dependant on the proportion of *silver iodide*: they extend further towards the longer wavelengths as the iodide content increases. In practice, however, 5% AgI is rarely exceeded.

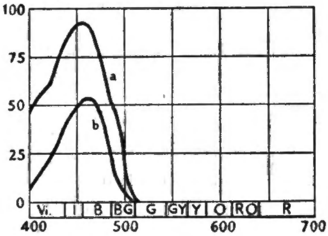


FIG. 82. Pure silver bromide emulsion
(a) sensitivity to daylight
(b) sensitivity to artificial light.

Pure silver bromide is normally sensitive from 300 to 510 mμ with a maximum at 460 mμ. A second zone of sensitivity stretches from 260 mμ to 520 mμ; a third, much weaker, extends to the short wavelengths. Different curves are obtained by exposure to daylight and to artificial light (Fig. 82), the latter showing a sharp drop in sensitivity. Commercial unsensitized emulsions containing silver iodide have a region of low sensitivity extending to 560 mμ.

Pure silver iodide is mainly sensitive from 415 to 450 mμ with a maximum at 425 mμ.

Orthochromatic emulsions. These emulsions are sensitive up to about 600 mμ. Generally there is a depression in the blue-green (500 mμ), the junction of the intrinsic and induced sensitivities (Fig. 83).

Panchromatic emulsions. Sensitivity extends to 700 mμ. The ratio of the general sensitivity to daylight to the general sensitivity to electric light can reach 1:4, that is, a highly sensitized emulsion can be four times as rapid in artificial light as in daylight (Fig. 84).

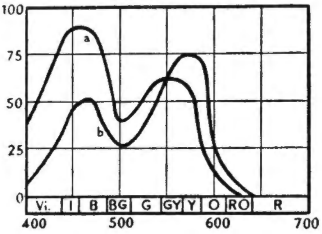


FIG. 83. Orthochromatic emulsion
(a) sensitivity to daylight
(b) sensitivity to artificial light.

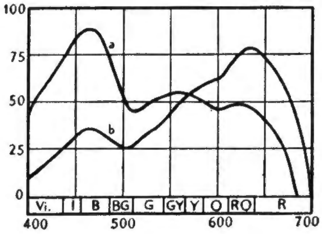
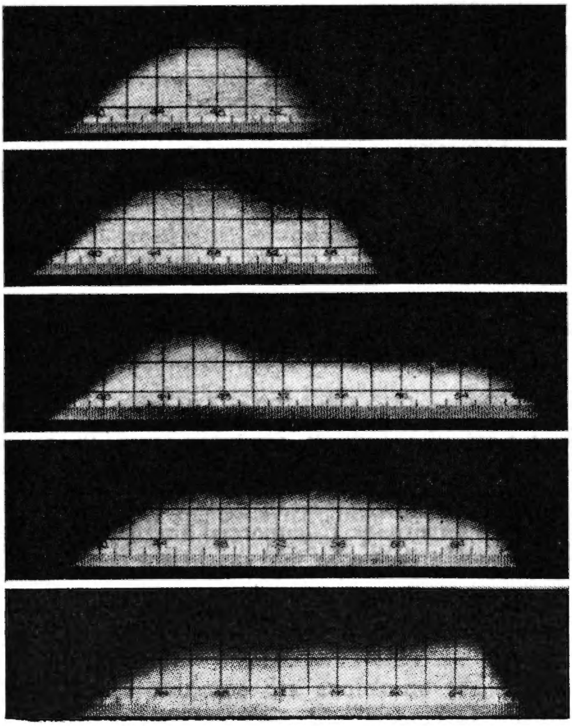


FIG. 84. Panchromatic emulsion
(a) sensitivity to daylight
(b) sensitivity to artificial light.

Ortho-panchromatic emulsions have their maximum sensitivity in the green. They are less sensitive to changes in light than panchromatic ones. They are very useful for daylight photography. They give less good results in artificial light portraiture for they strongly accentuate facial details and wrinkles.



Non-chromatic emulsion

Orthochromatic emulsion

Panchromatic emulsion type A

Panchromatic emulsion type B

Panchromatic emulsion type C

FIG. 85. Spectrograms of ordinary, ortho and pan emulsions (Eastman Kodak).

Various spectrograms of ordinary, ortho and pan emulsions obtained by exposure in a grating spectrograph are shown in Fig. 85.

478. Absolute spectral sensitivity

We have already seen that by allowing for the spectral *energy* distribution of the light source the absolute spectral sensitivity curve can be obtained.

The figures below show the energy in ergs/cm^2 necessary to produce a density of 1 at a γ of 1.

The lower the energy required, the greater the corresponding sensitivity.

		Wratten-Wainwright Pan	*Eastman D.C. Ortho*
Ultra violet	300 mμ	1.1	0·43
Ultra violet	350 mμ	0·24	0·18
Violet	400 mμ	0·59	0·41
Blue	450 mμ	0·74	0·67
Blue-green	500 mμ	2·5	2·9
Green	550 mμ	11	8·3
Orange	600 mμ	15	134
Red	650 mμ	17	—
Extreme red	700 mμ	97	—

The curves of Fig. 86 show the variations in absolute sensitivity on a log scale. It emphasizes that the *maximum of absolute sensitivity* in ergs/cm^2 is situated, not at 460 mμ, but at 350 mμ in the ultra-violet (Fig. 87). G. A. Morisson and H. O. Hoadley define the sensitivity as the reciprocal of the number of ergs/cm^2 to produce a density of 1.(43)

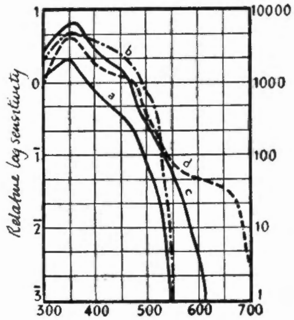


FIG. 86. Energy sensitivities of Eastman Plates. (a) 33; (b) 40; (c) D.C. Ortho; (d) Wratten-Wainwright Pan.

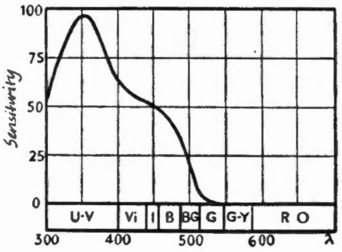


FIG. 87. Intrinsic absolute sensitivity of silver bromide.

The sensitivity decreases rapidly towards the short wavelength ultra-violet due to the absorption of the gelatin, considerable at 250 mμ and complete at 200 mμ. Without gelatin, the extreme ultra-violet sensitivity becomes much greater.

479. Effect of wavelength on contrast

The strongly absorbed short wavelength radiations effect only the silver bromide crystals which are on the surface. The longer wavelength radiations produce, on the contrary, an image deep in the emulsion. The way in which the two images are formed is therefore different, resulting from different grain distributions, even more so as the absorption of the longer wavelengths occurs through the intervention of a sensitizing dye.

The photographic contrast varies from the ultra-violet to the infra-red. Most frequently the red is more contrasty than the green, itself harder than the blue (Fig. 88). This is not always the case however.

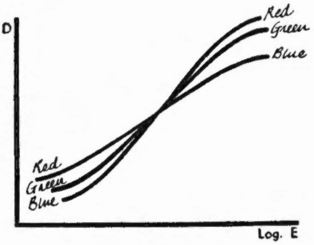


FIG. 88. Influence of colour on contrast.

To a certain extent it can be expected that the contrast of the sensitized region should be greater than the region of natural sensitivity as the sensitizer is adsorbed preferentially by the small grains which generally give higher γ than the large grains.

Effect of development. At each wavelength a contrast variation with development time is produced, which is normal (Fig. 89); it should be noted that there is a minimum in the curves in the blue-green at 500 mμ.

The phenomenon of variation of contrast with wavelength is important in colour photography: as it is necessary to have *three separation negatives*—blue, green and red—*having the same* γ, it is necessary to increase the development time of the green and to a greater degree the blue, from 25 to 100%. Without this correction the neutral scale cannot be correctly reproduced throughout its length. The light greys will be brownish and the dark greys bluish.

The problem is more complicated if the *three separations* are made *on the same film* when it is necessary to develop them all for the same time. Now it has been stated that the effect of colour on the contrast becomes negligible when the region of γ_∞ is reached: in other words, if development is complete, the contrast is approximately constant through the whole spectrum. We have seen (para. 177) that a *low gelatin concentration* facilitates development to γ_∞.

480. Influence of temperature

Studying the sensitivity of emulsions, as a function of increasing temperature, shows that:

(*a*) The sensitivity generally increases.

(*b*) The extent of this increase varies with the emulsion and the wavelength.

(*c*) At each wavelength, and for a given emulsion there is a more or less definite optimum temperature.

(*d*) The induced sensitivity is increased to a greater extent than the intrinsic sensitivity.

(*e*) The contrast increases, particularly at long wavelengths.

(*f*) The increase in sensitivity is limited in practice by the tendency to fog.

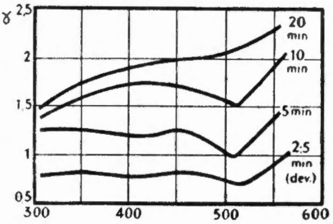


FIG. 89. Influence of development on colour contrast (Eastman 40 plates).

Thus, for example, the red sensitivity of panchromatic plates can be doubled or trebled at 60–70°C. It is the same with sensitized infra-red plates.

Conversely, at *low temperatures* the sensitivity decreases. The results obtained by different workers are not always in agreement, but in all cases a slight drop between $+20°$ and $-70°$ is found, and becomes great between $-70°$ and $-180°$. At the latter temperature the emulsion has only about 5% of its sensitivity.

The induced sensitivity drops more quickly than the intrinsic sensitivity. In blue light the γ_∞ remains almost unchanged, whilst in red light the γ_∞ is progressively reduced and the D max slightly decreased.

The effect of temperature on reciprocity failure is the same at all wavelengths: at low temperatures, reduction of sensitivity at high intensities; for low intensities, an increase follows a decrease. At high temperatures, the excitation necessary to produce a given density decreases, passes through a minimum, then increases. The temperature corresponding to this sensitivity maximum is lower with low intensities (at least in most cases).

---

1. Shown by the letter K or degrees Kelvin.
2. At the absolute zero, the molecules become static for $pv = RT = 0$, pv decreasing 1/273 for each reduction in temperature of 1°C.
3. *Brightness:* energy emitted in a solid angle equal to unity (cone of 1 radian opening) per cm^2 of the projected area of the source.
4. Neale D. M.: *Jl. Brit. Kin. Soc.*, 1946, 140.

5. Harding H. G. W.: *Jl. Sci. Instr.*, 1952, 145.
6. Dawson G. H., Grant and Ott.: *Jl. Soc. Mot. Pic. Tel. Eng.*, 1952, 309.
7. Crandell, Freund and Moen: *Jl. Soc. Mot. Pic. Tel. Eng.*, 1951, 386–397.
8. Finkelburg W.: *Illum. Eng.*, 1950, 625. Gretener E.: *Jl. Soc. Mot. Pic. Tel. Eng.*, 1950, 391–413.
9. Dejardin G., and Jamin J.: *Jl. Phys.*, 1952, 343–350.
10. Thorington L. (Westinghouse): *Sci. Ind. Phot.*, 1951, 19.
11. *Rev. Techn. Philips*, 1951, 113–128.
12. Bourne and Beeson: *Jl. Soc. Mot. Pic. Tel. Eng.*, 1950, 299–312; *Brit. Kinema*, 1950, 92–95.
13. Cumming: *Phot. Jour.*, 1949, 58.
14. *Intern. Proj.*, 1949, 10 or *Sci. Ind. Phot.*, 1950, 265; *Jl. Soc. Mot. Pic. Tel. Eng.*, 1950, 567–584.
15. 4000 flashes of 5μ sec duration per sec (*Proc. Inst. Electr. Eng.*, 1951, 619–634).
16. Marsal and Potter: *P.S.A. Jl.*, 1952, 21–26.
17. Rebikoff D., *Sci. Ind. Phot.*, 1952, 289.
18. Laporte: *Jl. Phys.*, Dec. 1950; *Sci. Ind. Phot.*, 1951, 281.
19. Bingham and Hoerlin: *P.S.A. Jl.*, 1951, 52–56.
20. Cloud G. A.: *Brit. Jl. Phot.*, 1950, 668.
20b. Davis and Gibson: *VII Int. Congress of Phot.*, London 1928.
21. Made by Eastman Kodak. These filters are of dyed gelatin.
22. Gelatin is readily detached from glass if the latter is first treated with a little sulphoricinate and thoroughly polished with a dry rag before coating.
24. Zolster and Kriukova: *Jl. Tech. Phys. U.S.S.R.*, 1944, 373–384.
24b. Bostwick and Mackey (Ansco): *Phot. Sci. Techn.*, Feb. 1955 p. 11–13.
23. Nicholas and Pollack, *Jl. Sci. Inst.*, 1951, 23; *Sci. Ind. Phot.*, 1950, 136.
25. Dense flint absorbs the ultra-violet above 350 mμ. Yellow cerium glass absorbs all the ultra-violet.
26. The letter (B) indicates "Badische-Anilin"; (By) = "Bayer"; (S) = Sandoz; (L) = Leonhardt.
27. F.P., 867, 411.
28. F.P., 868, 266.
29. For the technique of this operation see: Hadley and Dennisson: *J.O.S.A.*, 1948, 438–496 and Hermansen: *Nature*, Jan. 1951, 104–106.
30. Widdop E.: *R.C.A. Review*, March 1952, 27–33; *Jl. Soc. Mot. Pic. Tel. Eng.*, 1953, 357–366.
31. Koch G. J.: *Jl. Soc. Mot. Pic. Tel. Eng.*, 1950, 439–442.
32. For a study of Lippman monochromats see Delcroix J. L.: *Rev. d'Optique*, 1948, 493–509. Merland and Schonne, *Compt. Rend. Ac. Sc.* Paris, 1947, 1105.
33. Kaseman E.: *Optik*, 1948, 521–536.
34. Hicks H. F.: *Phot. Eng.*, 1951, 61–71.
34b. Korolev and Klementeva: *Dokl. Ak. Nauk. SSSR.*, Feb. 1954, 1025–1027; *Sc. et Ind. Phot.*, 1955, 143.
35. F.P.: 919,006 (1945).
36. The Backstrom and Basberg filter (*J.O.S.A.*, 1947, 89) transmits the red from 690 mμ, and the infra-red: *superimpose* 3 gelatin filters containing respectively per m^2; (a) Carmine blue 3·2g; (b) Rose Bengal 2g; (c) Tartrazine 4g + aesculine 10g. E. H. Mynster (*Zeit. Wiss. Phot.*, Aug. 1951, 84) used (a) tartrazine 4·4g + Solid red D 4·4g; (b) Naphthol green 7·4g + Carmine blue 1·47g.
37. F.P.: 898,519 and 898,614.
38. Turner A. F. and Benford J. R.: *J.O.S.A.*, 1947, 642.
39. Zehden W.: *Vacuum*, Jan. 1951, 38.
40. Banning (*J.O.S.A.* 1947, 686) used "Chromel A" containing 80% Ni and 20% Cr.
41. *Sci. Ind. Phot.*, 1929, 3.

42. The *Eder-Hecht* sensitometric wedges have, alongside the normal scale, 4 parallel bands coloured respectively blue, green, yellow and red which permits an approximate measurement of the orthochromatism of photographic materials. Correction tables are provided with the instrument.
43. *P.S.A. Jl.*, 1950, 64.

Chapter XXVII

PRINCIPLES OF COLOUR REPRODUCTION

COLOUR VISION

481. Characteristics of colour

Colour is defined by three fundamental properties: hue, intensity and saturation.

Hue is the sensation produced by radiation of one, or a group of, definite wavelengths. Between 430 and 640 mμ, small wavelength differences produce pronounced differences in the sensation of colour. On the other hand, the extreme violet (400–430 mμ) and red (640–700 mμ) appear of uniform hue: these are the unitonal regions of the spectrum.

The different colours are situated in the spectrum as follows (the change from one colour to another being gradual):

Violet	395–435 mμ
Blue	435–490 mμ
Blue-green	490–505 mμ
Green	505–545 mμ
Yellow-green	545–570 mμ
Yellow	570–595 mμ
Orange	595–625 mμ
Red	625–685 mμ
Deep red	685–740 mμ

Pink and *purple* are mixtures of red and violet. *Magenta* is formed of equal parts of red and violet-blue.

Intensity. Each primary radiation which constitutes a complex colour has its own intensity. For the intensity of a colour to increase or decrease without variation of hue, each primary variation must vary in the same direction. Intensity is often called brightness or brilliance.

Saturation. When a simple or complex colour is not mixed with white light, the colour is said to be pure or *saturated*. The spectral colours are saturated, but in general, the colours of objects are to a greater or less extent diluted with white.

482. Visibility of colours

We have already shown that at equal mechanical energy the luminous sensation is not equal throughout the spectrum, and that the visual maximum is in the yellow-green at about 555 mμ. From the visibility curve we can take the following coefficients, taking 1000 for $\lambda = 555$ mμ.

Colour	λ	*Visual coefficient*
Violet	400 mμ	0.4
Violet	440 mμ	23
Blue	460 mμ	60
Blue	500 mμ	323
Green	540 mμ	954
Yellow-green	555 mμ	1000
Yellow-green	560 mμ	993
Orange	600 mμ	631
Red	640 mμ	175
Red	660 mμ	61
Red	700 mμ	4·1
Far red	740 mμ	0·2

Thus a green object is brighter than a red object which in turn is brighter than a blue one.

For correct colour rendering in monochrome, the yellows and greens must be reproduced in the positive by very light areas, which necessitates a negative emulsion with its maximum sensitivity in the green (ortho-panchromatic emulsions). The use of a light green correction filter enables the same end to be achieved, by losing general sensitivity.

In colour photography on the other hand, it is useless for the emulsion sensitivity to follow the visibility curve, as this is done automatically by the coloured pigments which replace the silver image. It is therefore necessary to have the colour sensitivity as even as possible.

483. Complementary colours

The term complementary is applied to two colours which produce a sensation of white when mixed together. Thus orange at 610 mμ is complementary to blue at 490 mμ, whilst yellow-green at 572 mμ is complementary to indigo blue at 460 mμ. Figure 90 shows the simple complementary colours; the absence in it of pure green will be noted, as its complementary is in the hypothetical purple region (violet + red).

The complex colours have the following complementaries:

Blue-violet : yellow.

Green : magenta (violet-red)

Red : blue-green.

484. Mixtures of colours

The quantities of two complementary radiations necessary to produce the sensation of white are not equal, due to the *apparent saturation* particular to each radiation (result of the difference of visibility). In order of increasing apparent saturation they are:

Yellow-green, green, orange, blue, red, indigo, violet.

Also, mixtures of red with radiations above 520 mμ are always saturated, whilst mixtures of violet and blue below 495 mμ are *almost* saturated.

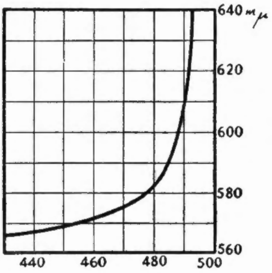


FIG. 90.
Curves of complementary colours.

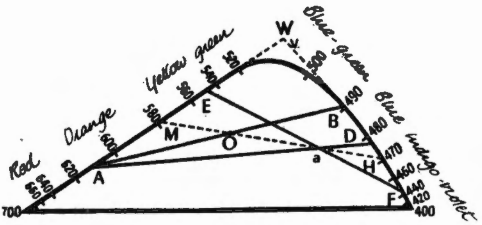


FIG. 91
Colour mixture diagram.

Finally, purple hues obtained by mixing red and violet always appear saturated.

All these considerations have led us to the preparation of a colour mixture diagram shown in Fig. 91 in which it can be noticed that mixtures of radiations between 520 mμ (deep green) and 495 mμ (blue) are never saturated.

Two radiations are complementary when the straight line joining them (AB for example) passes through the centre, O. The lengths OA and OB show the reciprocals of the proportions which must be used to produce the sensation of white: $\frac{1}{OA}$ of A and $\frac{1}{OB}$ of B.

The result of mixing any two colours A and D in the proportions $\frac{1}{aA}$ and $\frac{1}{aD}$ is a complex desaturated colour whose dominant wavelength approaches H.

The same tint 'a' can be produced by mixing the two colours E and F in the proportions $\frac{1}{aF}+\frac{1}{aE}$.

If with 'a', it is desired to produce white, it is necessary to add to it M, the complementary of the dominant H in the quantity $\frac{1}{OM}$, that is, one must in fact use $\frac{1}{aA}$ of A (orange, for example), $\frac{1}{aD}$ of D (blue) and $\frac{1}{OM}$ of M (green).

The point W in the diagram represents a hypersaturated green whose existence is effectively stated by the *contrast* of the colours.

When dealing with a *very complex colour* as is generally the case, it always has a *dominant* which gives the apparent hue, resulting from the components brought into play, and which depends on the many factors which will be shown. The apparent hue of a complex colour is therefore, so to speak, the '*centre of gravity*' of a system in equilibrium; thus a colour composed of a mixture of *red* and *green* appears *yellow*, although yellow itself occupies only a small region in the spectrum. Similarly, a colour composed of a mixture of blue and green gives the illusion of being solely a certain monochromatic spectral blue-green situated between 495 and 505 mμ.

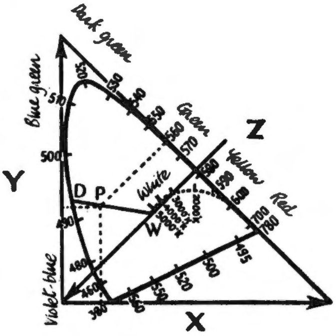


FIG. 92. Colour triangle C.I.E. system.

485. C.I.E. System

The diagram chosen by the International Congress of Lighting in 1937 is shown in Fig. 92.

In the *C.I.E. system*, or international colorimetric system, it is assumed that a mixture of colours can be reproduced by a combination of three colours arbitrarily chosen as blue, green and red which are used as co-ordinates. The three primary colours, or *coefficients of colour distribution* x, y, z are shown by the curves of Fig. 93. Their maxima are situated at 435·8 mμ, 546·1 mμ

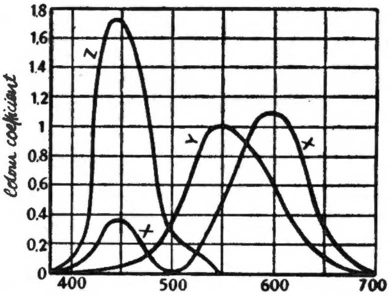


FIG. 93. Red, green and blue components of C.I.E. colorimetric system.

and 600 mμ. It is noticed that x, the red component, has a second maximum in the blue-violet, and that y, the green component, follows the visibility curve, in this way showing the brightness of the light studied.

The three trichromatic coefficients x, y, z are measured by the three peaks of the triangle, starting from each base, thereby defining a complex colour.

The centre of the triangle x, y, z corresponds to an equi-energy source (see para. 475) which is, as we have seen, purplish. A point representing a colour and situated in the interior of the curve becomes less saturated as it approaches the centre. The true white is situated away from the centre W on a line (dotted) which goes towards the green then the red as the colour temperature is reduced.

Any line passing through W joins two complementaries.

The point of intersection D of the line WP with the chromatic curve, where P represents a complex colour, shows the dominant wavelength of the colour P. The degree of saturation (or purity) is given by the ratio PW/DW. It varies between 1 (saturated colour) and 0 (equienergy white).

486. Physiological phenomena

Purkinje's phenomenon. The sensitive part of the eye, the *retina*, is made up of *cones* and *rods*: the former are used at high intensity levels and the latter at low levels. This results in a decrease of the work done by the cones and an increase in the effectiveness of the rods when passing from high levels to low levels. The maximum sensitivity of the eye which is at 555 mμ in the yellow-green is at the same time shifted towards the blue until it reaches 500 mμ. This is why blues seem more intense at low levels whilst reds become darker, and poorly lit objects appear more blue than they in fact are.

Persistence of colour impressions. The retinal cones are excited more rapidly by red light. On the contrary, the persistance of red light is less when the eye suddenly receives no light; less intense, but more lasting than the blue or green impressions. A residual white image very quickly becomes greenish, grey, violet and finally dull red before dying out completely.

Successive contrast. The fatiguing of the eye is a function of its ease of excitation: the red fatigues much more easily than the green or blue, especially if the surface illuminated is large. Successive contrast is principally due to this fatigue.

When the gaze is fixed for some time on a colour then on white, the complementary is seen. This phenomenon, however, is very irregular. It has been observed that, in general, an eye fatigued by red sees violet as blue-green; fatigued by violet, it sees green as blue-green and red as orange; fatigued by green it sees red as purple, and fatigued by blue, the same red appears orange.

Simultaneous contrast. Simultaneous contrast is a very important factor in the vision of natural colours, as it often falsifies judgment. Thus red and yellow appear more intense against a dull background, whilst green and blue lose some of their brilliance. A white or grey object against a yellow background appears bluish; against a blue background, yellowish; it appears greenish against a red background whilst against a green background it seems rather red.

Abnormal vision. Achromatopic eyes are insensitive to colour. To them, everything appears black and white. *Colour blind* eyes see badly, or not at all, certain spectral regions: red (protanopes), green (deuteranopes) or blue (tritanopes); this results in a serious alteration of colour judgment.

Variations in the visibility curve. Preston, Dressler, then Kohlraush have stated that the visual sensitivity to different radiations is subject to periodic variations, daily or weekly, which can amount to 5%. This phenomenon appears to be due to internal physiological changes of the individual, which are closely linked with feeding.

Fidelity of colour reproduction. Suppose we have to reproduce an original scene in colour: the colour sensation which it brings about in us does not correspond completely with the radiation system which it sends to the photographic plate, for, as we have seen, our appreciation of colour values enters into the way we see the scene. This appreciation is particularly affected by the *contrast of each coloured area with the surrounding areas.* Also, the saturation of each area increases when the illumination increases, up to an optimum value, which varies the brilliance, and hence the apparent corresponding shade.

It becomes obvious that the colour characteristics of each part of the original are intimately connected with their nature, that is with the situation of these areas, and their intensity of illumination. In colour vision there is, therefore, firstly a physical base represented by the group of radiations, and secondly a psychological modification process which depends at the same time on the nature of the scene examined, on the surroundings and on the faculties of the observer.

For the reproduction to be a faithful replica of the original, the same physiological processes must take place in viewing the colour image. It is however apparent that the brilliance of the various parts of the image, not being necessarily the same as the original, the colour contrast in the two cases will not be absolutely identical. Now experience has shown that the alteration is at a minimum when the reproduced image has a spectral composition identical with that of the subject. Whatever the light level, the rendition of colours will then be acceptable within reasonable limits.

In current practice the image rarely reproduces the colours of the original according to their spectral composition. Therefore all variations in brilliance affect the saturation and hue of the colours which leads to a more or less great modification in the colour accuracy. Also, when the colour reproduction is examined with uniformly illuminated surroundings the dense parts appear more dense. The apparent maximum saturation is reached in the image areas whose density is equal to that of the surroundings. This is why the reproduction appears appreciably different depending on whether there is a white, grey or black border. The size of the image also has an influence and the brilliance appears to change with the surface.

COLOUR ANALYSIS

487. Trichromatic analysis

According to a hypothesis formulated by Young in 1807, and revived by Helmholtz, the retina has three receptors capable of receiving three different groups of radiations. The combination of the sensations produced by each group enables complex colours to be seen and explains the fact that with three fundamental colours the majority of existing hues can be produced.

Thus the extremities of the spectrum affect only one receptor and appear uniformly coloured (monochromatic red and violet regions) and when only two of the three receptors function, the eye is afflicted with partial colour blindness.

The supporters of the three-colour theory present, to help Young's hypothesis, the work of von Studnitz who was able to isolate the three analysing pigments of the retina, blue, green and red which behave as receptors. The absorption maxima of these pigments were situated respectively, for the frog, at about 465, 560 and 600 mμ. On the other hand, Granit was able to record, among the nerves of the retina, the response of a single nerve and measure its characteristics depending on wavelength: the different nerves provided three excitation curves for the three primary colours.

488. Polychromatic analysis

Whatever the truth of *trichromatic colour vision*, it should be stressed that it it is, in fact, *independent* of the problem of *photographic analysis*; for before the eye sees the colours presented to it, they must be as near as possible to the original, if not there is a double alteration, first by the analysis then by the ensuing appearance which multiplies the causes of error.

Three-colour reproduction is imitative reproduction of approximate correctness, by which it is tried to *suggest* colour.(1) In general, it is only by chance that rare scenes are rendered correctly.

Contrary to the generally held opinions, we think that although vision is trichromatic, photographic analysis and reproduction must approach as closely as possible the spectral rendering.(2)

In this connection we would note a remark by R. P. Loveland on three-colour reproduction of two dyes used in biological micrography, eosin and fuchsin. Specimens treated with these dyes are very poorly reproduced by a three-colour system, and it is necessary to filter the light with a liquid filter of neodymium acetate.

This alteration of colours can have its uses: a film having two superimposed emulsion layers sensitized to green and to the near infra-red can be used to detect camouflage; leaves and green paint are reproduced in different colours.(3)

If the spectrum is divided into n separation regions going from violet to red, the reproduction of this spectrum becomes more exact as n becomes greater. For two-colour analysis $n = 2$; for three-colour, $n = 3$, and this is still not enough.(3b) Going further, we have *four-*, *five-* and *six*-colour analysis. Without going to $n = \infty$, tests have shown that satisfactory results are obtained with $n = 5$.

The use of polychromatic systems is in practice restricted by certain difficulties, the most important of which are the number of emulsion layers, and, for subtractive processes, finding pigments having the narrow absorption bands which correspond to the transmission of the separation filters (Fig. 94). The colour of the positive pigment is in fact complementary to the separation filter band in any layer.

489. Three-colour separation

The three spectral regions used in three-colour analysis are the ***blue-violet***, the ***green*** and the ***red***, whose maxima are generally quoted, after Maxwell's work, as 460, 528 and 630 mμ.

When a coloured spectrum is examined, it is seen that the two parts—extreme violet (400–415 mμ) and red (685–700 mμ) are hardly visible, and have little effect on the sensation of colour. They can be easily omitted from the analysis. We therefore have a spectrum divided into three unequal parts:

Blue-violet: 415–490 mμ with max. at 460 mμ.

Green: 500–570 mμ with max. at 530 mμ.

Red: 600–685 mμ with max. at 630 mμ.

The transmissions of the red and green filters can fall off on each side of the yellow at 585 mμ. Some processes, such as Dufaycolor, even use transmission bands which overlap each other, each filter covering half the normal spectrum; the exposure time is appreciably reduced in this way, but the results are less exact than with narrower band filters.

Separation filters for three-colour work are made of dyed gelatin (para. 465) or optically worked glass (para. 464).

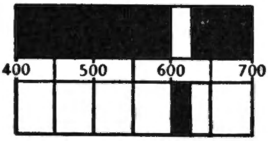


FIG. 94.

Red gelatin filters are usually easy to make with red dyes, to which a yellow dye is preferably added to eliminate any violet transmission: the triphenylmethane derivatives (fuchsines), the rhodamines, safranines, ponceaus are suitable for this. For example, a mixture of *rhodamine B* and *auramine O* gives good results. Depending on the dye concentration the limit of transmission is between 580 and 600 mμ.

The *green* and *blue filters* are more difficult to make as the corresponding dyes transmit more or less extreme red which must be eliminated.(4) Thus indigo sulphonate and iodine green have high red transmissions; methylene blue, acid brilliant blue and Victoria blue are better, but the preferred dyes (amongst others) are *toluidine blue*, *toluidine green*, *naphthalene green* and *erioglaucine*. The green transmission of a blue filter is limited by adding a little violet or magenta dye (methyl violet, rhodamine, rose Bengal); finally green filters can be made by adding a yellow dye to a blue or blue-green one.

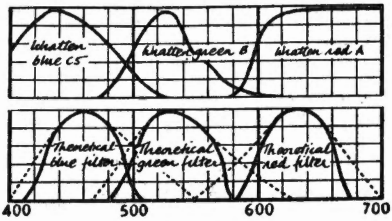


FIG. 95. Filters for tricolour selection.

Whatever colour the filter, it is advisable to incorporate an ultra-violet absorber in it: aesculine, β-methylumbelliferone, β-naphtholdisulphonic acid or one of the yellow dyes listed in the previous chapter (para. 466).

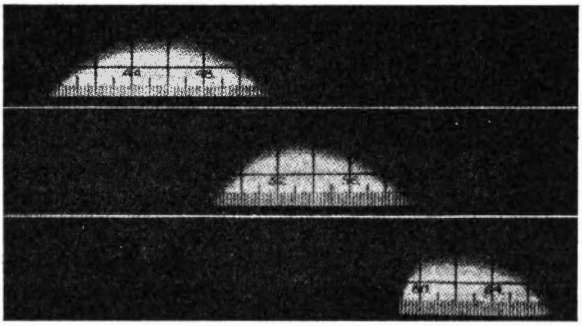


FIG. 96. Separations with Wratten tricolour filters in daylight, C5-blue, B-green, A-red (Eastman-Kodak).

For those who prefer ready-made filters, the Wratten tricolour set should be noted, A (No. 25), B (No. 58) and C5 (No. 47). Their transmissions are shown in Figs. 95 and 96.

Glass separation filters are more difficult to obtain than coloured gelatin filters as the choice of suitable spectral curves is very limited. Among the glasses suitable for three-colour work are:

Red: Corning 246RH; Jena 2745 (0·32 mm thickness).

Green: Corning sextant green 401 (th. = 1 mm). It transmits a large proportion of blue. Jena 4930 (th. = 1 mm) transmits blue and a little orange.

Blue: Corning signal blue 556. Transmission limit at 500 and maximum at 430 mμ; transmits ultra-violet. Jena 8780 (th. 0·60 mm) transmits green also, which can be eliminated with a Corning purple glass (th. 2–3 mm).

A photographic layer exposed to white light through each of the three separation filters blue, green and red, must give, on development, identical densities. Furthermore, the sensitometric curves obtained with each filter must be exactly superimposable to give a *grey scale*. The exposure times and the development γ corresponding to the three images must therefore be very carefully controlled.

Practical advice on the choice of dyes.

(*a*) Never mix acid dyes with basic dyes.

(*b*) To obtain a sharp cut green filter with no yellow and red transmission, choose a blue dye (in preference to a single green one) and add to it enough yellow dye to remove all the blue to 505 mμ (see para. 466). The more violet the blue, the narrower the green band, and the nearer to 500 mμ. To remove the red which is frequently transmitted by blue dyes add a bluish green dye (the greenish blue dyes generally absorb in the red but they transmit orange). To sum up, green filter = blue dye + yellow dye + bluish green dye.

(*c*) A monochromatic bluish green filter is obtained by combining a magenta dye whose transmission ends at about 520 mμ in the green (Rhodamine B for example) with a bluish green filter which removes the red and the violet. The orange is absorbed by a greenish blue dye such as methylene green whilst the rest of the blue is absorbed by a yellow dye. Bluish green monochromatic filter = magenta dye + bluish green dye + greenish blue dye + yellow dye. Such a filter is useful as a safelight for panchromatic materials.

(*d*) A yellow monochromatic filter is made by combining a green and orange-red filter. The filter generally appears brown because of the absorption throughout the spectrum.

490. Two-colour systems

The division of the spectrum into two regions gives dull inferior results due to the total disappearance of violet, pink, pure green and pure yellow. Only the brown, orange, blue and olive colours are reasonably correct. Two-colour systems are, on the other hand, simple to operate and are pleasing when well controlled, and this has led many experimenters to work this way for colour films.

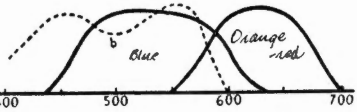


FIG. 97. Two-colour analysis.

The separation filters have uniform transmission without a prominent maximum. Two spectral regions are used (Fig. 97):

$$\begin{matrix}\text{Blue-green} \\ \text{Orange-red}\end{matrix}\left\{\begin{matrix}440\text{–}625\ \mathrm{m}\mu \\ 550\text{–}700\ \mathrm{m}\mu\end{matrix}\right. \quad \text{or} \quad \left\{\begin{matrix}470\text{–}580\ \mathrm{m}\mu \\ 570\text{–}700\ \mathrm{m}\mu\end{matrix}\right.$$

The blue-green filter can be replaced by a separate orthochromatic emulsion and no filter: the spectral extent of the blue is then 400–600 mμ (curve b).

491. Additive synthesis

By additive synthesis is meant the formation of complex colours by *mixing coloured light* (*without a solid support*): it is carried out by superimposing on a screen several beams of monochromatic light, or observing at a distance several side by side coloured objects whose images are confused by distance.

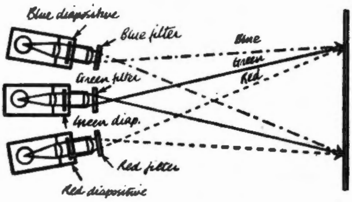


FIG. 98. Additive synthesis.

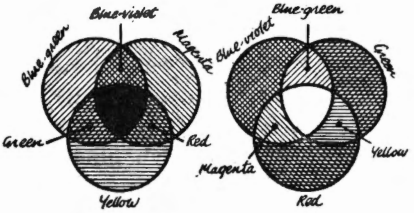


FIG. 99.

All colour mixtures described so far in this chapter are additive mixtures. The synthesis is carried out by the eye.

To reproduce photographic colour images additively, it is sufficient to project on to a screen (in exact register), positive prints of the separation negatives, each print being projected through a similar filter to the one with which the negative was made. Depending on whether two, three or more colours are used for the system, two, three, four, etc., projectors are used (Fig. 98) each fitted with the appropriate colour filter.

With a three-colour system, the colours are reproduced by *addition* of the three primaries: blue, green and red are produced directly without mixing; blue and green together give *blue-green*, blue and red give *magenta* and green and red give *yellow*, whilst a mixture of the three produces *white* (Fig. 99).

492. Subtractive synthesis

Colours are said to be formed subtractively when they are formed by *absorption* of certain radiations. Contrary to additive synthesis where monochromatic light is used to produce white, subtractive synthesis starts with white and subtracts the unwanted radiations; it is therefore an analysis rather than a synthesis.

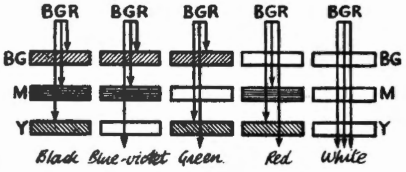


FIG. 100. Formation of colours in a three-layer subtractive film with subtractive primaries blue-green, magenta and yellow: the white light (BGR) passes through three superimposed differently coloured layers which each absorb the complementary colour.

Light is subtracted by mixtures of dyes or pigments. The subtractive primaries are not the colours used for analysis, but their *complementaries*.

Thus with two-colour work, the analysis filters being blue-green and orange, the subtractive synthesis colours are the opposite ones, *orange* and *blue-green*. For three-colour work the subtractive primaries are *blue-green*, *magenta* (or red-violet) and *yellow* which are, respectively, the complementaries of the analysis filters, red, green and blue (Fig. 99). We would note that the subtractive colours have a transmission spectrum twice that of the analysis colours. By combining in pairs they give colours with narrower bands (Fig. 100):

Blue-green + yellow = green;
Blue-green + magenta = blue;
Magenta + yellow = red.

A mixture of the three colours absorbs all light to give black or grey. Where the three colours are absent the light which is transmitted or reflected remains white.

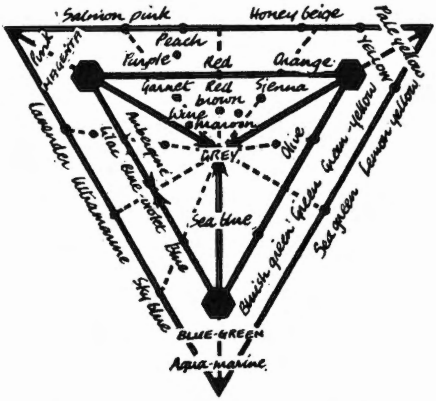


FIG. 101. Production of colours in a subtractive three-colour film by mixing *blue-green, magenta* and *yellow* in various proportions. On the perimeter of the inner triangle are the pure colours; inside the triangle are grey and the degraded colours obtained by mixing grey with a dominant colour, that is the simultaneous use of the three colours. Outside the central triangle, the addition of white (by a lower colour density) gives the pale hues becoming less saturated as they get further from the line of pure colours. These are the light neutrals formed from white and a dominant in low concentrations whilst the deeper neutral hues are formed from white (or grey) and a relatively strong dominant colour.

Subtractive synthesis applies to all colour materials: dyeing, painting, coloured images on the same support.

The reproduction of the principal hues takes place following the scheme of Fig. 101, where the proportions of the dyes are given by the reciprocals of the relative distances. For example:

Red = 1 yellow + 1 magenta;
Maroon = $\frac{2}{3}$ grey + $\frac{1}{3}$ red = 1 magenta + 1 yellow + $\frac{2}{3}$ blue-green;
pink = $\frac{1}{2}$ magenta (+ white).

The transmissions of the dyes or pigments which are usable in practice are never ideal. In photomechanical reproduction the magenta and blue-green inks leave much to be desired, particularly the magenta; only the yellow approaches the ideal (Fig. 102).

COLOUR REPRODUCTION

493. Direct methods

The direct reproduction of colours without using filters has been achieved or attempted by three main methods: the silver chloride process, the dispersion process and the interference method. Only the latter is of interest.

Silver chloride process.(5) This is based upon the supposed selective decolorizing of silver chloride, already blackened, by light: silver chloride paper (without gelatin) is treated with a reducer (5% stannous chloride) then 'blackened', still wet, in diffuse light, until it is deep violet. It is sensitized by an oxidizing agent (for example, potassium dichromate in the presence of copper sulphate) before exposure. The colours obtained are actually somewhat reddish or violet and the images cannot be fixed.

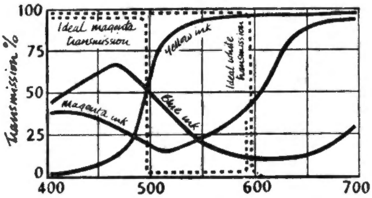


FIG. 102. Transmissions of three printing inks.

The blackened silver chloride, formed of particles of silver dispersed in excess chloride, results in a coagulation of particles. In fact R. Formstecher obtained slight coloration starting from a complementary negative using *violet silver alcosols* dispersed in collodiochloride, and exposing 8 days in bright sunlight:(6) the alcosols are obtained by reducing silver nitrate with glycin in a mixture of collodion and alcohol.

Dispersion process.(7) This process, which is purely optical, uses the dispersion by a prism, of an image, already divided by a screen into vertical elements. Studied mainly by Rheinberg and Chéron, it requires cumbersome apparatus. The results must be viewed in the same apparatus.

Interference method. Interference colour photography was conceived by G. Lippmann before 1891. A plate coated with a grainless emulsion (para. 342) is placed in a dark slide which can be filled with mercury, the gelatin surface forming one of the sides of the container. The plate is then exposed through the glass in a camera.

The rays which penetrate the sensitive layer are reflected by the mercury mirror; they *interfere* with the corresponding incident rays forming nodes and antinodes. The developed plate has through the gelatin layer (very thin) a *series of layers* of metallic silver separated by distances equal to the wavelengths of the incident light.

The stratified image is examined with incident light against a black background and appears in natural colour.(8) The stacks of silver layers behave as a sort of mould to the radiation striking them and therefore select only the suitable wavelengths. To view the image in the best way, a prism of about 10° should be stuck to it with Canada balsam. The glass surface is coated with matt black paint.

It is obvious that if the gelatin swells, due to dampness, the interstrata distances will vary and the colours change due to an increase in wavelength.

Interference photography can give perfect colour reproduction. There are, however, several practical disadvantages which limit its use; grainless emulsions are extremely slow (exposures of the order of 30 secs. at f 3·8 in bright sunlight are necessary); the use of a mercury container is inconvenient; development is extremely critical; finally, the *photographs are unique* and can only be examined at certain critical angles.

Rothé was able to obtain results without the mercury backing, simply using the reflection of the gelatin-air interface, the plate being exposed through the glass. We ourselves have tried the evaporation of an aluminium mirror on the gelatin, which is dissolved after exposure.

Complementary colours which are seen by transmitted light are obtained when dichromated colloids are used, due to the absence of the absorbing silver deposit: the colours appear in the wet state due to the formation of differentially swollen layers. Lippmann also disclosed the production of complementary colours by transmission, by precipitating silver iodide in place of the layers of silver. In these phenomena lie possibilities of contact printing processes.

The grainless plates are developed in pyro, glycin, or preferably amidol. Examples:

A	Pyro 1%	100 cc
	Water	350 cc
	Ammonia S.G. 0·920	20 cc
	Potassium bromide 10%	100 cc
B	Amidol	0·05 g
	Sodium sulphite	0·3 g
	Water	10 cc
	Water	800 cc

Development time: 10–30 secs.

Some writers prefer to underdevelop and intensify with mercury.

494. Additive processes

The additive synthesis of colour images is carried out, as we have seen, by projecting on to a screen with several projectors, the different separation positives each fitted with a colour filter. Thus for a three-colour process, the subject is photographed three times on three different plates through three separation filters, respectively blue, green and red. The negatives are developed and three positives are printed and placed in three projectors: the positive from the blue filter negative is equipped with a blue filter, the green filter positive with a green filter, and the red filter positive with a red filter. This method is purely experimental.

For practical results, the three (or other number) images must be on the same film, such as a *cinematograph film*. Now images made with different lenses have *space parallax* as they do not see the objects from the same angle. On the other hand, images taken successively through the same lens show a moving subject in different positions and result in time parallax. This makes it impossible for the three separate images to correspond exactly and it follows that for one reason or another there will be *colour fringes* around the objects on the screen.

These considerations have resulted in a host of optical combinations, more or less ingenious, but usually very complex, without fully achieving the desired result in spite of frequently excellent colour reproduction. The complication of a multiple lens is a serious practical obstacle, for it demands constant supervision and accurate adjustment to register the images. Furthermore it is necessary to modify all projectors and there is *a great loss of light*.

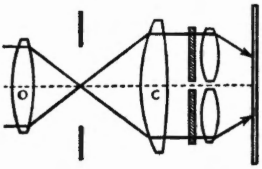


FIG. 103. Scheme of process of the Roux camera (longitudinal section).

It is not possible for us to describe the apparatus for additive taking and projection which has been thought of, for this would occupy the whole of this volume.(9) They have but a theoretical or historical interest. We will only note those which have actually been used.

Francita process. Three separation images are formed in the space of one normal image using two lenses and two mirrors at 45°: the green and blue images, for example, are exposed together. The film is then moved half a frame and the red separation is exposed, with time parallax.

Roux process. The image formed by a normal lens is returned to infinity by a collimating lens. It is received and separated by four smaller secondary lenses arranged in a square (Fig. 103).

It should be said that in the majority of additive systems, the single images are necessarily small, for the whole set must occupy the space of an ordinary image. This results in an appreciable loss of definition.

We would finally note, as a memoir, the attempt made formerly by Wood, to replace the colour filters by three defraction gratings, each with a different number of lines.

495. Lenticular films

The process using lenticular films is an *additive system* using a film with a *goffered* support. Invented by Berthon and applied by Keller-Dorian, it has been taken up by many workers, because of its apparent simplicity.

The principle is as follows: the film support has on the reverse side a multitude of grooves or hexagonal points having the shape of a honeycomb resembling miniature lenses (Fig. 104). The foci of these lenses are at the gelatin face (coated with panchromatic emulsion). The film embossed in this way is placed in the camera with the embossed face to the lens. This is equipped with a filter divided into three horizontal regions red, green and blue. The rays of each colour meet the film at different angles which produces three sets of contiguous separation images for each point or corrugation (Fig. 105). In projection the light passes the developed and *reversed* film along the same route in the opposite direction.

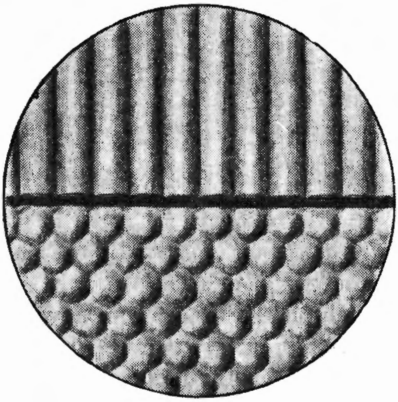


Fig. 104. Lenticular, ridged and hexagonally embossed film.

To emboss the film an engraved cylinder is used which is itself obtained mechanically with tools of special steel or, better, of diamond. The corrugations are easier to produce than the dots and have been generally adopted. The dimensions of the embossed elements are about 30 μ or 35 lines/mm.

Lenticular films need strong projection light and this is a serious objection. Furthermore, there is a double loss of definition, first by each separation image not occupying the whole frame, and secondly by the diffusion which inevitably takes place at the corrugation borders, this being great as the shape of the latter is never perfect.

As the embossing is not geometrically perfect, accidental variations in the scene are produced, and overlaps, which result in *colour fringes*. Furthermore, as each element is formed by a simple lens, *chromatic aberration* is present which reduces the sharpness of the image.

There are also certain difficulties in printing copies. There is generally a further loss of saturation over that already present in the original. To avoid moiré patterns, a prism must be turned between the two lenses of an optical printer, to oscillate the images to a degree equal to the corrugations.

Lenticular film was at one time used in 16 mm for the old *Kodacolor* and *Agfacolor* processes.

496. Colour screen processes

The use of coloured reseaus(10) is mainly applicable to still work, for, on projection, the pattern appears on the screen.

A plate or film support is covered with a *reseau* or *mosaic* of minute filters coloured blue, green and red. Over the reseau, which is protected by a layer of varnish, is a panchromatic emulsion coating. The plate is exposed through the base and receives the light via the reseau which in this way analyses the light. For example, the red rays are stopped by the blue and green elements but are transmitted by the red ones; they can only effect the emulsion and give a deposit of silver behind the latter. The developed plate is therefore opaque before the red elements, but if reversed, it becomes, on the contrary, transparent in these precise areas and opaque before the red and green ones: light can only pass through the red elements, and the plate therefore appears this colour. When the plate is transparent to both red and green together, yellow is formed as the eye cannot see them separately.

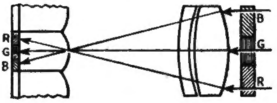


FIG. 105. Principle of colour analysis on lenticular film.

The reseau can be made up of an *irregular mosaic* of independent elements formed of starch grains, shellac, powdered glass or celluloid chippings; or it can be a *geometric screen* obtained typographically or photographically. Generally the regular reseaus have a finer pattern than the mosaics, as in the latter the single grains tend to form *clusters* which has the effect of producing, in practice, elements which are 5–10 times larger than the individual grains.

Lumière Alticolor.(11) Lumière Alticolour film is the successor to the widely known *autochromes*. It has a coloured mosaic made up of potato starch grains of a few thousandths of a millimetre. The grains are sorted, sifted and divided into three lots, and dyed respectively blue, green and red. They are then mixed to form a grey powder which is spread out on to a tacky varnish covering the film. The excess starch is blown off with a current of air so that only a single layer of grains remains (formerly the interstices were filled in with finely divided carbon) and the film is then compressed in a calender. The mosaic produced in this way is protected by an impermeable varnish with a refractive index near that of starch, after which it is coated with a thin layer of panchromatic emulsion of constant thickness. The reverse side is coated with a layer constituting a correction filter.

The exposed film is developed, reversed and fixed. Because of the low transparency of the starch mosaic the exposure time is much greater than with a normal material, and a strong light is needed to examine the transparency.

497. Dufaycolor film

The English Dufaycolor film succeeds the Dufay Dioptichromes made in 1908: it has a geometrical reseau formed of red lines alternating with blue and green squares. The blue squares are bigger than the green to balance the colour transmission of the film with the sensitivity of the panchromatic emulsion (Fig. 106). The width of each line is about 1/40th mm.(12) The reseau is made with wide band transparent dyes, each transmitting half the spectrum, which enables short exposures to be made, three times greater than for a very fast film. For example, in bright sunlight at f 6·5, 1/100th sec. is enough.

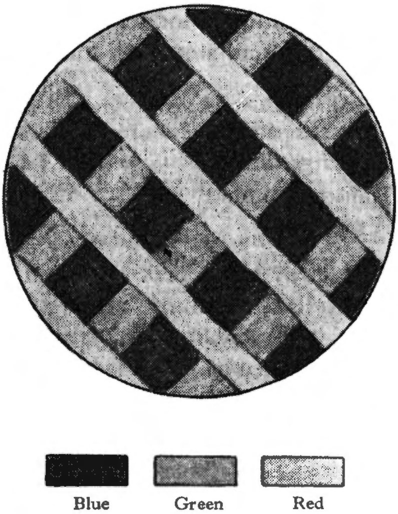


FIG. 106. Dufaycolor reseau.

The lack of saturation of the reseau colours, however, produce sensitivity to variations in the colour of the taking or viewing light which can modify the colour rendering.

The film is made by first coating the base with a layer of green collodion. A finely engraved steel roller then prints a series of greasy ink lines on the collodion, about 20 to the millimetre. After drying, the film passes into a bleaching bath which bleaches the parts not protected by the greasy ink. These areas are then dyed blue, and the greasy ink is removed in benzene. The film is then printed again with a series of lines at right angles to the first; after decolorizing the unprotected parts, these are dyed red. The red lines obtained in this way are not as clearly defined as the blue ones.

The reseau is then coated with a protective synthetic resin varnish a few μ thick, containing a substratum. Over the varnish, a low gelatin content emulsion is coated in a very thin layer, so that the reseau elements can be completely blocked by the corresponding silver deposits without loss by diffusion $R = \frac{\text{gelatin}}{\text{Ag}} = 0{\cdot}9 - 1.$

One of the proposed processing techniques is:

The exposed film is first desensitized by treating for two minutes in 1:2000 phenosafranine and rinsed. It is then developed for 2½–3 minutes in complete darkness, then by the weak light of a Wratten No. 3 safelight for a total of 4–6½ minutes. The image must be hard and the shadows full of detail. The developer is a metol-hydroquinone-thiocyanate bath (para. 161). Development is stopped with an acetic acid stop bath followed by a 2-minute wash. It is hardened in:

Formalin 40%	28 cc
Caustic soda	1·5 g
Sodium sulphate	150 g
Water	1000 cc

A two-minute wash is followed by reversal for 4 minutes in a bath containing 3 g permanganate and 10 cc sulphuric acid (S.G. 1·87) per litre. After washing for 2 minutes, it is cleared in 2·5% bisulphite, again washed and exposed for 1 minute at a distance of 1 foot from a 100 W lamp and redeveloped in an M.Q. developer.(13) After rinsing it is fixed for 3 minutes in a 360 g.p.L. hypo solution containing 12 g potassium metabisulphite. It is finally thoroughly washed.

Because of the low gelatin content $\gamma\alpha$ is quickly reached and the contrasts of the three-part negatives are substantially equal.

For optical printing of cine prints a mercury cadmium arc light source can be used, filtered by a solution of didymium chloride, giving three emission bands at 436, 546 and 643 mμ which enables each filter to be affected without interfering with the others (para. 514). The original is developed to a negative; it is therefore in complementary colours. Spencer has shown that by replacing the thiocyanate by hypo, as the solvent in the developer, development takes place nearer the reseau, at the bottom, thereby diminishing the loss in saturation of colours by better blocking of the coloured elements. A metol-caustic soda-hypo developer is used for this.

To avoid a moiré pattern produced by combining the negative and positive reseaus, the negative reseau has its red lines at 27° to the edge of the film whilst the red lines in the positive reseau are at 45°. This produces, nevertheless, an inevitable colour dilution because of the overlapping of the negative elements of one colour by the positive elements of another colour.

498. Other screen processes

The manufacture of geometrical reseaus can be advantageously carried out photographically: with dichromated glue or gum as in the old Warner-Powrie process, dyeing in a series of three vertical differently coloured bands, or better, by colour development of a very fine emulsion exposed under a screen (process disclosed in 1914 by Fischer and Seigrist). The unprinted portions are developed after exposure in another colour.

Finally we would mention the *Finlay process* in which the geometric reseau was independent of the sensitive layer. It was provided with two black supplementary reseau screens for the separation of colours, then the printing of separation positives for use in photogravure. A fourth reseau, this time coloured, called 'visual', enabled the colour rendering to be controlled when placed in register on the developed plate.

1. One can, in principle, imitate a colour with a mixture of several primaries, *whatever they are*. It is a simple question of proportions. (See colour mixtures.)
2. For R. M. Evans (*J.O.S.A.* 1943, 579) the actual value of the colours is of little importance, only their brilliance and apparent chromaticity matter, the colours being more plausible than exact due to the adaptation of the eye. However, in our opinion, spectrally correct images alone are satisfactory under all the varied illumination conditions, even though they do not match the original exactly. Brilliance plays an important, but secondary, role.
3. Zeiss–Ikon F.P. 896, 571–2 (1943).

3b. According to McAdam, the additive synthesis by projection is perfect if the three primary radiations are simple.

4. Instead of dye, ferric ferrocyanide (Prussian blue) or ferrous ferricyanide (Turnbull's blue) can be used precipitated in gelatin. These pigments are opaque to red. They must be combined with a violet or magenta dye.
5. Disclosed by Poitevin and taken up by Colson and Saint-Florent. The latter tried collodiochloride papers.
6. *Phot. Ind.*, 1932, **30,** *No.* 8.
7. See Thovert: Photographie en Couleurs (Doin, Paris).
8. An analogous phenomenon to the iridescence of mother of pearl.
9. See, on this subject, the works of Wall *History of three-color photography* and Friedmann *History of color photography* (American Photography, Boston, Mass.) (Translator's note: also Cornwell-Clyne *Colour Cinematography* Chapman and Hall, London).
10. Used by Joly in 1893 and studied by Ducosdu Hauron and Bercegol.
11. For Autochrome processing see the detailed operations given by Cuisinier in *Leçons de photographie* 2nd Vol. (P. Montel, Paris).
12. This fineness is inadequate for large screen projection.
13. 4 mins. in the following bath: methol 1 g, Hydroquinone 5 g, sulphite anh. 50 g, carbonate anh. 20 g, bromide 1 g, water to 1000 cc.

Chapter XXVIII

SEPARATION NEGATIVES FOR COLOUR REPRODUCTION

499. Reproduction methods

The subtractive colour reproduction processes give images which are themselves coloured, and which can be examined directly, without any aid. These are the only ones at the moment which have any practical application, for no projector modification is necessary, and frequently, ordinary cameras can be used. On the other hand, the subtractive processes are very critical to operate and continuous rigorous control is essential in all stages of production.

There are two distinct stages in a subtractive process, which must not be confused: (*a*) making the separation negatives on one or more bases; (*b*) preparing from these negatives a positive, each element of which is necessarily coloured to give the final print.

The *separation negatives* are either on separate supports or are superimposed on a single support.

When *separate negatives* are used, they are simply developed to black and white images following normal practice. If the emulsions are *superimposed on the same support* they can be developed to silver or to colour images. In the first case, special techniques are used to separate the layers. In the second, more usual case, the three layers are simultaneously developed to colour images; frequently separate separation positives are obtained from them.

For amateur cinematography where only one copy is required, the first superimposed images on a single base are *reversed* to give a colour positive.

Generally, any copying operation results in a change, however small. Also, any *conversion of a silver image to a colour image* brings about a change which is often considerable. The obvious result of this is that the copy is always inferior to the original, particularly when the original is itself coloured or when a coloured intermediate is used. Furthermore, the *control of the primary separation images* is not as simple when the three images are developed separately, as it is when three superimposed layers are developed simultaneously. The difficulty of balancing several systems as unstable and variable as photographic emulsions is well known. The most faithful colour reproduction is obtained with direct separation negatives developed to black and white with no colour processing, and with the minimum of intermediate stages, and avoiding the use of a colour original.

Despite this, the method which is most widely used to obtain negatives is to use several superimposed layers on a single support, which are simultaneously developed by a colour developer. The reasons for this choice are the convenience—particularly the use of a normal camera—demanded by the user. They are not justified by the mediocrity of the results—with a few exceptions due to chance—which is out of proportion to the enormous technical means which are involved.

500. Direct separation negatives

The best and simplest way to produce separate separation negatives is to make three successive negatives in a camera using a blue, green and red filter for the three exposures (see para. 489). The three negatives are developed to the same gamma and can be used for the preparation of colour prints. The exposure time must be adjusted for each filter so that the whites and greys have the same density on each negative.

Unfortunately this method can only be used for static subjects. Where there is movement, and for snapshot exposures in general, more complex methods must be used:

(*a*) Recording on multipacks (or superimposed films), particularly bipacks.
(*b*) Use of a beam-splitter camera.

501. Bipacks and tripacks

The problem of obtaining separations for *two-colour* work is easily solved by the use of bipacks (para. 490). A bipack is made up of two separate films held together during exposure, face to face (Fig. 107). The front ortho film records the blue-green and the rear panchromatic film records the orange-red. The orthochromatic emulsion is coated with an orange-red filter layer to prevent the blue-green light from affecting the panchromatic emulsion. The front emulsion is as thin as possible, so that its light absorption is kept low, and it is essential that perfect contact between the two films is maintained during the exposure. After development and fixing, the red filter layer is bleached in fresh 2% hydrosulphite. Resolution of rear element: 20 lines per mm. Lighting necessary at f 2·8: 3000 lux (or 300 ft. candles).

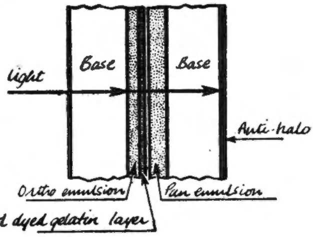


FIG. 107. Schematic cross-section of bipack.

Bipacks are used for trichromatic analysis together with a third film (for the green) in beam-splitter cameras, which will be considered later.

Tripack. An ordinary tripack was produced by Du Pont under the name 'Tripac'. It was made up of an assembly of three separate films: an ordinary film and an ortho film face to face, with a pan film behind the resulting bipack. The ordinary film was dyed yellow for the first filter, and the rear face of the ortho film was dyed red for the second filter. The definition of the rear film—the red record—was very poor and the system was only applicable where reduction prints were made.

Note on the term 'tripack'. As L. P. Clerc has remarked to us, the word tripack has more than one meaning and can lead to some confusion, therefore it is desirable to give a more precise definition: *Tripack* as designated in the present chapter is a combination of three emulsions on *separate supports* and kept in intimate contact. The prefix mono-, bi- or tri- therefore indicates in this case the number of separate elements which are combined; this is in keeping with the term 'bipack' by which is understood the use of two films with their emulsion faces together. A 'monopack' will therefore be a single support having several superimposed emulsions.

This is not a universally accepted definition, and the term 'tripack' is used to describe three superimposed emulsions on a single support (which we, on the contrary, describe as a 'monopack'). A paradoxical case is the Du Pont 'tripack'—S. T. Tripac—which will be described later, having three emulsions on *two* separate supports. It can therefore be assumed that in this case it is the number of emulsions and not the number of supports which determines the meaning of the terms 'tripack', 'bipack' and 'monopack'. Our personal preference is for the former system, which covers the current use of motion picture bipack on two separate supports.

502. Beam splitting systems

The production of direct separation negatives, on separate bases using beam splitting systems is indisputably the best possible method, and it is regrettable that, as far as motion picture work is concerned, this method is being abandoned in favour of colour development films.

For colour photography there are many types of camera which will simultaneously produce three separation negatives: they may contain two lenses behind a semi-reflecting mirror, the beam emerging from one lens being again divided into two, as in the Cunningham camera; or a single lens may be used with two differently oriented partial reflectors behind it; for this purpose, pellicle mirrors which do not produce double reflections are used, made of thin pellicles stretched on a metal frame.

For cinematography a parallax-free optical system like the *Technicolor* one can be used: the light passed by a *single lens* is divided in two by a *cube* whose diagonal is a semi-reflecting mirror (by partial silver or gold deposition). One of the two beams passes through a yellow or green filter to expose an *ortho film* and give the green negative. If a gold partial reflector is used the green filter is unnecessary due to the dichroic characteristics of the reflector, which transmits green. The second beam exposes a *bipack* or system of two films assembled emulsion to emulsion (Fig. 108). The front non-colour-sensitive film records the blue; its emulsion face is coated with a red-dyed gelatin layer which filters out the unwanted blue and green and transmits the red to the rear panchromatic film which records it.

Although the principle is simple, in practice very exact adjustment of the optical and mechanical components is necessary if the three images are to register perfectly. The complete camera is quite heavy due to the presence of three films passing through it simultaneously, with all the necessary accessories. The back-focus of the lens must be sufficiently great to enable the dividing prism to be accommodated. The tolerance of positioning the two elements must not exceed ·0001 inch.⁽¹⁾

A camera using only two films as a bipack for three-colour analysis was described in Warner Bros. U.S.Ps. 2,353,797; 2,366,578 and 2,374,015. The bipack is moved two frames at once; it forms a loop and passes through a second gate for the third record to be exposed in the unexposed gap. Any camera for additive work will provide separation negatives if the parallax is negligible. *Multiple lens systems with fixed dividing mirrors* in front can be used, or rotating mirrors with a single lens as in the Brewster camera.

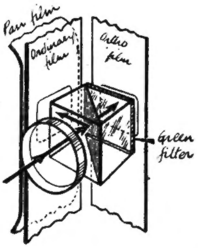


FIG. 108. Principle of the Technicolor type beam-splitter.

Instead of recording the three images on separate films, they can be brought together as a number of small images occupying the space of a normal frame on a single film. Many special lenses for additive synthesis can be used for this. We would mention, among others, the Roux, Cristiani, Opticolor, Italcinecolor and Dugromacolor.

As far as *cartoon films* are concerned, the problem of movement does not occur. The three separation negatives can be made successively on the same film, the camera being equipped with a rotating filter disc, carrying the three colour filters. From this original negative, the individual separations can be printed on to separate supports.

503. Preparation of separation negatives from images in superimposed layers, developed but not coloured

From the preceding paragraphs, two features should be retained.

1. Making direct separation negatives in a special camera gives results of the highest quality as the images are simply developed to black and white.
2. The use of a single film with superimposed layers is more convenient in practice than a cumbersome camera which requires careful adjustment.

It is, however, possible to combine the advantages of the two methods.

In 1933 the writer perfected a method of preparing separate separation negatives from a single original pack of three superimposed layers which was only developed to black and white.(2) With it, an ordinary camera could be used, and undistorted separation negatives could be obtained.

A *cellulose triacetate* film base is coated on one side with three superimposed emulsions which are separated by a *semi-permeable cellulose lacquer*, that is, one which is permeable to water, but not to the large developer molecules. The lacquer layers are extremely thin. Before coating the next emulsion, each of these layers is treated with a special substratum which brings about *limited adhesion* of gelatin so that development can be carried out. The emulsions are colour-sensitized and filters are included in the usual way.

The film is exposed in an ordinary camera, and is developed normally. As the two lower emulsions are protected by the lacquer, only the upper layer—the blue record—is developed. The fixed, washed and rapidly dried film is then *optically printed with infra-red* radiation which has no effect on the underlying emulsions: a blue separation positive is obtained.

The layer carrying the first image is then destroyed in dilute hypochlorite, rinsed, and after drying for two minutes is treated in a mixture of *amyl acetate and ether*. The excess is removed and the film passes into a drier and the surface is treated with an *alcohol-acetone* mixture applied by roller. It is then ready for second development. These operations are carried out on a single continuous machine.

During the permeating treatment, the lacquer is not removed, but is made porous. The reason for the limited adherence of the emulsion to the varnish is now apparent: too much adherence would result in a gelatin skin which would prevent the action of the amyl acetate.

The second development, similar to the first, gives the green record negative which is printed by the method already given. The same sequence of operations is carried out, and then the red record is developed, so that finally three separation positives are obtained. If the printing process requires negatives, these can easily be prepared.

There are two reasons for using a triacetate base: firstly, it is less liable to stretch and shrink during processing, and secondly, the film can be treated in the amyl acetate bath without danger of the base dissolving.

The same process can be applied to a bipack, the rear film containing only the red record.

504. Layers separable after development

Several emulsions superimposed on the same support but separated by layers with controlled adhesion can be separated after *development of the pack* in certain cases. For this method to be practicable, the separating layers must be permeable to the processing solutions, and retain their adhesion, but this adhesion must be nil in pure water. Austin and Coote disclosed the use of regenerated cellulose for these layers.(3) Layers of polyvinyl acetophthalate which is soluble in water, but not in alkaline sulphite solutions can also be used.

S.T. Tripac. The Du Pont S.T. Tripac is actually a *bipack* whose front element contains two layers separated by a polymer which is soluble in water but not in processing solutions. The layer next to the front film base is not sensitized and is dyed yellow for use as a filter in front of the following green sensitive layer. The pack is balanced for 3200°K light, to which it has an A.S.A. index of 12. The daylight speed index is 8 with an orange 85B filter.

The two films are developed together for 10 mins. at 20°C in: water to 1000 cc, metol 1·5 g, anhydrous sulphite 60 g, hydroquinone 15 g, potassium carbonate 64 g, potassium bromide 4·5 g. Stop bath: water to 1000 cc, borax 120 g, sodium sulphate crystal. 10 g for 30 sec. Fixing 10 mins. in a hardening fixer. The front two layer film is immediately immersed in a fresh stop bath then *stripped.*

The excess solution is removed, and the film is agitated for two minutes in a transfer solution which reduces swelling: water to 1000 cc, glacial acetic acid 20cc, 32° Bé aluminium chloride solution 7 cc, 70% alcohol 800 cc. It is then rolled into contact with a gel coated support and left for two minutes. By pulling off at an angle, the two layers can be separated, the green record being transferred to the new support. It only remains to wash the three films for 20 mins. and dry to produce the three separate separation negatives $\gamma = 0{\cdot}8$.

The principle of the S.T. Tripac is based upon the patent of R. S. Potter, applied for in 1936(4) which disclosed the use of soap base intermediate layers.

Chromart-Tricolor Process. Fraunhofer and Coote have worked out a process for separating the developed and fixed layers by *diffusion-transfer* (see para. 406). The silver image of the outer layer is rehalogenated and transferred to a gelatin-coated film containing cadmium sulphide development centres. This layer and the separating layer are of soft gelatin which can be washed off in warm water to uncover the middle layer (green record) and enable it to be transferred to another support. The red negative remains after elimination of the second layer. Transfer takes 30 seconds and is carried out on a metal pin belt. Total processing time—2 hours.(5)

505. Layers separable before development

Three superimposed emulsion layers separated by a substance which is only slightly adhesive, such as methyl cellulose(6) can be successively separated when wet *before development* by *mechanical transfer* on to subbed films.

This process was studied by Capstaff and culminated with the separable layer motion picture film, Eastman 5249,(7) made up of three emulsions in very thin layers respectively sensitive to blue, green and red, and separated by intermediate layers.

The exposed film is treated in pure water at 21°C for about ten seconds, then applied to the subbed film after registering the perforations. The adhesion of the outer emulsion is complete after a minute on a stretching drum moving at a speed 5% greater than that of the film, which is 30 ft. per minute. After separating and drying, the transferred layer is developed. The same operations are carried out on the second layer.

In this way the blue and green separate records are reversed compared with the red record. The thin layers necessarily give very flat images.

The separation of the layers is of course carried out in the dark. It is a very critical operation.

506. Separation by additive methods

The additive systems which can, in practice, give separation negatives are the colour mosaic films or plates and lenticular films (see para. 495–498).

Coloured or mosaic reseau layers. Coloured mosaic layers have been used for a long time for the preparation of separation negatives for photogravure with distinctly better results than those obtained from subtractive colour originals. This is due to the fact that the individual images are free from unwanted absorptions (as is the case with subtractive images) and need no correction by masking.

The transparency with a mosaic (*Lumiere Alticolor*) or with a colour reseau (*Dufaycolor*) is used for printing the three separation negatives by contact onto fine grain panchromatic plates or films, the light in each case being filtered by sharp-cut narrow band filters. Dufay supply for this purpose the filters 1S, 2S and 3S which are respectively red, green and blue, and whose transmissions are 600–700, 530–575 and 400–450 mμ. To achieve correct reproduction the transmission band of the filter must not encroach upon the transmission of the other two elements of the reseau. The loss of colour saturation due to the presence in the final print of a triple screen which is not registered, since it is always diffused, is practically negligible.

Finlay plates were also used for photomechanical reproduction (see para. 498).

The preparation of separation negatives for motion picture work gives poor results due to the non-coincidence of the screens, which produces an effect of 'rain' formed of small spots on the positive colour print. The writer has obtained better results with a bipack made up as follows:

A front film with a reseau is in contact with a rear red sensitive element. The reseau is made of a series of vertical (or horizontal) lines in *yellow* and *magenta*, produced optically on a very fine grain film followed by colour development, with a width of 1/100 mm. The reseau is coated with a thin layer of an orthochromatic emulsion which is supercoated with a layer of red gelatin. The reseau film records the blue and green whilst the rear element records the red. The system gives clear images with only slight loss of saturation. It is possible to increase the width of the yellow lines (corresponding to the green image) at the expense of the magenta ones whose corresponding image is the less important yellow. The two films can be used directly as colour separation negatives merely printing the reseau film with green and blue monochromatic light onto colour sensitive positive emulsions.

Use of lenticular film. For cinematography, many proposals have been made for the preparation of separation negatives from images on lenticular film. The reduction of the total area of the actual image to a third or a quarter and the diffusion resulting from the diffusion of the lenticular element results in poor definition and appreciable loss of saturation which greatly reduces the quality of the results.

Results can be improved by using a bipack with a lenticular front film and a panchromatic film. The lenticular film records the blue and green, and two separation negatives on normal base are made from it.

507. Complementary colour negatives

The use of complementary colour negatives for the printing of positive prints on paper or motion picture film is the most widely used method, although it is subject to many faults.

A negative film for direct development to a complementary colour image is made up of *three superimposed emulsion layers* each separated by a thin gelatin layer (Fig. 109): these are, starting from the base, a red sensitive emulsion, a green sensitive emulsion and a non-colour-sensitized emulsion sensitive only to blue. The 'red' emulsion is more sensitive than the 'green', which in turn is more sensitive than the 'blue' to compensate for the loss of light absorbed by the overlaying layers.

The non-sensitized emulsion receives the light first; it records the blue, which it absorbs and allows the green and red to pass on. To prevent the passage of blue light which would affect the underlying emulsions, a yellow filter is included, either in the blue emulsion itself or in the gelatin separating layer.

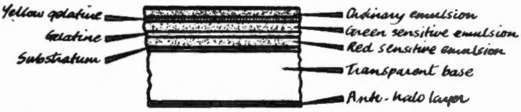


FIG. 109. Multilayer-film for colour photography (schematic cross section).

The following orthochromatic emulsion records the green, and transmits the red which is recorded by the third emulsion, next to the base. If the latter emulsion is only sensitive to red and not to green, it is unnecessary to include a red filter in the second emulsion; in the opposite case the excess green is absorbed by a red filter dye in the green layer or in the separating gelatin.

The *thickness* of each layer is about 6 μ. That of the yellow layer about 2 μ. The second separating layer is 0·5–1 μ, but is often omitted. The rear anti-halo soluble layer is less than 1μ. It can be replaced by a grey dyed base.

The colour sensitivity maxima of the three emulsions are generally at about 450 mμ for the blue, 555 mμ for the green and 655 mμ for the red. It is, however, beneficial to shift the green and red maxima towards the shorter wavelengths (see para. 489): 530 mμ for the green and 630 for the red.

Colour couplers. Each emulsion of the negative monopack contains a colour coupler—or former—which differs for each layer: the outer blue sensitive emulsion contains a *yellow coupler*; the middle green sensitive emulsion a *magenta coupler*, and the bottom emulsion, a *cyan* (or blue-green) *coupler*. The three colours do not appear until the layers have been developed in a *colour developer*, which produces dyes at the same time as the silver image (see Chap. XXIX). The image in each layer is developed to a colour complementary to the colour sensitivity. The dyestuff absorptions are: yellow 440 mμ, magenta 540 mμ, cyan 660 mμ.

As the emulsions are so thin, the maximum amount of silver which can be developed is much less than with an ordinary emulsion. Fortunately the tinctoral strength of the dyes is high, 4–5 times that of the equivalent silver image, which enables the required maximum density to be obtained.

On the other hand, the thin layers result in *a very small exposure latitude*. The image is recorded on a short curve, necessarily close to the threshold. It is therefore impossible to under expose without losing shadow detail (50% is the maximum permissible under-exposure) and it is not possible to over-expose without losing the highlights: maximum 100%.

508. Sensitivity of colour films

The *relative sensitivity* of the three layers differs depending on the light for which the material is balanced—artificial light or daylight. In Chapter XXVI we saw that the emission spectra of sources of different colour temperature vary: artificial light, rich in red, needs a bottom red sensitive emulsion which is less sensitive than a daylight material (para. 477). This is why commercial colour films are generally made in two types: type A for photography in daylight and type B for artificial light work. Some negatives are, however, only made in one type which can be used both in daylight and artificial light (Eastman, Gevaert, Ferrania, Tellko) provided that a compensating filter is used with one of the two sources. Thus a film balanced for daylight (Ferrania) will be corrected for artificial light with a bluish filter; a film balanced for artificial light (Eastman) will be corrected for daylight with a yellowish filter. If the sensitivities of the blue and red emulsions are adjusted to a mean value, the film can be used without filters with any light source, correction being made during printing (Gevaert, Tellko).

The *total sensitivity* of a multilayer film is about one-tenth that of a high-speed ordinary film, giving an ASA index for daylight of 10–16 and 16–10 in 3400°K illumination. Average speed in degrees DIN: 13/10, and Scheiner 23°. This speed has recently been increased. For example, Eastman Color 5248 has an ASA index at 3400°K of 32, and 24 in daylight. The latter figure, although obtained with a correction filter, is still greater than that of a normal film in daylight, which is 16.

Contrast. The similarity of the characteristic curves of the three emulsions must be as great as possible otherwise the colour balance will be ruined. If one emulsion has a higher contrast than the other two, it will result in a colour cast of the colour to which it is sensitive, above the cross-over of the characteristic curves, and of the complementary colour, under this point (cf. Fig. 88, para. 479). It frequently happens that the gammas of the three emulsions are all different; this results in colour inaccuracies which are impossible to correct. In this case, the curves can cross at three points which is a sign of complete colour unbalance. The unequal contrast of the three emulsions can be due to a manufacturing defect, incorrect exposure or faulty development.

The gamma of each layer of a colour negative film should be 0·7. Some manufacturers prefer a higher contrast, about 1, however, to avoid loss in saturation—Ansco 843 for example. On the other hand, if there is a contrast loss in one of the images during printing, the contrast of the original is suitably adjusted. Thus in the quoted example, the contrasts are: blue 1·15, green 1·00, red 1·00.

Reciprocity failure. Because of reciprocity failure (see para. 207) a colour film must not be exposed to light intensities which differ greatly from those for which it was designed. Not only does a substantial change in exposure time (for equal exposures) produce a general variation in sensitivity, it changes the relative sensitivity of the individual layers of the system, necessitating the use of correction filters. This happens when electronic flash is used, whose exposure time is very short (para. 458), making it necessary for the manufacturers to give correction factors. A short exposure results in under-exposure which is particularly noticeable in the red, giving a blue cast.

The production of multilayer materials for direct colour photography involves problems of manufacture and development, which make consistent results chancy.

In manufacture, the simultaneous production of three emulsions which closely conform to given standards is very difficult to achieve. It is also difficult to coat them to a constant thickness. With drying faults, the production waste can be as much as 30%.

509. Resolving power

The resolving power of a colour film is relatively high. The figures given by different writers do not agree very well, but a total resolving power of the order of 50 *lines per mm* can be counted on, compared with a fast negative film which will give 65 lines. However, the three layers do not have the same resolving power. That of the outer blue recording layer is by far the highest; that of the bottom red record is naturally the lowest. Now the most important are the middle and bottom layers which give the magenta and cyan images.

The figures obtained by Eggert and Grossmann(8) are:

		Lines/mm		
		Yellow	*Magenta*	*Cyan*
Negative films:	Agfacolor	80	33	27
	Eastman color	118	45	30
	Gevacolor	120	40	30
	Telcolor	120	43	31
	Ferraniacolor	120	45	32
Reversal films:	Agfacolor	120	55	38
	Anscocolor	122	60	33
	Ektachrome	80	45	30
	Kodachrome	120	75	52
Positive films(9)*:*	Agfacolor	100	42	30
	Eastman color	37	200	100
	Du Pont color	35	190	52

The adoption of wide screens necessitates the highest possible resolving power. Gevaert have been able to increase it by 50% using a negative film coated on both sides.(10) The green and red layers are superimposed on one side whilst the blue-sensitive layer is on the opposite side. However, an optical beam splitter must be used for exposure, which loses the great advantage of a negative colour process.

510. Reversal films

So far, primarily the characteristics of negative colour development films have been described. These films are used for the printing of *positive colour prints* on paper or 35 mm motion picture film.

Another group includes the *reversal films* intended to give *positive colour transparencies* or sub-standard motion picture films. Here the colour development process has a great advantage over the preceding ones, enabling a single copy to be simply and quickly obtained. They have, furthermore, a higher quality as the problems of printing are non-existent, provided that they have received correct treatment, for faults can only be corrected by masks, due to the same absence of a printing stage.

The reversal films, like the negative ones, have three superimposed layers. However, as they are necessarily developed to a *higher gamma*, 1·6–1·8, the silver content of the layers must be increased, which results in a greater thickness, and hence a generally lower sensitivity due to the increased light absorption by the upper layers.

The colour development reversal films are of two types:

(*a*) *Reversal films containing non-diffusing colour couplers: Agfacolor reversal* and *Ektachrome* are two examples of different types.

(*b*) *Reversal films not containing couplers.* These are used in the developing solution. Typical example: *Kodachrome* used for sub-standard cinematography and miniature work.

All of these films will be described in detail in the following chapter.

It is, of course, possible to make copies of these colour transparencies. Because reversal makes corrections difficult the results are inferior to those made by the negative-positive method.

511. Constitution of a colour development film (example)

Referring to Fig. 109 of para. 507, the outer layer of the colour development film is not colour sensitized as it only records the blue. The middle layer contains a *colour sensitizer* for the green, and the bottom layer a red sensitizer (these sensitizers will be studied in the 4th part). For practical reasons, the sensitizers are not necessarily the same for negative, reversal or positive films; for use in artificial or daylight, or for copying.

The same is true of the couplers, whether they are incorporated or not.

By way of example, we include a table of the colour sensitizers and corresponding couplers for the three layers of *Agfacolor* films.(11)

Film	Top Layer	Middle Layer		Bottom Layer	
	Yellow coupler	Green sensitizer	Magenta coupler	Red sensitizer	Cyan coupler
Negative					
Daylight	a	A+B	c	E	f
Electric	a	A+B	c	E	f
Reversal					
Daylight	a	A+C	c	F	f+g
Electric	a	A+C	d	F	f+h
Duplicating	a	A	d	G	f+h
Positive	b	A	c	G	h
Paper	a	D	e	H	h

Colour sensitizers (see 4th part):

A	green	mesoethyl-phenyloxacarbocyanine (ethyl thiocyanate).
B	green	mesoethyl-phenyloxadimethylthiacarbocyanine (ethyl perchlorate)
C	green	dichlorimidazoleselenacarbocyanine (acetoxypropylthiocyanate)
D	green	mesoethyl-phenyloxacarbocyanine (propyl nitrate).
E	red	Complex merocyanine: hydronaphthothiazole + diphenylthiazole
F	red	Complex merocyanine: methylethoxybenzthiazole + diphenylthiazole.
G	red	Complex merocyanine: lepidine + dimethylbenzoxazole.
H	red	chloroquino-dimethylbenzthiacarbocyanine (ethiodide).

Couplers (see para. 541)

a	yellow	p′-stearoylamidobenzoylacetamido-3 : 5-isophtalic acid.
b	yellow	p′-anisylacet-o-methyloctadecylamino-p-carboxyanilide.
c	magenta	1-sulphophenoxyphenyl-3-stearyl-5-pyrazolone.
d	magenta	1-sulphomethylenephenyl-3-stearyl-5-pyrazolone.
e	magenta	octadecenylsuccino-(p-cyanaceto)-anilide.
f	cyan	1-hydroxy-2-naphthoyl-0-methyloctadecylamino-anilido-4′-sulphonate.
g	cyan	1-hydroxy-2-naphthoyl-α-octadecyl-naphthanilido-4-sulphonate.
h	cyan	1-hydroxy-2-naphthoyloctadecylamido-4-sulphonate.

These sensitizers and couplers are not the only possible ones, there are many others.

Important note. The developed dye, in each layer of the negative, must have an absorption maximum corresponding to the colour sensitivity maximum of the corresponding positive layer. It is not essential for it to form an image in natural colours, for it is only an intermediate stage. The coupler in the positive layer must, on the contrary, give a dye of the correct subtractive hue.

The couplers are introduced into the emulsions in 3–10% solutions in caustic:

a. 4·5 g + 16·2 cc N.NaOH + water to 150 cc (pH 10·1).
b. 4·5 g + 81 cc N.NaOH + 18 cc 20% Nekal BX + water to 150 cc (pH 10·5).
c. 7·5 g + 20 cc N.NaOH + water to 150 cc (pH 9).
d. 7·5 g + 20 cc N.NaOH + water to 150 cc (pH 10·1).
f. 4·5 + 9·45 g NaOH in 4·5 cc methanol + water to 150 cc (pH 9·8).
g. 15 g + 0·75 g NaOH in 1·5 cc water + methanol to 150 cc (pH 9·1).
h. 7·5 g + 5·25 cc N.NaOH + water to 150 cc (pH 9·5).

512. Emulsions

Each film has three emulsions whose sensitivities increase from the outer to the inner layer, to compensate for the absorption losses. In preparing the middle and bottom emulsions, the changes in speed due to the use of colour sensitizers and the calculated thickness of the overlying layers must be taken into account.

The amount of silver in each layer is much less than that in an ordinary emulsion layer. If the latter is fixed at a minimum of 6 g of silver per sq. m. it will be about 2 g per sq. m. This average value, however, must be modified according to the coupler, as all the couplers do not produce the same amount of colour.

Emulsion contrast. Colour development has a high contrast increasing effect which necessitates the use of *extra soft* emulsions. If the gamma of a single negative image is fixed at 1 and if the contrast factor of colour development is 2·5 for example (under given processing conditions) the gamma of the emulsion must only be 0.4.

On the other hand, the developed positive film can have a contrast of 2·4 which, with an intensification factor of 2·5, brings the gamma of the positive emulsion back to about 1. Maximum densities after colour development: negative 2, positive 3. Maximum densities of the emulsions developed to silver: negative 0·8, positive 1·2.

Reversal emulsions have the characteristics of the positive film although the speed and colour sensitivity are those of the negative.

Composition of the emulsion for coating with the sensitizers and couplers which have already been given:

	Negative		
	Top layer	Middle layer	Bottom layer
Emulsion	1 kg	1 kg	1 kg
Sensitizing dye 1 : 1000	—	35 cc	30 cc
Coupler 3–10% daylight	500 cc	200 cc	330 cc
tungsten	830 cc	200 cc	330 cc
Antifoggant 1%	30 cc	30 cc	30 cc
Anti-oxidant (pyrocatechin) 1%	—	6 cc	6 cc
Wetting agent 4%	5 cc	5 cc	10 cc
Wetting agent used	Nekal BX	Dismulgan T	Igepal C
Thickness of dry layer	6·5 μ	4 μ	9 μ

	Reversal		
	Top layer	Middle layer	Bottom layer
Emulsion	1 kg	1 kg	1 kg
Sensitizing dye 1 : 1000	—	80 cc	60 cc
Coupler 3–10% daylight	417 cc	200 cc	366 + 30 cc
tungsten	417 cc	200 cc	366 + 80 cc
Antifoggant 1%	30 cc	10 cc	10 cc
Anti-oxidant (pyrocatechin) 1%	—	6 cc	6 cc
Wetting agent 4%	37 cc	20 cc	20 cc
Wetting agent used	Nekal BX	Saponin	Saponin
Thickness of dry layer	5 μ (6 μ tungsten)	5·5 μ	9 μ

	Positive		
	Top layer	Middle layer	Bottom layer
Emulsion	1 kg	1 kg	1 kg
Sensitizing dye 1 : 1000	—	23 cc	25 cc
Coupler 3–10%	120 cc	200 cc	240 cc
Antifoggant 1%	30 cc	30 cc	30 cc
Anti-oxidant (pyrocatechin) 1%	—	6 cc	6 cc
Wetting agent 4%	5 cc	5 cc	10 cc
Wetting agent used	Dismulgan T	Dismulgan T	Igepal C
Thickness of dry layer	8·5 μ	5 μ	6 μ

The reversal duplicating film may contain 10 cc of 10% tartrazine in the top layer.

The antifoggant is preferably an indolizine (para. 350), especially when the emulsion is gold sensitized.

513. Yellow filter

The yellow filter which separates the top and middle layers is composed of a gelatin layer containing yellow colloidal silver. There are many ways of preparing colloidal silver.

(*a*) *Reduction of silver nitrate* in aqueous solution with ferrous sulphate: addition of sodium nitrate followed by purifying and drying at a low temperature.

(*b*) *Reduction with ammoniacal ferrous sulphate:* pour 1 L of 372 g.p.L ammoniacal ferrous sulphate into 1 L of solution containing 200 g of citric acid neutralized with ammonia. Add 3 L of distilled water then pour in slowly 200 cc of 20% silver nitrate solution. The brown precipitate is quickly washed and dried *in vacuo*. Add to a solution of gelatin.

(*c*) *Reduction* of silver nitrate in gelatin in the presence of sulphite with *pyrogallol*. Wash after setting and mix with gelatin.

(*d*) *Dispersion of the metal with an arc* formed between two silver electrodes with alternating current, in slightly alkaline iced water (Electrargol).

(*e*) Colloidal dispersion in *sodium lysalbinate* (which is formed by decomposing egg albumen in warm dilute soda): this is collargol. The method of preparation given in the BIOS Report is: to a solution of water 122 L, caustic soda, 350 g, sodium lysalbinate 2200 g, add 4200 g of silver nitrate dissolved in 17·5 L of water in 10 minutes. Then simultaneously in 30 minutes at 65°C add 1225 g caustic soda dissolved in 8·8 L of water and 228 g of tannin dissolved in 13 L of water. Leave for 10 minutes and add 2600 g of ammonia in 105 L of water. Then add 28 kg of dry gelatin. Cool after digesting for 25 minutes. Preferably shred and wash for two hours.

The intermediate yellow layer has the following composition: silver dispersion 1 kg, water 1 L, 1% hydroquinone (antioxidant) 50 cc, wetting agent (Dismulgan T) 4% 50 cc, 4% gelatin to the required amount. For reversal film the Dismulgan is replaced by Igepal C. Thickness: negative 3 μ, reversal 2–3 μ, positive 3–3·5 μ.

Protective layer. Instead of a simple gelatin layer, roll and sheet film can be coated with an emulsion of medicinal mineral oil in gelatin: water 1 L, gelatin 20 g, 4% Nekal BX 7·5 cc, paraffin emulsion 4 cc. The latter is obtained with 1·5 L of distilled water, 50 cc of 4% Nekal BX, 80 g of gelatin and 80 g of paraffin oil containing propyl alcohol.

Anti-halo layer. For negatives, halation is reduced either by using a grey-dyed support or by a layer on the back 1 μ thick. For reversal films, an undercoating 2 μ thick containing black reduced silver can be used (see para. 440).

REPRODUCTION

514. Printing from complementary colour negatives

A developed negative contains three layers in subtractive primaries, complementary to the analysis colours: yellow, magenta and cyan corresponding to the blue, green and red separations. The positive, on which the prints are made, also has three layers sensitive to blue, green and red which are developed to yellow, magenta and cyan.

The printing operation therefore comprises the copying of the *yellow negative image* on to the blue sensitive positive emulsion with *blue light*, the *magenta negative image* on to the green sensitive positive emulsion with *green light*, and the *cyan negative image* on to the red sensitive positive emulsion with *red light*. Each single image can only be copied with light of the complementary colour, for the dye deposit is transparent to light of other colours.

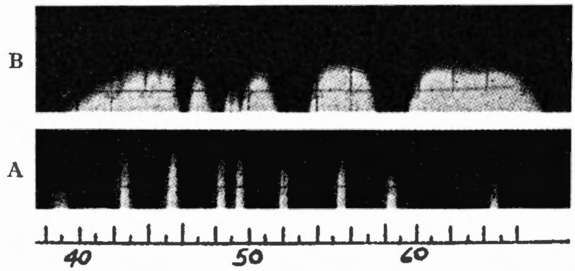


FIG. 110. (A) Emission spectrum of a mercury cadmium lamp. The percentage of light is as follows:

Line	Low pressure	High pressure
468mμ	6·1%	5·4%
480 ,,	23·7%	14·1%
508 ,,	61·0%	58·0%
643 ,,	9·2%	17·8%

The red emission increases with the pressure at the expense of the blue-violet.

(B) Absorption spectrum of didymium chloride saturated solution which only transmits the four main lines (T. Thorne-Baker, *J.S.M.P.E.*, September 1938).

The single images, viewed in light of the complementary colour, appear black. The coloured light used for printing must be completely transmitted by the two other layers, passing through as if the latter do not exist—at least in theory.

How is the exposure of the negative made on to the raw positive material? An ordinary electric lamp can only give acceptable results if it is equipped with a set of *three filters*, blue, green and red—which are as nearly as possible *monochromatic*. Three separate exposures are then made, the amount of light being adjusted according to the particular filter, the sensitivity of the positive layer and the density of the particular negative image. Low and high negative densities are compensated during this operation. The three single exposures can be made simultaneously if a colour integrator with semi-reflecting mirrors, or a rapidly rotating filter disc are used.

Another solution is to use a mercury-cadmium light source in combination with a didymium chloride liquid filter (Fig. 110).

Direct printing of the complementary colour negative on to a positive is only used for printing *ordinary photographs* on paper or film. For commercial motion picture work the production of release prints requires a more complex system involving the use of *duplicates*. There are, in fact, five alternative ways of producing a positive print from a negative:

(*a*) *Direct* negative-positive printing. Best results.

(*b*) Printing from a colour *duplicate negative* made on *reversal film*. Useful for the poorly equipped laboratories.

(*c*) Printing a *colour positive* then a duplicate negative which is used for release printing. This is the worst method.

(*d*) Printing 3 separate *separation positives*, then 3 separate *separation negatives*, then the positive colour print. Whilst it gives good results, this method is not used, as three printing operations are needed for the final print.

(*e*) Printing 3 separate *separation positives* which are used to make a *colour duplicate negative* which is used for release printing. This is the method which is generally used.

515. Printing duplicate colour negatives (method (*e*))

The first stage is to make three *separation positives* on panchromatic film known as 'Separation Panchro' or 'Interpositive', using blue, green and red filters. These films are developed to black and white. The exposure times are determined after sensitometric tests.

The three positives are then printed on to a *duplicating colour negative*, also called 'Colour Internegative', using three primary light sources and taking care to maintain perfect register. The duplicate negative has the same structure as the original negative. The same couplers are used, but as it is much slower, the grain is much finer. Also, the colour sensitivity must correspond to the transmission maxima of the three primary colours used for printing it.

To increase its resolving power, *Eastman Internegative* 5248 has been modified as follows: the magenta image is formed in the blue sensitive outer layer; the cyan image in the green sensitive middle layer, whilst the yellow image, which has least effect on the sharpness, is formed in the red sensitive bottom layer.

The contrast and the extreme densities of the duplicate negative should be as nearly as possible the same as those of the original. The *gammas* of the three primary images undergo variations in contrast during the printing operations, and the high contrast Ansco Color films(12) serve as an example:

	Yellow	*Magenta*	*Cyan*
Colour negative 843	1·15	1·00	1·00
Separation positives	0·75	0·75	0·75
Duplicating negative 846	1·20	1·10	1·10
Colour positive 848	3·00	2·70	2·70

If printing is carried out optically, there is an increase in contrast of 25%.

Storage of raw stock. The characteristics of the three emulsions change easily, with loss of sensitivity. To avoid these changes, it is recommended that the material should be kept in a refrigerator at 5°C.

516. Duplicating colour transparencies

Colour transparencies, which are generally obtained with reversal materials (roll-film or 16 mm films), can be duplicated on similar materials. Special films like *Duplicating Kodachrome,* for use with a 3000°K light source, are available for this. The duplicating material is slower than the normal type and has finer grain, whilst its colour sensitivity corresponds better to the dyes in the original. Despite this, however, it is impossible to obtain a copy which is as good as the original. We shall see later, when considering masks, that this cannot be otherwise.

A *second method which is widely used for prints from transparencies* is to make separate *separation negatives* using the usual tricolour filters, on a panchromatic material. The separation negatives are preferably made using masks. The negatives obtained in this way can either be used to print dye transfer matrices, or for photomechanical reproduction.

516b. Control of printing

When a colour original is copied, both the intensity and the spectral composition of the light source must be adjusted. The intensity is regulated by the insertion of neutral filters or diaphragms. The colour is adjusted by inserting yellow, magenta or cyan filters which balance the colour of the original image. To do this, the printer can be fitted with a black paper band, which contains punched-out holes of suitable size, each being covered by a thin colour filter, chosen after preliminary tests. The paper band is placed between the light source and the film. It is moved to the next opening at each change of scene.

When a grey scale is copied, it is not generally neutral. A filter is therefore chosen, from a series of 10 for example, which will give a neutral scale. This is the filter which is used for printing.

A system of correction filters used by Ansco consists of a collection of films dyed in various colours which are exposed and developed to give a central clear area of various widths. These films are selected according to the colour and light transmission required, and are spliced end to end corresponding to the different scenes in the roll.

Another recent system (Debrie) uses, as a printing source, three mixed beams of blue, red and green light, obtained with three vertical and contiguous filters placed in front of the lamp. The intensity of each coloured beam is modulated by means of a screen printed on a microfile film.

At the beginning of each scene it is advisable to photograph a grey scale. The original and the copy are compared with a reference film on an illuminated multiple rewind table.

Each image is examined through four discs, each containing about a dozen filters of increasing density in grey, yellow, magenta and cyan, selected by a push button system (Agfacolor), or through an additive light system (Debrie).

Printing colour photographs on opaque films is generally carried out on automatic machines where the print film is carried on spools containing, for example, 75 m of film 12·5 cm wide. The light from the lamp passes through the original and is divided into two beams, one of which exposes the print film, whilst the other is received by a photocell, which regulates the exposure time, taking into account the extreme densities of the transparency and the ratio of the average density of the important area to the total average density of the image.

A printer and a tester designed by Herrnfeld(13) use three light beams from three lamps, which are filtered blue, green and red respectively with narrow band interference filters.

For Agfacolor *paper prints* a multiple printer has been used containing 25 lenses equipped with 75 preselected filters. These filters are divided into three groups of 25 on movable carriers and it is therefore possible to print 25 images simultaneously from the same negative on to a 10 × 10 cm sheet, to choose the correction filter giving the best colour rendering.

1. Coote J. H.: *Jl. Soc. Mot. Pic. Tel. Eng.*, 1948, 543–553.
2. Glafkidès P.: F.P. 858,419 and U.S.P. 2,293,816.
3. B.P. 564,976 (1943).
4. U.S.P. 2,126,137 (1938).
5. *Brit. Kin.*, 1954, 79.
6. U.S.P. 2,367,665.
7. Capstaff J. G.: *Jl. Soc. Mot. Pic. Tel. Eng.*, 1950, 445–453.
8. Eggert J. and W. Grossmann: *Naturwiss.*, 1952, 132.
9. The low yellow values are due to the layer, giving this image, being at the bottom of the pack.
10. Meussen L.: *Brit. Kin.*, 1954, 56–58.
11. *B.I.O.S. report No.* 1355 (1945), H.M. Stationary Office, London. Although the information is relatively old, it is still valuable.
12. Duerr H. H.: *Jl. Soc. Mot. Pic. Tel. Eng.*, 1952, 465–479.
13. Herrnfeld F.: *Jl. Soc. Mot. Pic. Tel. Eng.*, 1955, 256–259.

Chapter XXIX

CONTROL AND CORRECTION OF COLOUR IMAGES

MASKS

517. Unwanted absorptions

For colour rendering to be perfect it is not only necessary for the individual colour images to absorb completely all the incident light of one primary complementary colour; they must also transmit completely the other two primaries. Thus blue-violet light will be absorbed to a greater or less degree by the yellow image, but will pass freely through the magenta and cyan images. Similarly green and red light will be absorbed only by the magenta and cyan images respectively, being the complementary colours. This happens with dyes whose spectral curves are ideal, with sharply defined bands and whose transmission region is completely transparent (Fig. 111, curve A).

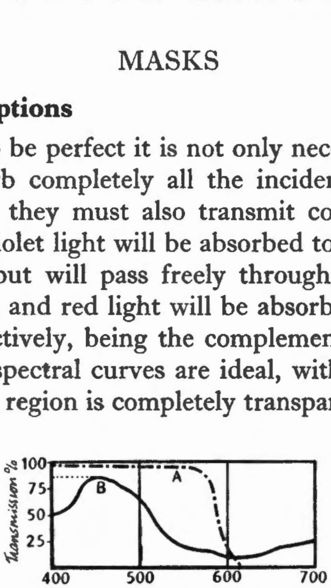


Fig. 111. (A) Ideal transmission of a cyan dye.
(B) Actual transmission of a cyan dye.

In practice the spectral curve is a wavy line whose absorption and transmission regions blend gradually, and which has a slight absorption even at the transmission maximum (curve B).

Generally a dye or a pigment has two principal absorption bands, whose *dominant wavelengths change with the concentration.* Cyan becomes blue, magenta becomes red and yellow becomes orange. The colour, in fact, tends towards grey or brown. The balance of a light grey with small concentrations of dye differs from a dark grey with high concentrations.

A colour image, being necessarily made up of unequally absorbing areas, due to the presence of more or less dye, therefore has a variable absorption even at the point of maximum transmission which should be transparent to light of that colour. The result of this is that, at the same time as the individual image is printed, *two residual unwanted images* provided by the other two layers are recorded. In the regions where these two images are absent, the printed image is pure; in regions where the other two images are present, the printed image is changed unequally.

Each single image is therefore accompanied by two unwanted images of complementary colour which darken it. This gives a total of 3 normal primary images, and in theory, 6 *unwanted images* as follows:

	Unwanted Images	
Yellow image absorbs blue	*magenta layer* strong blue absorption	cyan layer absorbs blue
Magenta image absorbs green	yellow layer absorbs a little green	*cyan layer* strong green absorption
Cyan image absorbs red	magenta layer absorbs very little red	yellow layer absorbs very little red

This table shows that

1. The cyan image corresponding to the red record is accompanied by no appreciable unwanted images.
2. The yellow image is accompanied by a strong unwanted image from the magenta, and a second fairly strong one from the cyan.
3. The magenta image is accompanied by a strong unwanted image from the cyan and a weak one from the yellow.
4. *The two most important unwanted images of the group are those from the magenta and cyan,* which correspond to the green and red records.

Consider the cyan image. Ideally, it should be transparent to green light. In practice, it absorbs about 33% at an overall density of 1·5. The unwanted image to green light will have a gamma of 0·5. The magenta image therefore only contributes a density of 1 in the total 1·5. With more concrete examples, the following figures are given:(1)

Density to coloured light

	Image	Blue	Green	Red
Kodachrome (transparency)	Cyan	0·45	0·45	1·5
	Magenta	0·45	0·90	0
	Yellow	0·60	0·15	0
	Total density	1·50	1·50	1·5
Ektachrome (transparency)	Cyan	0·20	0·45	1·5
	Magenta	0·45	0·85	0
	Yellow	0·85	0·20	0
	Total density	1·50	1·50	1·5

	Image	Blue	Green	Red
Ektacolor (corrected negative)	Cyan	0·10	0·20	1
	Magenta	0·30	0·85	0
	Yellow	1	0·15	0
	Total density	1·40	1·20	1
Agfacolor (negative)	Cyan	0·15	0·15	1
	Magenta	0·50	1	0·15
	Yellow	1	0·15	0·05
	Total density	1·65	1·30	1·20

Obviously, the *duplication of a colour image* on to a similar material will multiply the imperfections. A Kodachrome duplicate, for example, will give a cyan image with a gamma of 1·5 × 1·5 = 2·25, a true magenta image with a gamma 0·9 × 0·9 = 0·81 plus a false magenta image gamma 0·45 × 0·9 = 0·39, and a true yellow image with a gamma 0·6 × 0·6 = 0·36 increased by two false yellow images with gammas 0·45 × 0·6 = 0·27. Furthermore, the imperfections of the image dyes will produce, as with the original, unwanted images in blue and green light from false and from true images of the picture, which can be summed up this way:

Density to coloured light

	Image	Blue	Green	Red
Kodachrome Duplicate	Cyan	0·67	0·67	2·25
	Magenta	0·67	0·81 +0·41+0·13	0
	Yellow	0·36 +0·27 +0·27	0·22	0
	Total density	2·24	1·83	2·25

518. Masks

To some extent the imperfections of the image dyes can be corrected using *masks*.

This correction method consists in superimposing to the original colour image, *the reverse of the unwanted image* which is to be removed. Thus a transparency with an unwanted image D max 0·45 to blue light can be corrected by registering with it a negative of this unwanted image having the same D max to cancel it out during the printing of separations or direct prints.

The mask must be obtained from the image which has the unwanted absorption, using light which corresponds to its principal absorption: an unwanted blue light absorption due to the impurity of the cyan dye is counteracted by a mask obtained by red light. As the ratio unwanted absorption/principal absorption is constant, the mask is developed to a gamma equal to this ratio. However, the image from which the mask is made may itself be accompanied by a secondary image from another dye; for example, the magenta is accompanied by an unwanted image from the cyan layer. A mask made from the magenta image with green light will, at the same time, record the unwanted absorption of the magenta dye. To compensate for this, it would be necessary to first mask the magenta image with an auxiliary mask from the cyan image.

Consider Miller's figures for Kodachrome, given in the preceding paragraph, again. Print a negative of the cyan image, using red light, and develop to a γ of 0·3. Then, using green light, print a negative of the magenta image, also developed to a γ of 0·3. As the initial γ is 1·5, the resulting γ in the masks will be $1{\cdot}5 \times 0{\cdot}3 = 0{\cdot}45$. The first red light mask, superimposed to the original, will cancel out the unwanted absorptions of the cyan image to green and blue lights. The second mask, made with green light, will cancel out the unwanted blue absorption of the magenta dye, which can be shown in the following table:

	Image	*Contrast to*		
		Blue	Green	Red
Masked Kodachrome	Cyan	0	0	1·05
	Magenta	0	0·90	0
	Yellow	0·6	0·15	0
	Total γ	0·6	1·05	1·05

It should be noted that the blue light print necessary in this case requires the registration of two masks, which is not practicable. A single mask for each printing stage must suffice: either the red light mask for the successive separations in blue and green lights, or this same mask for the green separation and the mask obtained with green light for the blue separation. The figures given above will then be obtained, except that yellow will still have an unwanted image of $\gamma = 0{\cdot}45$, bringing the total yellow γ to 1·05. The Kodachrome copy developed to γ 1·5 will now have: cyan $\gamma = 1{\cdot}57$, magenta $\gamma = 0{\cdot}81 + 0{\cdot}13$, yellow $\gamma = 0{\cdot}36 + 0{\cdot}27$, instead of cyan $\gamma = 2{\cdot}25$, magenta $\gamma = 0{\cdot}81 + 0{\cdot}54$, yellow $\gamma = 0{\cdot}36 + 0{\cdot}54$.

519. Correction with two masks

In theory, complete correction (para. 517) necessitates the use of *six masks* (two for each image). However, the unwanted red absorptions are low enough to be ignored. This reduces the number of masks to *four*, two for the yellow and two for the magenta. However, their registration complicates all stages, and usually the number is reduced to two. Even so, the masking technique is laborious and extremely critical. Insufficient control of γ and density involves the risk of further changes in colour balance.

The two principal masks are:

1. *The magenta image mask* obtained by printing the original with red light, and developing to a γ of 0·12–0·3.
2. *The yellow image mask* obtained by printing the original in green light, and developing to $\gamma = 0{\cdot}3$.

Some writers recommend that the magenta mask should be developed to 40% of the original γ and the yellow mask to 60%. We, however, consider these figures to be too high. In any case, each make of film needs the use of particular contrasts.

For motion picture negatives, Gevaert have worked out the following procedure: prepare a red light mask on 'interpositive', which is developed to $\gamma = 0{\cdot}3$; prepare a green light mask on 'interpositive' which is developed to a 40% higher γ than the previous one, i.e. 0·42. Print the separation positive of the magenta, with the first mask in register with the negative, by green light. Print the separation positive of the yellow image using the second mask and blue light.

In all these cases it is advisable to print the separation of the cyan image, which needs no correction, with the red light mask of this same cyan image, to reduce the contrast to a value equal to that of the other two masked separations.

Correction with two combined masks. The above technique using two masks prepared with red and green light respectively produces only a partial improvement in colour balance. We have seen in para. 518 that the magenta dye is accompanied by an unwanted cyan absorption in green light, and if the yellow mask is printed from the magenta image, the unwanted cyan absorption interferes. This disadvantage can be overcome by using a certain order for printing the two masks as follows:

1. Print a mask A with red light and develop, for example, to a γ of 0·3 for Kodachrome.
2. Print with the combination (original + A), a mask B with green light, and develop to $\gamma = 0{\cdot}45$.
3. The magenta separation is made with mask A and green light (development to $\gamma = 1$).
4. The cyan separation is made with mask A and red light (development to $\gamma = 1$).
5. The yellow separation is made with blue light and masks A + B (development to $\gamma = 1{\cdot}75$). The diffusion produced by the superimposition of the two masks is of slight importance here.

The three Kodachrome separation negatives will then each have a γ of 1·05.

Note. The mask A can be used for operation 5 (yellow separation) only if the unwanted absorption of the cyan image is the same for blue and green lights. Otherwise the yellow separation must be made with a mask A′, also from the cyan image using red light, but with its γ altered to correspond to this unwanted absorption. For Ektachrome, A′ must be developed to a γ

50% lower than that of A; and for the yellow separation, a combination of A′+B is used.

520. Masks on two layer films

In blue and green light, there are usually two unwanted images. Those in blue light come from the cyan and magenta images, whilst those in green light come from the cyan and yellow images. To avoid superimposing two separation masks, a film having two superimposed layers can be used, sensitive respectively to red and green and to red and blue, or more simply to red and to blue and green for the two pairs of masks. It is, however, necessary to have different contrasts for the two emulsions.

The *Agfa 'Kombi films* invented by Hickethier have two superimposed emulsions as above, with the difference that each layer contains a colour coupler giving coloured masks.

Separation in in	Negative image	Colour of Kombi film images
Blue light	Yellow	Magenta + cyan
Green ,,	Magenta	Cyan + yellow
Red ,,	Cyan	Yellow + magenta

No filters are necessary for making these masks, as separation is carried out by sensitizing the layers.

Masked negatives on two-layer films. Carroll and Staud⁽²⁾ suggested the use of a separation negative material of silver chloride having a second emulsion on the surface of silver bromide, for printing the mask. After development and oxidation of the surface image with quinone in isopropyl alcohol, the silver chloride is removed with sulphite solution saturated with silver bromide, and the film is fogged and redeveloped to a positive, the residual bromide giving the mask.

Watter⁽³⁾ has described films having an emulsion for producing the separation negative, and an emulsion containing an orange azo coupler for the mask. On colour developing, the coupler produces a blue dye, transparent to the printing light. The residual orange coupler acts as a positive and therefore constitutes a mask. The masking layer for correcting the yellow is sensitive to green and red, whilst the masking layer for correcting the magenta is only sensitive to red.

Masking by supplementary exposure of long duration and low intensity. Maurer and Yule⁽⁴⁾ have suggested the possibility of forming on the negative latent image a positive image serving as a mask, by prior exposure of long duration and low intensity. If the supplementary exposure is given after the main exposure, the solarizing effect does not occur; on the contrary, the latent image is intensified. Furthermore, readily solarized emulsions which show particular reciprocity failure are needed.

521. Unsharp masks

Masks have the disadvantage that they produce an *edge effect* on the image. This defect is overcome by using unsharp masks. The unsharpness reduces the overall contrast, but not that of the fine detail. It eliminates errors in registration and consequently gives better detail than a sharp mask, contrary to what one would think.

The unsharpness can be produced in two different ways:

(*a*) By interposing a translucent sheet about 0·75 mm maximum thickness.

(*b*) By interposing a transparent sheet (or even the base of the original) about 0·2 mm thick at the most, and rotating the pack on a turntable, the lamp being 1·8 m above and 0·6 m off the axis. The image is bigger than the original if the lamp is too near. To some extent shrinkage of the base counteracts this enlargement.

522. Magenta coloured masks

Sharp masked negatives are prepared in the cameras used for *photomechanical* reproduction with masks developed to a magenta colour. These masks are mainly used when the image is to be enlarged, which avoids difficulties of registration. They reduce the gamma and increase the colour saturation.

The two masks are those normally obtained with a red filter (A, for the correction of the magenta image) and a green filter (B, for the correction of yellow image).

The exposure of each mask is made on a panchromatic plate placed in the screen holder of the camera. The mask is developed to magenta in a colour developer and then replaced in the holder. After this, the appropriate separation is made with the blue, green and red filters successively. For the separation of the yellow, the magenta-coloured mask B is used, whilst for the magenta separation mask A is used, and for the cyan, a clear glass sheet only.

The distance between the mask and the panchromatic plate is 3 mm. The emulsion must be soft, unless the document is too pale.

The masks must have a minimum density of 0·3 to 0·5. Gamma of A = 40–45% of the original; gamma of B = 55–65%.

If the masks are not developed to magenta colour, they must be made unsharp by interposing a diffusing film during their exposure.

When separating pictures for photogravure, there is no need to correct the cyan and black printer negatives.

It should be remembered that each original must be accompanied by register marks, a grey scale, and patches of each primary ink.

Magenta colour developing solution⁽⁵⁾ (can cause dermatitis):

A	Water to	1000 cc
	Diethyl-p-phenylenediamine hydrochloride	18 g
	Sodium carbonate	40 g
	Potassium bromide	1 g

B	Water to	1000 cc
	p-nitrophenylacetonitrile	1 g

Many other colour developing solutions can be used (see following chapter) including those using a sulphamido-diamine developer, which are non-toxic.

Alkaline stop bath S13-9a

Water to	1000 cc
Sodium carbonate anh.	50 g
Sodium sulphite anh.	50 g
Potassium bromide	200 g

Dilute with 9 volumes of water. Time 4 minutes.

Bleach bath R13

Water to	1000 cc
Sodium sulphate anh.	100 g
Sodium carbonate anh.	12 g
Potassium ferricyanide	20 g

Treatment time 2–3 minutes followed by fixing.

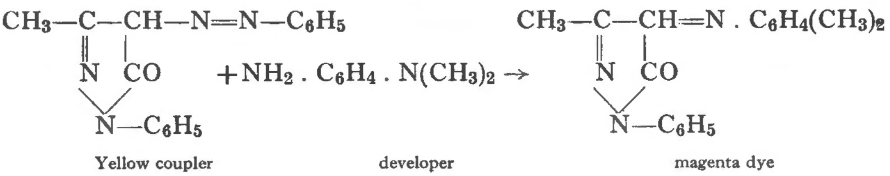
523. Masking with coloured couplers

The most practical method of automatically compensating for the imperfections of negative dyes is by means of coloured couplers, elaborated by Hanson and Vittum. The principle is to convert the unwanted absorption image of the single colour image to a uniform layer of this colour over the whole image, which is done by colouring the transparent parts with a dye which absorbs precisely those wavelengths which are insufficiently transmitted by the image dye.

The correcting effect is carried out by using *coloured couplers* which lose their colour when they combine with the developer. If, for example, we have an orange coupler which on development gives a cyan dye, the final image will be orange in the low densities and cyan in the high densities: the inefficient green transmission will then be spread evenly through the layer, having no effect but to increase the exposure time.

The coloured coupler correction process is used in the *Ektacolor* and *Eastman Color* films (cf. para. 517) where the emulsion which gives the cyan image (red record) contains an *orange* coupler, and the layer which gives the magenta image (green record) contains a *yellow* coupler. The yellow colour corrects the inadequate blue transmission of the magenta dye.

The coloured couplers are obtained by attaching to the colourless coupler a chromophoric group which can be split off by combination with the oxidized developer by rupturing the link. Thus a yellow coupler for the magenta image can be prepared by attaching the group $-N=N-C_6H_5$ to the reactive methylene group of the original coupler.



We have already shown the proportions of unwanted absorptions in Ektacolour film (para. 517). Although relatively small, they are still present, and for photomechanical reproduction it is recommended that the magenta separation should be masked. To obtain this mask, a panchromatic emulsion is exposed under the original negative first to blue light (Wratten 47+39A filters) then to red light (Wratten 70). The ratio of the two exposures is 2:3 (γ = 20–25% of the original). The magenta separation positive from the original plus the mask, is made with a Wratten 61 green filter to which is added a density 1 neutral filter, if the yellow separation positive is made with the 47+39A filters and the red separation with the 70 filter.

The separation positives thus prepared can be used to prepare screen negatives. A *black printer* must be added to them.

524. Black record

There are several methods of obtaining the black image used for photomechanical printing.

(*a*) *Use of a dense yellow filter.* The image is underexposed but completely developed.

(*b*) *Copying with three successive exposures* through blue, green and red filters. That made through the red filter is increased by 50%. Some people, on the contrary, prefer to expose much less to red light. Everything, in fact, depends on the density of the filters, the colour sensitivity of the emulsion and the nature of the subject.

(*c*) *Mask method.* A *temporary mask* is first prepared from the original negative with two partial exposures using blue then green filters. The minimum density should be 0·3 and the density difference the same as that of the Ektacolor measured in red light. The pack (original plus temporary mask) is copied with red light so that the *new mask* has a minimum density of 0·3 to 0·4 and a gamma of 1·6 to 1·8. By superficial reduction, the minimum density is reduced to 0·1. The black positive is obtained with this second mask combined with the original, using the deep red Wratten 70 filter. There must be no strong colour contrasts.

A theoretical study of the black image has been made by Yule.(6)

525. Actual separation of greys

The 'black printer' such as the one indicated above is only a device for covering up the imperfections inherent with three-colour half-tone. It has nothing in common with a true photographic separation.

The reason for an *actual grey separation* is quite different. The grey is an integral part of the colour reproduction system, and can be applied to all photographic, motion-picture and photomechanical processes. Although the method is not in current use, the grey separation method is a considerable advance on all other methods of colour separation.

The grey separation consists in removing from the normal set of tricolour negatives, the *complete grey image* (from white to black), then, which is most important, to *subtract* this from the three negatives of blue, green and red. Printing colour positive copies is carried out by exposing and developing a *grey image* (in other words, black and white), and three *reduced colour images* in cyan, magenta and yellow.

In normal three-colour subtractive synthesis the *grey* results from the superimposition of *equivalent amounts of the three dyes*—cyan, magenta and yellow. Any unequal combination of these three produces a *non-neutral tint* which is, in fact, a *mixture of grey with one or two of the colours*. The synthesis of the colours then becomes a *heterogeneous two-colour* system in which the two colouring elements are not always the same. This can be readily seen from Fig. 101, para. 492. The advantage of such a method is obvious: the neutrality of the greys is ensured by the use of a perfectly neutral dye or pigment, and the colours are given by the minimum amounts of dye (which are unavoidably imperfect).

If in a particular area of the colour image, the amounts of superimposed dyes, presumed pure, are $Q_C + Q_M + Q_Y$, corresponding to the cyan, magenta and yellow respectively, and if, for example, Q_M is the least of the three, the *amount of grey* Q_G used in the formation of the tint will be equal to Q_M. The amounts of dye actually used to give the colour will be $Q_C - Q_M$ and $Q_Y - Q_M$. In the present example the dominant colour is a grey which is more or less saturated according to whether Q_G has a low or a high value. The three-colour synthesis in this case is therefore reduced to a grey image Q_G, a cyan $Q_C - Q_G$ and a yellow $Q_Y - Q_G$.

How is the grey separation obtained? The best way is to use three separate black and white separation negatives. For each area of the image it is the *densest negative of the three* which gives the grey, on the *grey separation positive* (or separation of the least positive densities). Now if the three separation negatives are simultaneously *scanned point by point* with three light beams, it is possible, with suitable apparatus, to select the corresponding weakest electric signal, which in turn is converted to a luminous signal to expose the grey separation positive. The *reduced separation positives* of the three colours are either obtained using the grey positive as a mask on the original negatives, or directly in the electronic apparatus used for extracting the grey, by selective subtraction. The corrected separation negatives can also be obtained directly by electronic means.

If a colour original is used, the task is more complex, for corrections to eliminate unwanted absorptions must be included (corrections corresponding to masks). Scanning is therefore carried out with coloured light beams.

Printing colour images using a grey analysis was studied by the writer in

1935. Murray, Hall and Morse have also invented electronic apparatus to separate and correct the various images. Another method for dealing with transparencies has been perfected by Springdale Laboratories.(8) The original transparency is mounted on a transparent drum, whilst the four unexposed films are placed on a steel drum with the same axis. Scanning is carried out on a spiral track whose width is 50–100 μ. In addition to the systems for analysing, filtering and measuring the light beams, an electronic brain is used to resolve the various calculations.

To obtain the grey analysis, Yule(9) has given a further method, which is to print three *very contrasty separation positives*, and then copy them on to a single emulsion developed to a low contrast.

526. Contrast masks

It is sometimes desirable to reduce the excessively high contrast of some multilayer films. This is done with a contrast mask, preferably unsharp, having a density range about 25% of that of the original. The contrast mask is registered with the latter for printing the normal masks.

For duplicating saturated colour transparencies whose γ is 1·6–1·8, a mask with $\gamma = 0{\cdot}4$ and maximum density 0·5 is used. The γ is thus reduced to 1·2–1·4. During the preparation of the duplicate, the emulsion of the latter is in contact with the back of the original registered with the mask.(10)

Motion picture negative films can be corrected with a mask γ 0·3 (obtained on interpositive from the same negative without using filters).

The following method has been given for *Agfacolor* films:(11) the negative is developed in complementary colours to a γ of 1, instead of 0·65. The silver is rehalogenized and the sensitivity of the film is partly restored in a bath of sulphite. The emulsion face is exposed to red light, and the bottom layer is developed with a glycin developer containing a little potassium iodide (or an imidazole derivative) which converts the upper layers to undevelopable complexes. Maximum mask density: 0·6–0·7.

Highlight mask. The highlight mask is obtained from a *transparency*. It is developed to a low γ, and the density should not exceed 0·3. Together with the transparency, it suppresses the highlights; with the corresponding negative, it accentuates them.

Shadow mask. The shadow mask is obtained from a *negative*. Density 0·2–0·3. It reduces the contrast of the shadows on a negative, whilst it increases the contrast on a positive.

526b. Correction with fluorescent pigments

This method, evolved by Murray, is applied to the reproduction of coloured pictures and charts. Perfected by Yule, it is based on the following principle:

An image will be correctly reproduced if each original colour is altered in advance in such a way that the changes resulting from process imperfections are compensated. The same result can be achieved without altering the pigments themselves *by incorporating fluorescent substances in them*. This substance is almost invisible in white light, but is made visible by excitation with ultra-violet.

The pigments of the water-colour type are sold in tubes, and a suitable fluorescent substance is added to each. The artist must only mix them according to the manufacturer's instructions, otherwise false colours may be seen. The photographic analysis which follows painting is quite complicated, and must be carried out in accordance with the recommendations supplied, as ordinary three-colour filters are unsuitable.

In the same category as this method are the fluorescent pink, blue and green drawing inks for preparing multicoloured drawings and graphs. The blacks are made with Indian ink.

Among the fluorescent substances which have been disclosed(12) are pure chrysene (violet), impure chrysene (blue) and naphthacene (green).

The ultra-violet rays can be absorbed with two Wratten 2B filters.

SENSITOMETRY OF COLOUR IMAGES

527. Spectrosensitograms

A study of the *colour sensitivity* is very important (see para. 473–479), for which a spectrograph is essential. This can be constructed to produce *spectrosensitograms*.

The Evans *spectrosensitometer* is the best known:(13) the dispersing system is a moulded grating, whose spectrum is projected on to a slit, then on to the sensitive layer. A shutter disc and a revolving disc are used for the sensitometric exposures. The luminous energy received is measured with a thermocouple connected to a galvanometer, which enables the sensitivity to be expressed by the reciprocal of the number of ergs per cm^2 required to produce a given density.

The Morrisson and Hoadley *spectrosensitograph*(14) is derived from the Evans and the van Cittert(15) instruments. It enables 10 spectra to be printed whose exposure increases on a factor 2 scale. The light beam from a 7·5 A 6·5 V lamp is reflected by a mirror, collimated, intercepted by a 570 lines/mm grating; it is then reflected by a second mirror, projected on to a slit, reflected on to a third mirror and collimated before passing through a second grating, to be finally focused on to the exit slit combined with a sector disc rotating at 4000 r.p.m. A moving holder enables the complete spectrum to be traversed in 135 seconds.

528. Absorption spectrum

The first operation in any systematic study of sensitive materials for the production of colour images is the printing of the *sensitometer strips*. The various methods used for this were described in Chapter XV, para. 220. We would only remark that the exposure conditions (intensity, duration and colour temperature) should as nearly as possible be those encountered in practical use: variable intensity and constant time of about 1/50th second.

A developed and coloured sensitometer strip can give a *series of absorption spectra* whose determination enables the behaviour of the primary pigment used, to be seen.

The spectral transmission curve of a substance is the reverse of its absorption curve.

When a radiation of wavelength λ passes through an absorbing medium, of thickness d

$$\frac{I}{I_o} = e^{-Kd}$$

where I_o is the intensity of the incident radiation, I that of the transmitted part and $\frac{I}{I_o}$ the *transmission coefficient.* K is the *specific absorption coefficient* for the radiation under consideration and e is the Naperian logarithm base, 2·718. The intensity of a radiation passing through an absorbing medium decreases exponentially, following the thickness (*Lambert's law*). The preceding formula can be written:

$$\frac{I}{I} = e^{-iCd}$$

when the substance is dispersed in a solvent or a transparent support (*Beer's law*). The absorption coefficient K is therefore proportional to the concentration C

$$K = iC$$

if the concentration is expressed in gram-mols of the substance per litre, the constant i is called the *molecular absorption constant.*

To draw an absorption curve, the wavelengths are plotted on the abscissa, and the coefficients of absorption or their logarithms on the ordinates.

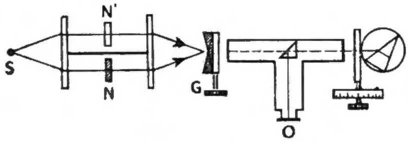


FIG. 112. Fery spectrophotometer. The two areas to be compared are examined at 0. The test solution is placed at N and balance is achieved by moving the wedges, G.

Measurements are made with a *spectrophotometer* in which the proportion of incident monochromatic flux passing through the coloured layer is measured. The monochromatic light beam is not produced with a filter, but with a prism (although narrow band interference filters can be used). An absorption compensating device enables the studied sample to be compared with a known density. This can be done with absorbing wedges, as with the Fery spectrophotometer (Fig. 112) or with nicol prisms as in the Konig, Martens and Grunbaum instrument, or even with shutters or rotating discs.

The receiver can be the eye or a photocell: the Yvon, Fery and Pulfrich instruments are visual; the Hardy, Boutry-Gillod, and Barton and Yoe ones are photoelectric. The latter is a 'zero' instrument: it comprises a monochromator whose light beam is divided between two barrier cells. A rheostat is used to balance the circuits.(16) Many other spectrophotometers are available.

A method of automatically recording the transmission curve is to expose panchromatic plates of *known sensitivity* in a grating spectrograph, in front of whose slit the coloured layer is placed. A neutral wedge is placed between the slit and the layer, or is fixed in front of the plate, to graduate the luminous intensity. Instead of using a wedge, a number of plates can be exposed for varying times or, better, one exposure can be given, and the density measured with a recording microdensitometer. The resulting values of transmission are then multiplied by the coefficients of colour sensitivity of the plate, corresponding to each wavelength. The figures which are finally obtained are not as exact as those obtained with a spectrophotometer, but two dyes can be readily compared to a first approximation.

529. Absolute density of coloured layers

The density of a coloured layer can only be actually measured with *complementary light*. Thus

A cyan layer is examined in red light;
A magenta layer is examined in green light;
A yellow layer is examined in blue light.

There are two cases which can be considered, depending on whether a single layer is measured, or whether the three single images are superimposed, and it is important that the two should not be confused.*

A *single layer* measured in complementary monochromatic light gives the pure or *absolute density* d_λ. If K is the coefficient of absorption—always less than 1—the quantity of dye necessary to produce the density d_λ is proportional to d_λ/K.

The same image, examined with the other two primary lights, gives the two *unwanted densities*, δ_λ, due to the unwanted absorptions, that is, the chromatic impurity (para. 517).

Thus the three primary images will give:

Cyan:	d_R	δ_G	δ_B
Magenta:	d_G	δ_R	δ_B
Yellow:	d_B	δ_G	δ_R

---

* *Translator's note*

There appears to be no definite correspondence between the absolute and total density used by M. Glafkides with the commonly used terms *analytical* and *integral* density used in English.

529b. Equivalent density

With a *multilayer* colour image the observed densities are always due to the group of three superimposed images, which mutually affect each other's purity. In the regions where only one layer is developed, then its measured density is the absolute density. In the majority of areas, however, this image is accompanied by a certain amount of the other two dyes which have unwanted absorptions in the spectral region of the other.

Suppose we have three primary images containing appropriate amounts of dye so that the resulting tint in *white light* of a given colour temperature is *neutral grey*. If the density of this grey is D_T, then

$$
\begin{array}{lllllll}
D_{TR} = & d_R & + & \delta_{Rm} & + & \delta_{Ry} & \text{in red light} \\
D_{TG} = & \delta_{GC} & + & d_G & + & \delta_{Gy} & \text{in green light} \\
D_{TB} = & \delta_{BC} & + & \delta_{Bm} & + & d_B & \text{in blue light} \\
 & \text{cyan image} & & \text{magenta image} & & \text{yellow image} &
\end{array}
$$

where δ_{Rm} and δ_{Ry} are the unwanted images in red light given by the magenta and lower layers; δ_{Gc} and δ_{Gy} the unwanted images in green light from the cyan and yellow layers; δ_{Bc} and δ_{Bm} the unwanted blue light images from the cyan and magenta layers.

The density D_{TR}, or D_{TG}, or D_{TB}, in white light of known colour temperature, but corresponding to an examination in red, green or blue light, represents the *total density*, also called combined density, practical density and more frequently *equivalent neutral density*. It is equal to the sum of an absolute density and two unwanted densities.

The equivalent density of a primary image is therefore the density of grey obtained by superimposing sufficient amounts of the other two dyes. It is necessarily greater than the absolute density.

The ratio of an unwanted density to the principal absolute density of one image is a constant value, for example $\delta_{BO}/d_R = 1/4$. By replacing the values of the unwanted densities in the above equations by those of the corresponding absolute densities modified by a suitable coefficient, we can calculate an absolute density, after having measured the equivalent density, and knowing the amounts of the other two images voluntarily introduced to obtain a neutral. Conversely, it is possible to calculate the equivalent densities after measuring the absolute densities, which is more useful. This calculation is sometimes performed electronically.(17)

530. Measurement of colour densities

The measurement of the densities of coloured layers is carried out with different instruments depending on whether the absolute density, or the equivalent density, is required.

(*A*) *Measurement of absolute densities:* The monochromatic light required for absolute density measurement can be obtained by a monochromater, or by a series of colour filters.

Lapley and Weiss colour densitometer.(18) This is a combination of a Coleman double monochromator and a Western Electric densitometer. The dispersing system consists of two transparent gratings. As the spectrum is focused on a slit, the wavelength can be selected by rotating a cam. An interrupter disc with 15 radial slits rotating at 1800 r.p.m. feeds a 450-cycle signal to the amplifier. The light passing through the sample is received by an electron multiplier cell.

The colour densitometers using filters are more numerous than those with monochromators. A refinement is to replace the customary colour filters by interference filters(19) with very sharp absorption bands.

To make an approximate determination of the density of a monochromatic coloured area, place it alongside a calibrated density scale, and illuminate it with a diffuse source of the complementary colour. The comparison density scale must have similar graininess to the test.

Behrendt colour densitometer.(20) This uses a 25 W lamp, a condenser with an iris diaphragm, and a filter disc having an 8 mm Schott BG 19 infra-red absorbing filter in addition to three 2 mm filters of Schott BG 12, red; VG 9, green; and RG 2, blue. The light is received by a barrier photocell and measured with a galvanometer.

Thiels colour densitometer.(21) The filters are mounted concentrically on a rotating disc and successively receive the light reflected by a movable prism, which is then transmitted to a lens. The light beams passing through the film are received by a photocell connected to an amplifier. The blue component is carried in one direction to a galvanometer, whilst the green and red are connected in reverse. The measurement of the three densities is given by the displacement of the two reflecting prisms. The equivalent density is obtained by combining the absolute and unwanted densities.

Sweet colour densitometer.(22) This instrument is designed to overcome the fatigue of photomultiplier tubes. It consists of a 6 V lamp, a condenser, two infra-red absorbing filters and a cell surrounded by a cylinder holding six filters. The three curves of a sensitometer strip are plotted in less than two minutes in three inks of different colour.

Herrnfeld colour densitometer.(23) The light, at 3000°K, from an 8·5 V 4 A lamp is condensed on an aperture fitted with an infra-red absorbing filter (Corning 9780, 2·5 mm) in front of which is an interrupter producing 360 c.p.s. A further disc, containing four filters is placed between this aperture and a lens which focuses the light on to the film. An integrating bar of transparent plastic material receives the diffuse light which is taken to a cell and an amplifier.

Eastman 31A electronic colour densitometer.(24) A lens A receives the light from a 100 W lamp and forms an image on lens B. After reflecting with a mirror the image is projected on to the film, followed by a photocell. A second similar cell receives the comparison beam from the lamp.

Frayne and Jacobs colour densitometer.(25) The Westrex model R.A. 1100 E, uses a selenium photocell which receives almost all the diffuse light.

(*B*) *Direct measurement of equivalent density.* These densities are measured by superimposing on the sample area, 2 or 3 *coloured wedges* made up of the same dyes as those of the film considered. A supplementary grey wedge is used to balance the system: *R. M. Evans*(26) and *Schneider and Berger*(27) instruments are of that type.

Heymer and Sundhoff colour densitometer.(28) Two identical beams are viewed simultaneously. The sample is placed in one path and one to three colour wedges are in the other.

(*C*) *Pavelle colour densitometer*(29) *for printing control.* The light from the source is filtered through $CuCl_2$ solution to remove the infra-red, and is condensed on to a cell connected to an amplifier and an oscilloscope. A disc rotating at 300–900 r.p.m. contains 3 filters in sectors with transmission maxima at 440, 540 and 660 $m\mu$. Neutral densities enable the light passing through the three filters to be balanced. By introducing a coloured area, a wavy line is produced on the oscilloscope screen. This can be straightened by introducing three filter discs, each containing 14 filters of the same type as the film dyes.

(*D*) *The measurement of paper densities* by reflection is generally complicated by surface reflections.

531. Colour balance

To achieve colour balance together with sufficiently accurate colour reproduction in the subject, several rules must be adhered to, and this is not always easy to accomplish in practice.

(*a*) The *colour sensitivity* of each layer of the negative material must be exactly established in order to make the analysis under the most favourable conditions.

(*b*) The *speed* of each negative layer, which differs with its position in the film, must balance that of the others.

(*c*) The *development* of the three separation negatives must be carried out to the same gamma, or to an equivalent gamma if a correction stage is introduced.

(*d*) If *masks* are used, they must be prepared with the greatest care or the results will be worse than if they had not been used.

(*e*) The *primary dyes* must be of the greatest possible colour purity. They are the source of many inaccuracies.

(*f*) The *average density* of each colour image must be carefully controlled, with respect to the colour temperature of the source, by standardizing the printing time and by ensuring correct development. A colour image which is too dense results in an overall colour cast.

(*g*) The three images which make up the final image must have the same *contrast* and the same shape of characteristic curve (by measurement of the *equivalent densities*). When the three images have the same contrast, the greys appear well balanced.

The importance of correct grey scale reproduction has been contested.(30) It is true that good grey reproduction does not necessarily mean that colours will be reproduced faithfully, for the adjustment of the three images to give good grey reproduction will not eliminate the unwanted absorptions of the image dyes. However, if the curves of the three images are not coincident, the situation will be even worse. The achievement of a grey scale is a sign of correct balance and careful work. Moreover, an image whose greys are coloured is not generally pleasing.

532. Taking colour photographs

As the exposure latitude of colour emulsions is small, errors must not be made as they are impossible to correct. The first thing, therefore, is to choose the main subject in the scene (from the visual point of view), and after measuring its average brightness, attempt to expose so that it is in the middle of the negative characteristic curve. If the subject has a brightness range which exceeds the acceptance of the negative, then it is necessary to decide which parts of the subject must be recorded and which can be lost.

The incident light necessary for photography with a 'daylight' type negative film ASA index 16 is about 500 sq. ft. candles at an aperture of f 2 and at 24 frames per sec. With the newer materials of higher sensitivity 300 sq. ft. candles is enough.

For ordinary photography, satisfactory results are obtained with summer sunlight with an exposure of 1/50th sec. at f 6·5 (16 ASA or 13/10 DIN film).

Exposure should be increased under the following conditions:

	Multiply by
Light cloud	2
Overcast sky	4
Dull heavy cloud	16
Winter	2
Shaded subject	8
Brilliant subject	Divide by 2

In artificial light, two 500 W lamps in ordinary reflectors (100 hour over-run lamps) at 10 feet from the subject enable exposures of 1/5–1/10 sec. at f 2 to be given.

For considerations of light sources, refer to Chapter XXVI. In the studio, daylight can be imitated with arc lamps corrected by a bluish filter (Brigham Y1 for example), or by filtered tungsten lamps.

A film balanced for 3400°K tungsten light can be used in daylight with a Wratten 85 filter.

Some negative films can be used with any light source without filters, corrections being made during printing.

In all cases avoid excessive brightness range; side lighting, shadows on the face, subjects partially in the shade and *contre-jour* effects.

Auxiliary exposure. The latent image of colour films can be intensified considerably by low intensity long duration post exposure until an extra 0·1–0·2 fog density is obtained. Three groups of light sources are used, each with a different colour filter.(31) Exposure time with Eastman Color: 20–30 minutes; film speed, 20 feet per minute. Blue filter = Wratten 213 + 47, green filter = 61 + 16, red filter = 70. 10 W lamps having an emission surface of 4–10 cm².

By latensification with post exposure the exposure time can be reduced 2–4 times. A reduction of 6 times has even been claimed for Ektachrome film.(32) Exposure time 1–2 secs. at 60 cm with a safelight containing a 7 W pearl lamp and an aperture 25 mm diameter. An orange Wratten G filter, a neutral density of 1 and if necessary a blue-green or pink correction filter are used. First development 18–20 minutes at 21°C. Leave 8 minutes in the colour developer before fogging, which is the least to reverse the film, followed by a further 7 minutes' development.

533. Measurement of subject luminosities

There are several exposure meters which measure the average subject brightness. For precision work, however, it is advisable to measure the *extremes of brightness*. For this, the subject can be compared with the extinction of a filament (Volomat apparatus, Paris) or a telescope photometer can be pointed successively at the shadows and highlights of the scene. The brightness of the deepest shadow to be recorded is important for exposing negative materials, whilst for reversal films, it is the brightness of the brightest necessary highlight which must be determined.

An important point which is frequently neglected is the measurement of the brightness of actors' faces in scenes of known brightness range. The ratio of this brightness to the brightness of the decor is a vital factor in the balance of the colour image, and in the print-making process.

'Norwood Director' exposure meter. This instrument comprises a hemispherical receiver of opal glass which is placed in the position occupied by the subject to be photographed. As the light is gathered from all directions, the effective illumination is recorded. A second receiver of clear glass enables the brightnesses to be measured, the instrument being pointed towards the control area. A perforated mask also enables the part played by each lamp in the total illumination of the subject to be determined.(37)

For colour temperature measurement see para. 451.

1. Miller T. H.: *Jl. Soc. Mot. Pic. Tel. Eng.*, 1949, 133–155.
2. F.P. 836,444.
3. Watter O.: *Zeits. Wiss. Phot.*, Dec. 1953, 228; *Sci. et Ind. Phot.*, 1954, 160.
4. *J.O.S.A.*, 1952, 402.
5. Note by L. P. Clerc in *Le Procedé* in an arrangement of the *Bulletin for Graphic Arts* No. 8 (1946) and No. 11 (1948).
6. Yule J. A. C.: *J.O.S.A.*, 1940, 322–331 (second part).
7. F.P. 834,838 (1937–38); 871,370 (1938–39). See also I.G.F. F.P. 873,706 and C. Add. 53,622 (1943–44).
8. *Photo. Engr. Bull.*, May 1950, 13.
9. Yule J. A. C.: F.P. 867,412 (1939–40) and *J.O.S.A.* 1940, 322 (Part 1).

10. Loessel E. H. (Ansco): *P.S.A. Jl.*, 1949, 14.
11. Zeh, Clever and Watter: *Bild u. Ton*, 1950, 315–319; *Sci. et Ind. Phot.*, 1951, 30.
12. Yule J. A. C.: F.P. 917,585–6 (1940–43).
13. Evans C. H.: *J.O.S.A.*, abstracted in *Sci. et Ind. Phot.*, 1940, 152. Jones and Sandvik had previously constructed a spectrosensitometer composed of a monochromator and a rotating disc: *Sci. et Ind. Phot.*, 1921 (1), 127.
14. Morrison G. A. and Hoadley H. O.: *P.S.A. Jl.*, 1950, 64–69.
15. Van Fittert: *Rev. d'Opt.*, 1923, 57.
16. Barton C. J. and Yoe J. H.: *Ind. Eng. Chem.* (Anal. Ed.) 1940, 166.
17. Bingham used the matrix calculation. *Sci. et Ind. Phot.*, 1946, 301.
18. Lapley A. C. and Weiss J.P. (Dupont): *Jl. Soc. Mot. Pic. Tel. Eng.* 1951, 23–29.
19. Letzer E. K. and Powers S. A.: *J.O.S.A.* 1954, 870.
20. Behrendt W.: *Veroff. Wiss. Photo-Labo. Agfa*, 1951, 32–36.
21. Thiels A. F. (Gevaert): *Jl. Soc. Mot. Pic. Tel. Eng.*, 1951, 13.
22. Sweet M. H.: *Jl. Soc. Mot. Pic. Tel. Eng.*, 1950, 35–62.
23. Herrnfeld F. P.: *Jl. Soc. Mot. Pic. Tel. Eng.*, 1952, 184–190.
24. *Jl. Soc. Mot. Pic. Tel. Eng.*, 1953, 696–708.
25. Frayne J. G. and Jacobs J. H.: *Jl. Soc. Mot. Pic. Tel. Eng.*, 1955, 67–71.
26. Evans R. M.: *Sci. et Ind. Phot.*, 1938, 340.
27. Schneider and Berger: *Sci. et Ind. Phot.*, 1944, 316.
28. Heymer and Sundhoff: *Sci. et Ind. Phot.*, 1938, 22.
29. Varden L. E.: *Jl. Soc. Mot. Pic. Tel. Eng.*, 1951, 197–204.
30. Williams F. C.: *Jl. Soc. Mot. Pic. Tel. Eng.*, 1951, 112.
31. Carey K. M.: *Jl. Soc. Mot. Pic. Tel. Eng.*, 1954, 61.
32. Eyerman J. R. (Life): *Photography*, 1953, 50 and 206–209.
33. Woolsey R. A.: *Jl. Soc. Mot. Pic. Tel. Eng.*, 1947, 548.

Chapter XXX

COLOUR DEVELOPMENT

534. Theory of colour development

The formation of coloured images by colour development was disclosed in 1906 by Homolka. In 1912, R. Fischer tried to obtain three coloured images in blue, magenta and yellow simultaneously in three superimposed emulsion layers. His experiments were not successful, due to the diffusion of the colour couplers into neighbouring layers. This difficulty was not overcome until much later, by means of several different devices which will be examined in the following paragraphs.

The organic compounds, or systems of organic compounds, which can form *coloured pigments or dyes* when oxidized by the latent image are very numerous. Fischer drew up a fairly complete list of types.

Once the colour image has been produced, the *accompanying silver image must be dissolved* to reveal the true dye image.

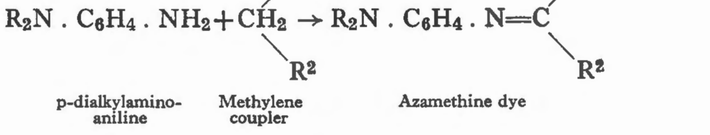
Colour development takes place when a latent image is developed with an unsymmetrical *dialkyl-p-phenylenediamine* in the presence of a ***phenol*** or a compound containing a *reactive methylene group* CH_2. The phenylenediamine is the developer, and the phenol (or reactive methylene compound) is the coupler or former.

The most common dialkyl-p-diamine is diethyl-p-phenylenediamine (or p-diethylamino-aniline). By *oxidizing* in the presence of 1-naphthol, an insoluble blue indophenol is produced, following the reaction:

$$\underset{\text{p-diethylamino-aniline}}{(C_2H_5)_2N\,.\,C_6H_4\,.\,NH_2} + \underset{\text{1-naphthol}}{C_{10}H_7OH} \rightarrow \underset{\text{Indophenol}}{(C_2H_5)_2N\,.\,C_6H_4N{=}C_{10}H_7{=}O}$$

For the reaction to take place, the para position of the naphthol is free, or is occupied by a displaceable group.

If the coupler is a reactive methylene compound with the formula $R' - CH_2 - R^2$, the reaction is:



$$R_2N\,.\,C_6H_4\,.\,NH_2 + CH_2\begin{matrix}\diagup R^1\\ \diagdown R^2\end{matrix} \rightarrow R_2N\,.\,C_6H_4\,.\,N{=}C\begin{matrix}\diagup R^1\\ \diagdown R^2\end{matrix}$$

p-dialkylamino-aniline   Methylene coupler   Azamethine dye

In this case the azamethine group $-N=C\!<$ is the chromophore of the dye produced.

The production of a dye by colour development is not, however, a simple reaction. In fact, it takes place in several stages:

A. The N-substituted p-aminoaniline is first oxidized to a *semiquinone ion* (or quinhydrone) by the latent image, whilst metallic silver is formed:

$$R_2N.C_6H_4.NH_2+2Ag^+ \rightarrow R_2N^+ = C_6H_4 = NH+H^+ +2Ag$$

The semiquinone is a resonance hybrid with six possible extreme structures (due to the positions of the electrons around the nitrogen atom). Its existence is only possible if the two alkyl radicals and the benzene nucleus on the same nitrogen atom are coplanar. This coplanarity can be disturbed by the adsorption of the developer on the halide, resulting in a reduction of development rate.⁽¹⁾

B. The semiquinone ion reacts with the coupler (anion) to give a *leuco derivative*:

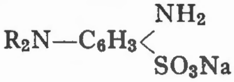
$$\underset{\text{semiquinone}}{R_2N^+{=}C_6H_4{=}NH}+\underset{\substack{\text{Methylene}\\ \text{compound}}}{CH_2:R'R^2} \rightarrow \underset{\text{leuco derivative}}{R_2N\,.\,C_6H_4{-}NH{-}CH:R'R^2}$$

C. The leuco derivative, oxidized by other semiquinone ions produces an *insoluble dye*

$$R_2N.C_6H_4-NH-CH{:}R'R^2+\text{oxidizing agent}\rightarrow R_2N.C_6H_4-N = C{:}R'R^2+2H^+$$

Colour development can even take place effectively if the coupler is isolated from the silver bromide by a resin film.

According to Jordanski and Arbusof⁽²⁾ the complete reaction requires 4 atoms of silver. In some cases, $2Ag^+$ is sufficient.⁽³⁾ The dye yield can be reduced to secondary reactions: with sulphite, the semiquinone forms a sulphonate:⁽⁴⁾



$$R_2N{-}C_6H_3\!<^{NH_2}_{SO_3Na}$$

which is oxidized by an excess of Ag^+. The speed of formation of the sulphonate is, however, much lower than that of dye formation. The latter is therefore always produced.

Properties of the dyes. The dyes produced by colour development have, for the most part, faulty spectral characteristics (see para. 517). The yellows have too flat a slope from the violet to the green, as the line separating the absorption from the transmission should be as steep as possible, and situated at 500 mμ. The *cyans* absorb part of the blue, which they should transmit completely whilst their green transmission decreases gradually towards the orange, and the transmission rises again in the far red. The *magenta* dyes have an unwanted absorption band in the blue.

Light stability is mediocre. Some dyes, such as the β-naphthoylacetanitrile pink are decolorized by several hours' exposure to an arc lamp. The pyrazolone dyes are more stable than the nitrile dyes. As a general rule, prints obtained in this way should be kept in an album.

Chemically, the simpler azamethine dyes and the indophenols are sensitive to oxidizing and reducing agents; but some are more resistant than others. Thus the dyes in Eastman Color film are difficult to decolorize. Acids and alkalis only produce reversible changes.

535. Colour developing agents

The dialkyl-p-phenylenediamines are useful as colour developers. They are quite numerous, but only a few are used, as the colour is primarily determined by the coupler.

An increase in the molecular weight of the diamine results in a deepening of the resulting colour: thus a diethyl-diamine gives a greener hue than the dimethyl compound in the case of a cyan dye, more blue in the case of a magenta dye, and a more orange colour in the case of a yellow dye.

As for the reducing power—in other words the tendency to part with electrons—this depends on the electron donating groups attached to the nitrogen of the substituted NH_2 group or on the benzene ring in the orthoposition relative to the primary NH_2 group. Weissberger has correlated the reducing power with the half-wave polarographic potential at pH 11 using a platinum micro electrode.(1)

The most widely used p-diamines are *diethyl-p-phenylenediamine* $(C_2H_5)_2N-C_6H_4-NH_2$, *diethyl-p-toluylene diamine* $(C_2H_5)_2N-C_6H_3(CH_3)-NH_2$ and certain derivatives of reduced toxicity which will be described later. It is also possible to use some *aminophenylene-piperidines* and *pyrrolidines*. Peterson(5) has suggested the use of *alkylaminoindols* and N-substituted *tetrahydroquinolines*.

The p-diamines are added to the developer as the *hydrochlorides* (or sulphates—translator).

For their preparation see para. 111: the corresponding dialkylaniline, dissolved in iced hydrochloric acid is nitrosated with sodium nitrite solution. The p-nitrosodiakylaniline is then reduced with zinc powder until the yellow colour just disappears. After filtering, the solution is made alkaline and the dialkyl-p-phenylene diamine is extracted with benzene.

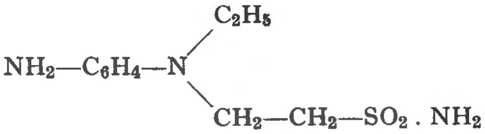
Another method of preparation starts with a p-2 : 5-dichlorophenylazo-N-dialkylaniline.

Low toxicity developers. The p-phenylene diamines can cause severe dermatitis, brought about by allergenic properties. This can, however, be considerably reduced by the introduction of chemical groups which increase the solubility.

(*a*) *Sulphonamido derivatives* (Eastman Kodak) (para. 111) such as:

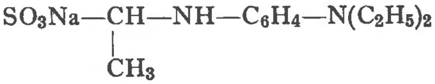
$$NH_2—C_6H_4—NH—CH_2—CH_2—NH—SO_2 . CH_3$$

and



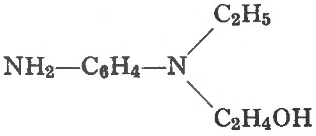
$$NH_2—C_6H_4—N\begin{matrix} / \, C_2H_5 \\ \backslash \, CH_2—CH_2—SO_2 \, . \, NH_2 \end{matrix}$$

(*b*) *Alkylsulphonates* (Gevaert).⁽⁷⁾ Obtained by the action of sodium bisulphite and an aldehyde on a dialkyl-p-phenylenediamine. The alkylsulphonate group is attached to the reducing NH_2



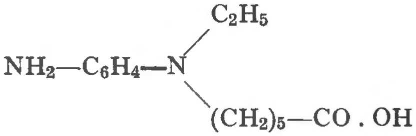
$$SO_3Na—\underset{\displaystyle CH_3}{\underset{|}{CH}}—NH—C_6H_4—N(C_2H_5)_2$$

(*c*) *Hydroxyalkyl derivatives* (Agfa) such as hydroxyethylethyl-p-phenylenediamine:



$$NH_2—C_6H_4—N\begin{matrix} / \, C_2H_5 \\ \backslash \, C_2H_4OH \end{matrix}$$

(*d*) The reducing energy of a p-phenylenediamine type of developer is a function of the basicity of its molecule. Thus the diethyl derivative, which is more basic than the dimethyl, is more active. If *solubilizing groups* $-SO_3H$ or $-COOH$ are attached to the alkyl radicals, the basicity drops as these groups are electron acceptors, and diminish the transfer of electrons to the oxidizing silver ions. Raasch⁽⁸⁾ overcame this difficulty by isolating the acid group, that is, by interposing a group $(CH_2)_n$ where n is less than 5, between the acid group and the nitrogen atom.



$$NH_2—C_6H_4—N\begin{matrix} / \, C_2H_5 \\ \backslash \, (CH_2)_5—CO \, . \, OH \end{matrix}$$

(*e*) An aminophenol, 2:6-diiodo-4-aminophenol, has also been disclosed as a non-toxic colour developer.⁽⁹⁾

536. Cyan couplers

The condensation of the substituted p-phenylenediamines with *phenolic compounds* produces the blue indophenols: *cresols*, *thymols*, 1-*naphthols*, *thiophenols*, *selenophenols*, etc. An increase in the molecular weight of the phenol produces a bathochromic effect, therefore a shift to the green. Thus 1-naphthol and dimethyl-p-phenylenediamine produce a blue-violet dye, whilst dichloro-1-naphthol gives a clear blue dye. Replacement of $-OH$ by $-SH$ has the same effect.

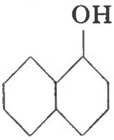
If the para position of the phenol is occupied by a readily displaceable group, the condensation can still take place.⁽¹⁰⁾ Examples: p-chlorophenol, p-hydroxy-benzoic acid, sodium phenol-p-sulphonate, hydroquinone monomethyl ether, etc.

Among the cyan couplers which have been disclosed are:

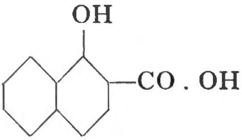
1-naphthol
1-thionaphthol
2:4-dichloro-1-naphthol
3:5-dibromo-o-cresol
4-chlorophenyl-phenol

m-hydroxybiphenyl.(11)
5:7-dibromo-8-hydroxyquinoline.
Dihydroxydiphenylmethanes.(12)
1-hydroxy-2-naphthoyl-o-chloranilide.
p-nitrobenzylpyridinium chloride.(13)
3-hydroxyguanazopyrazolone.

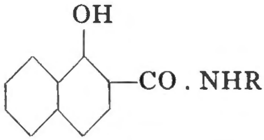
1-*naphthol*, however, is the starting point of the most important couplers, particularly *hydroxynaphthoic acid* used as the *amine* (Agfa) or the *hydrazone* (Gevaert).(15)



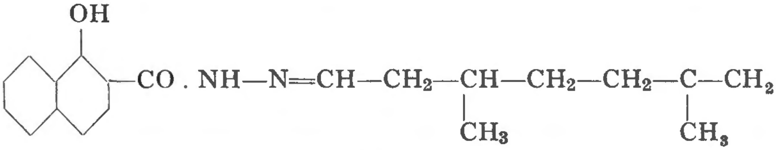
1-naphthol



1-hydroxynaphthoic acid

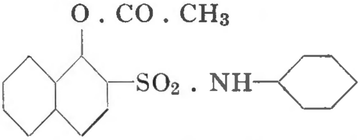


1-hydroxynaphthoic acid amide



Hydrazone of 1-hydroxynaphthoic acid and citronellal.

The lateral chain can also be a sulphonamide (Du Pont):



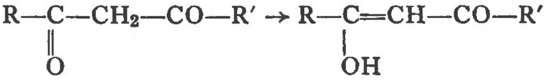
1-acetoxy-2-naphthalene phenylsulphonamide

Another group of cyan couplers are derived from *naphthaquinoline*, having an auxochromic group in the β position, preferably RNH, and an OH group in the third nucleus (General Aniline: F.P. 939,497 and Add 61,005, 1954, U.S. priority 1947).

537. Yellow couplers

Yellow couplers are compounds with a *reactive methylene group* of the type $R-CO-CH_2-CO-R'$.

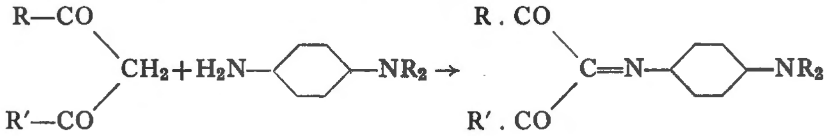
When being condensed, the keto group is changed to the isomeric *enol* group (tertiary alcohol form), which converts the methylene group CH_2 into the group CH, one of whose valencies becomes free.



$$R{-}\underset{\underset{O}{\|}}{C}{-}CH_2{-}CO{-}R' \rightarrow R{-}\underset{\underset{OH}{|}}{C}{=}CH{-}CO{-}R'$$

Keto Enol

The yellow dye is formed in the following way:



Acetylacetone derivative Dialkyl p-phenylene diamine Yellow azamethine dye

The simplest ketomethylene compounds are only of theoretical interest:

Acetyl-acetone $CH_3-CO-CH_2-CO-CH_3$.
Benzoyl-acetone $C_6H_5-CO-CH_2-CO-CH_3$.
Ethyl acetoacetate $CH_3-CO-CH_2-CO-O-C_2H_5$
Benzoylacetic ester $C_6H_5-CO-CH_2-CO-O-C_2H_5$
Ethyl α-chloracetate $CH_3-CO-CHCl-CO-O-C_2H_5$

Anilides. The acetoacetanilides with the general formula CH_3—CO—CH_2—CO—NH—Ar are good yellow couplers. They are obtained by condensing the corresponding acetoacetic ester with a cyclic amine for 20 minutes at 190°C.(15b) The product is recrystallized from alcohol.

The simplest members: *acetoacetanilide* and *acetoacetotoluidide* give brownish-yellow images. The phenetidide and the β-naphthalide give colours which are too orange. Acetoacet-2:5-dichloroanilide CH_2—CO—CH_2—CO—NH—C_6H_3—Cl_2 is preferable.

The benzoylacetanilides are frequently used, various radicals being finally attached to the extreme benzene nuclei of the molecule.

$$R{-}C_6H_4{-}CO{-}CH_2{-}CO{-}NH{-}C_6H_4{-}R$$

These include *benzoylacet-p-chloranilide*, the *m*- and *p-aminobenzoylacetanilides*, *m-aminobenzoylacet-p-bromanilide*,(16) *p-methoxybenzoylacet-m-dialkylanilide* (Agfa).

Malonic hydrazones. The derivatives of *hydrazine* NH_2—NH_2, will combine with the acetoacetic esters to give the *hydrazones*,(17) for example, the cyanacetyl-hydrazone of acetoacetic ester.

$$CN{-}CH_2{-}CO{-}NH{-}N{=}C(CH_3){-}CH_2{-}CO{-}O{-}C_2H_5$$

Malonic acid $HO—CO—CH_2—CO—OH$ forms a *hydrazide* with hydrazine $NH_2—NH—CO—CH_2—CO—NH—NH_2$. This malonic hydrazide can be condensed in alcohol with two molecules of acetoacetic ester to give the yellow coupler *malonyldihydrazone of acetoacetic ester*:

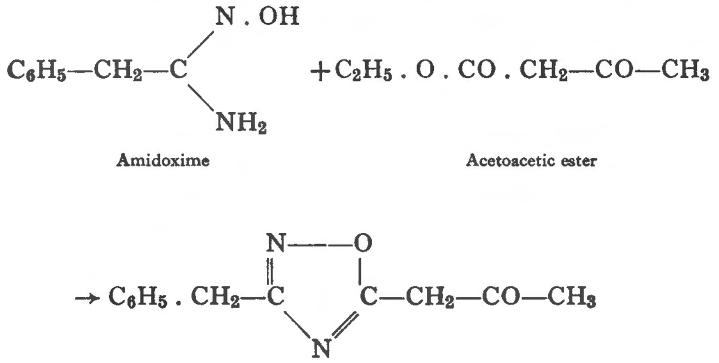
$$C_2H_5—O—CO—CH_2—C(CH_3){=}N—NH—CO—CH_2—$$
$$CO—NH—N{=}C(CH_3)—CH_2—CO—O—C_2H_5$$

The reaction can be carried out with many ketones and aldehydes (in place of the acetoacetic ester);(18) benzaldehyde $C_6H_5—CHO$ and the o- and p-hydroxybenzaldehydes, acetone, etc. If the condensation is carried out successively with two different aldehydes or ketones, an assymetrical dihydrazone is obtained: for example, o-hydroxybenzaldehyde and o-chlorobenzaldehyde. On development all these compounds give yellow to golden-yellow images.

Other simpler hydrazones have the structure(19) $C_6H_5—CH{=}N—NH—CO—CH_2—CO—O—C_2H_5$. They also give yellow images.

Malonic diamides. The malonic diamides $R—NH—CO—CH_2—CO—NH—R'$ were disclosed as couplers in 1936(20) but only give images when they are impure. Thiers and Van Dormael(21) have obtained strong images even after purification, with malonic diamides having on the nitrogen atoms, *thiazole* or *benzthiazole* nuclei; for example, the symmetrical malonic amide of 2-amino-benzthiazole.

Heterocyclic ketomethylene compounds. In these compounds the reactive CH_2 group is linked to a nitrogenous heterocyclic nucleus, which is a cyclammonium base, especially the derivatives of 1:2:4-*oxodiazole*, (Gervaert)(22 produced by condensing acetoacetic ester with amidoximes. For example:

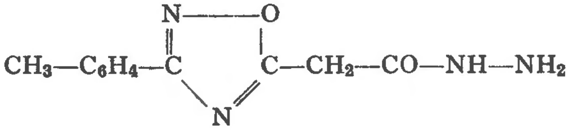


Amidoxime

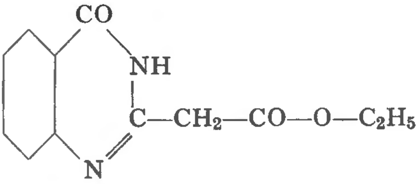
Acetoacetic ester

2-benzyl-5-acetonyl-1 : 2 : 4-oxodiazole

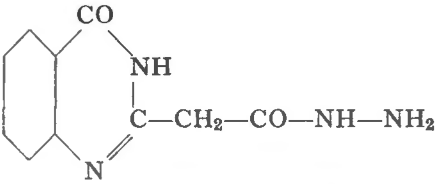
If the amidoxime is condensed with a chlorinated derivative, such as $Cl—CO—CH_2—CO—O—C_2H_5$, the corresponding ethyl oxodiazoylacetate is formed, which under the action of hydrazine is converted to the—*carbohydrazinomethylene* derivative,(23) for example:



The *carbethoxy* and *carbohydrazino* derivatives of *quinazolone*(24) are also yellow couplers



Carbethoxymethylene quinazolone



Carbohydrazinomethylene quinazolone

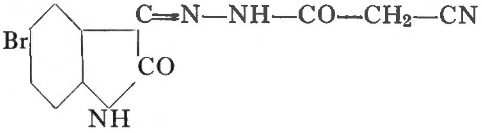
538. Magenta couplers

Although a purple-red dye (abs. max. 545 mμ) can be obtained from 3-(1-*hydroxynaphthoyl*-2-*amino*)-*benzoic* acid,(25) the magenta couplers generally belong to 4 main groups: *phenylacetonitriles*, *cyanacetylureas*, *cyanacetylhydrazones* and *pyrazolones*.

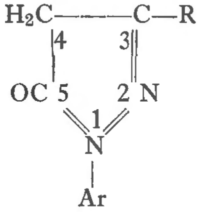
(*a*) *Phenylacetonitriles*—principally *p-nitrophenyl-acetonitrile* (or p-nitrobenzyl cyanide) $CN—CH_2—C_6H_4—NO_2$. Other derivatives are *benzoylacetonitrile* $CN—CH_2—CO—C_6H_5$ and *p-phenylbenzoylacetonitrile* $CN—CH_2—CO—C_6H_4—C_6H_5$.

(*b*) *Cyanacetylureas*. These are compounds with the structure $R—NH—CO—NH—CO—CH_2—CN$, whose corresponding dyes have a relatively high blue transmission (Kodak).(26)

(*c*) *Cyanacetylhydrazones*. These also give dyes whose blue transmission is substantial. Their structure corresponds to the formula $R{=}N—NH—CO—CH^2—CN$. For example, R can be indazolone (Gevaert):(27



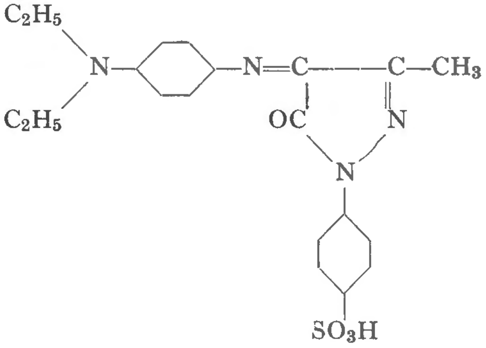
(*d*) *Pyrazolones*. These magenta couplers with the structure



are very widely used for colour films. Their disadvantage is that they have an undesirable blue absorption between 440 and 450 mμ, due to the negative charge of the oxygen atom of the —CO group. The main absorption band in the green, between 530 and 550 mμ, is due to the negative charge of the second nitrogen atom. The unwanted blue absorption can be reduced by introducing electron attracting substituents in the benzene nucleus: NO_2, NH_2, SO_3K, COOK, or by replacing the benzene with naphthalene.

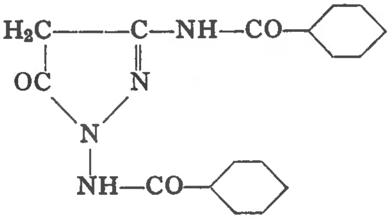
The pyrazolones are prepared by hot condensation of a phenylhydrazine Ar—NH—NH_2 with a keto compound such as acetoacetic ester CH_3—CO—CH_2—CO—O—C_2H_5 in the presence of water and alcohol. They are insoluble in water, but soluble in caustic soda. Their sulphonated derivatives are soluble.

The simplest coupler is 1-*phenyl*-3-*methyl*-5-*pyrazolone*. The aryl sulphonated compound is prepared from sulphophenylhydrazine.(29) With diethyl-p-phenylene diamine, a magenta dye is obtained with the formula:

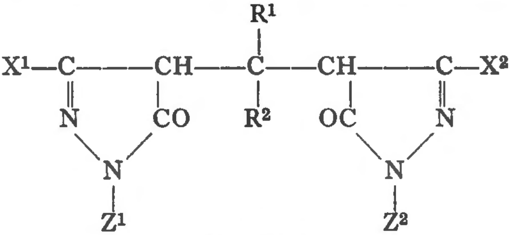


Before coupling, the keto group —CO—CH_2— is isomerized to the enol form —C(OH) < CH—.

1-*phenyl*-3-*amino*-5-*pyrazolone*. This pyrazolone gives a dye which is transparent in the blue, and is prepared by the action of phenylhydrazine on cyanacetic ester in benzene, followed by cyclization of the resulting ethyl-β-imino-β-phenylhydrazine propionate. Kuminine and Itano obtained it in greater yield by condensing in pyridine, the alcohol being eliminated with NaOH.(30) The phenlyhydrazine can be replaced by sulphophenyl-, bromophenyl- or toluyl-hydrazine, and the amine group by a benzoylamido, nitrobenzoylamido, laurylamido or palmitylamido group (see para. 540). With two amido groups, in positions 1 and 3, compounds similar to the following are obtained:(31)

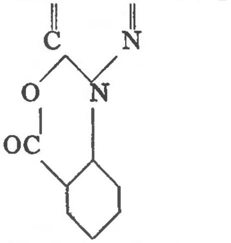


The use of *bis-pyrazolones* joined in the 4-position by a —CH_2— or —$CR'R^2$— group has been patented by Jennings (Du Pont) and by Kodak(33) and also the 4:4′-anisylidene derivative.(34) Some simple pyrazolones can also have their reactive methylene groups substituted. Dye formation is facilitated when the substituent in position 3 is an aminoheterocyclic group. The *imino-bis-pyrazolones* have been patented by Kodak (F.P. 1,081,140–1954, U.S. prior. 1952).



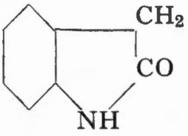
Bis-pyrazolone

Another system includes a complex nucleus between the CO and the neighbouring nitrogen of an aminopyrazolone, such as 3-*amino-pyrazo-coumarazone*(35) prepared from o-carboxyphenylhydrazine and ethyl β-amino-β-ethoxy-acrylate:

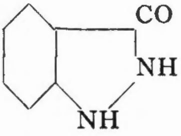


3-amino-pyrazo-coumarazone

Other heterocyclic magenta couplers. These include, chiefly, the *oxindoles* and the *indazolones:*(36)



Oxindole



Indazolone

In the case of the indazolones the link with the p-phenylenediamine is *via* the middle NH group. The benzene ring can have a chain such as $R'R^2N.SO_2$— in the β-position (to the CO) (I.C.I.: F.P. 1,089,328 Brit. prior. 1952).

Magenta couplers derived from *quinoline* have been patented by General Aniline (F.P. 939,497 U.S. prior. 1947 and Add. 61,004 and 61,006; 1954) with: in position 2, an alkyl, aminophenyl, stearoylaminophenyl, octadecanesulphonamidophenyl group; in position 4, a COOH or CONHR group; in position 6, a sulphonated aliphatic radical containing at least 10 carbon atoms and an OH in position 8. There are many variations.

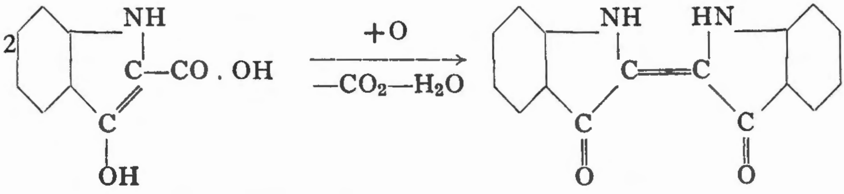
539. Other colour coupling systems

The direct formation of colour images by development does not necessarily involve the presence of two reagents. There are systems in which the developer, by simple oxidation produces a coloured substance *in situ.*

In this way *pyrocatechin* and *pyrogallol* in the absence of sulphite, produce, in addition to the silver image, a residual brown organic image which tans the gelatin strongly.

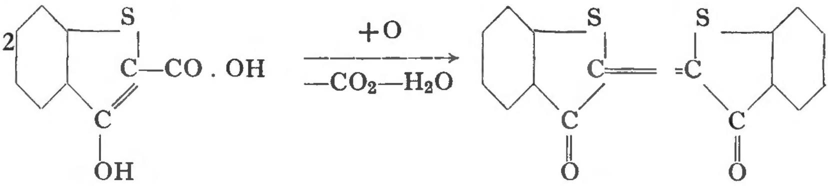
The following systems which can be used for the production of colour images are of greater interest:

A. Indigo derivatives. Indoxyl and *thioindoxyl* are respectively oxidized to the blue *indigo* and the magenta *thioindigo.* They are the basis of the discovery of colour development by Homolka. Their acid derivatives bring about the same result more easily:



Indoxyl-carboxylic acid

Indigo (blue)



Thioindoxyl-carboxylic acid Thioindigo (magenta)

The introduction of substituents into the benzene nucleus brings about a modification of the colour. 4:4′-dichloroindigo is greener than indigo, whilst 6:6′-dichloroindigo is more violet. 5:6:5′:6′-tetrachloroindigo is violet, whilst the 5:7:5′:7′-tetrachloro derivative is bright blue. 5:5-dimethyl indigo tends towards the violet, whilst 7:7′-dimethyl indigo has a greenish shade.

A substituent in the 5-position of thioindigo changes the colour towards violet, whilst in the 6-position the change is towards red and orange. Thus 5:5′-dichlorothioindigo is magenta whilst 6:6′-diethoxy thioindigo is orange.

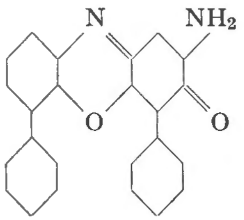
Instead of an indoxyl, 4-*hydroxyisocarbostyryl* (or 1:4-dihydroxyquinoline) can be used(37) which develops an orange-red carboindigo.

The developing solution contains the indoxyl derivative, caustic soda and sulphite. Example:(38) thioindoxyl carboxylic acid 4 g, caustic soda 5 g, anhydrous sulphite 10 g, water to 1000 cc. As these solutions are readily oxidized, it is advisable to work in an inert atmosphere.

It should be noted that the *indoxyl derivatives couple with the substituted p-diamines*. They can therefore be used for normal colour development, as blue and magenta couplers.

B. Naphthols and phenols. An orange-yellow image is obtained by developing in a sulphite solution of 1:2:4-*trihydroxynaphthalene* (Pavolini). The resulting compound is a β-hydroxy-α-naphthoquinone. K. and L. Schinzel(39) have disclosed the 2:5-*diphenoxy*-, 2:5-*diphenetyl* and 2-*phenyl-α-naphthohydroquinones* to obtain lemon yellow images. 2:5-*dibenzoylaminohydroquinone* and other similar polyacylamino derivatives give yellow or orange images. 1:4-*dihydroxynaphthalene* monomethyl ether gives blue images.

C. Autocoupling of the aminophenols. Fischer and Jones stated in 1894 that the o-aminophenols, oxidized with mercuric chloride, form aminophenoxazone dyes. Henn(40) obtained a similar reaction by developing with 2-*amino-6-phenylphenol* which gives a sepia image. After dissolving the silver, an intense yellow-orange image is left. Its constitution is:



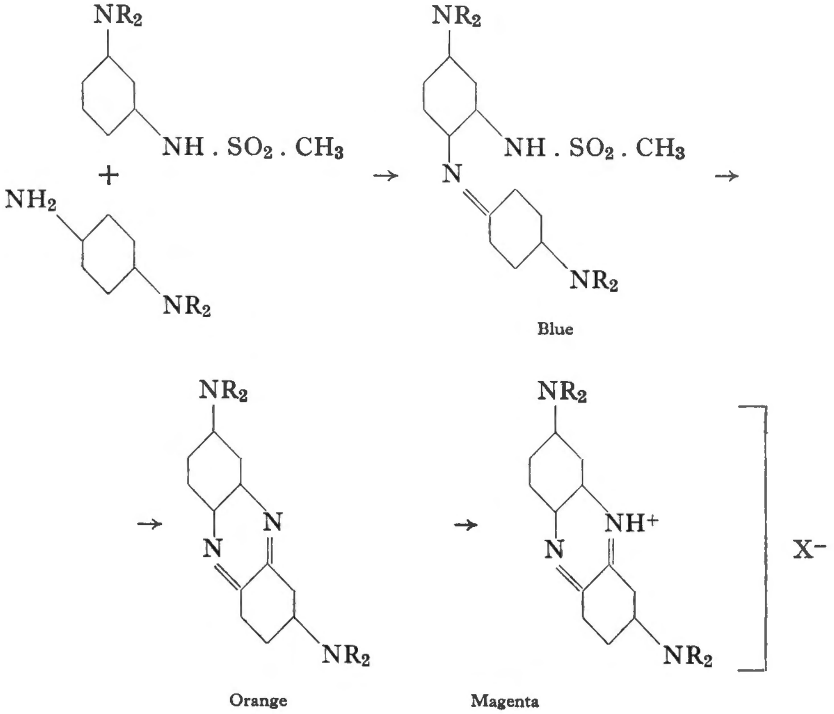
D. Combination of phloroglucinol with phenolic developers. Phloroglucinol, 1:3:5-trihydroxybenzene, will condense with phenolic developers in the presence of an oxidizing agent to give coloured pigments. Henn and Fassett(41) obtained an orange image by developing in a solution containing *phloroglucinol* and *hydroquinone*, a green image with *pyrogallol* in place of *hydroquinone*, yellow with *gentisic acid*, and orange with *nordihydroguaiaretic acid* $(OH)_2—C_6H_3—CH_2—(CH—CH_3)—CH_2—C_6H_3(OH)_2$, or 'N.D.G.'

In the same way, 'N.D.G.' and 1:3:5-triaminobenzene give an intense orange image. With resorcinol, orcinol or m-aminophenol, the image is also orange. It is pinkish orange with N.D.G. + 4-chlororesorcinol.

These colour development systems can only be used with films as a colour fog is produced with papers.

N.D.G. is extracted from a desert plant, *Larrea divaricata*. It is used as an anti-oxidant.

E. Azine couplers. Diethyl-p-phenylenediamine with an azine coupler such as m-diethylamino methylsulphonamidobenzene gives a transitional blue compound which is changed spontaneously to a brown-orange compound. The latter, on acidifying, changes to a magenta dye (Ansco).(42)



The three subtractive primaries can be obtained with analogous coupler systems.

F. Reduced forms of indophenols can be used as colour developers. Rzymkowski obtained them by electrolytic reduction of mixtures of phenols or phenols and acetoacetic esters.(43)

540. Non-diffusing couplers

The couplers which have so far been described cannot be incorporated as they are into emulsions, as they would quickly diffuse throughout the different layers of the film. To ensure their immobility in gelatin, chemical groups which have a strong affinity for gelatin must be added to their molecules. Currently, the main method used is to attach long carbon chains which is one system of anchoring the molecules.

(1) *Diffusion preventing carbon chains.* The *dodecyl* (or lauryl) —$C_{12}H_{25}$, *hexadecyl* (or palmityl) —$C_{16}H_{33}$, *heptadecyl* $C_{17}H_{35}$, *octadecyl* (or stearyl) —$C_{18}H_{37}$ radicals are attached to the coupler molecule, preferably *via* an amide linkage —CO.NH—.(44)

As the resulting compound is insoluble, *it is solubilized by adding a sulphonic or carboxylic acid group.*

With the *pyrazolones*(45) the antidiffusing chain is attached in the 3-position whilst the sulphonic acid solubilizing group is linked to the phenyl nucleus in the 3′- or 4′-position, preferably via a methylene group —CH_2—. In the first case, one could have, for example, 1-(3′-sulpho-4′-methyl-phenyl)-3-heptadecyl-5-pyrazolone, and in the second, 1-(3′-sulphomethylphenyl)-3-heptadecyl-5-pyrazolone. Magenta images are obtained from their sodium salts.

Examples of the preparation of long chain non-diffusing couplers are given in the following paragraph.

The following antidiffusing groups are rarely used:(46)

(2) *Nuclei with an aldehyde function* combined with phenols.(47) Phenol, p-cresol, m-cresol or xylenol are condensed at the boil with salicylaldehyde in the presence of hydrochloric acid. The product is diluted with ether and precipitated with benzene. Blue images.

(3) *Terpenes* condensed with phenols. The resulting product is solubilized by sulphonation.(48) In this way camphene or pine oil can be combined with phenol, cresol, xylenol, o-chlorophenol, pyrocatechin, pyrogallol, etc. Blue images.

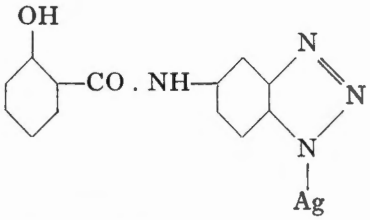
(4) *Carbon chains containing atoms of oxygen, sulphur* or *nitrogen,*(49) generally prepared by polymerizing the oxides of *ethylene*, propylene, dimethylethylene, bromoethylene, ethylene sulphide, etc. These anchoring groups are attached to the molecules of phenols, acetoacetic and benzoylacetic esters, and pyrazolones.

Thus a cyan coupler (2-pentaethoxy-1-naphthol) is obtained by heating 1-nitro-2-naphthol in toluene with ethylene oxide in the presence of caustic potash in an autoclave at 150°C under pressure. Similarly, by condensing ethylaniline with ethylene-imine, nitrosating, reducing and combining the product with acetoacetic ester, a yellow coupler is produced.

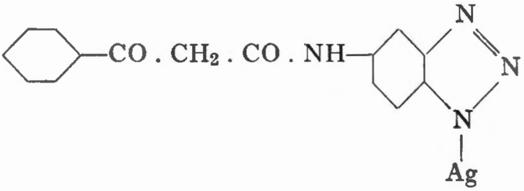
(5) Chains of *polypeptides*, *resins*, *menthene cyclic compounds*, groups like the *substantive dyes*, *polyisatin* groups (Gevaert),(50) or the sulpho or carboxy monoarylides of hydroxynaphthalic acid in which the aryl is linked to an aliphatic chain. Example:(51)

$$HO\,.\,C_{10}H_6{-}CO\,.\,NH{-}C_7H_{15}\,.\,SO_3H$$

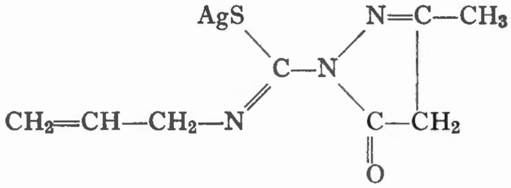
(6) The couplers are introduced as insoluble metallic salts on condition that they contain an —SH or —NH group in which the H is replaced by an atom of metal.(52) The following compounds have been proposed for three-colour work:



Silver salt of 5-salicoylaminobenzaldehyde
(cyan image)



Silver salt of 5-benzoylacetaminoindazole
(yellow image)



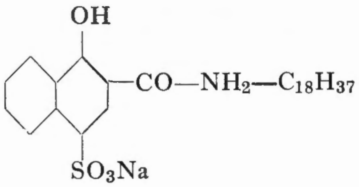
Silver salt of 1-(N-allylthiocarbamido)-3 methyl-5-'pyrazolone
(magenta image)

541. Preparation of long chain non-diffusing cyan couplers

Non-diffusing couplers were first studied and made by Schneider and his collaborators in the Agfa laboratories. The following preparation sequences of certain non-diffusing couplers are given as examples:

The cyan coupling function is an α-naphthol (see para. 536). The anti-diffusing group is a long octadecyl chain which may be attached via a cyclic amine.

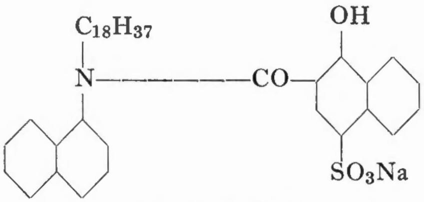
The simplest cyan coupler is 1-*hydroxy*-2-*naphthoyloctadecylamido*-4-*sulphonate*:



(para 511: coupler h)

prepared by condensing octadecylamine with the internal anhydride or the phenyl ester of 1-hydroxy-2-naphthoic acid. The purified product is sulphonated and converted to the sodium salt.

Sodium-1-*hydroxy*-2-*naphthoyl-α-octadecylnaphthanilido*-4-*sulphonate*.



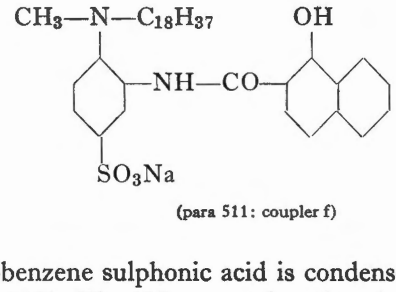
(para 511: coupler g)

The octadecylnaphthylamine is first prepared by reacting α-naphthylamine with octadecyl chloride in the presence of calcined magnesia of suitable fineness. M.Pt. 61–62°C after recrystallization. Yield 87%.

The octadecylnaphthylamine is condensed with the phenyl ester of 1-hydroxynaphthoic acid. A molecule of phenol is eliminated. Yield 59% after recrystallization.

Sulphonation, decolorization with carbon and recrystallization. Yield 73%.

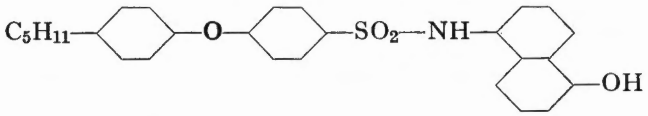
1-*hydroxy*-2-*naphthoyl-o-methyloctadecyl-amino-anilide*-4′-*sulphonate*.



(para 511: coupler f)

2-nitrochlorobenzene sulphonic acid is condensed with methyloctadecylamine. Yield 83–90%. The NO_2 group is reduced to NH_2 with iron and HCl (in 5 reductions in aqueous alcohol). Yield 83%. The resulting diamine is then condensed with 1-hydroxy-naphthoic acid (previously converted to the anhydride with thionyl chloride).

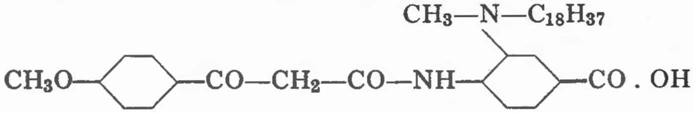
Alternative cyan coupler



541b. Yellow non-diffusing couplers.

The basis of these couplers is *benzoylacetanilide* (see para. 537) and the anti-diffusion group is *heptadecyl* or *octadecyl.*

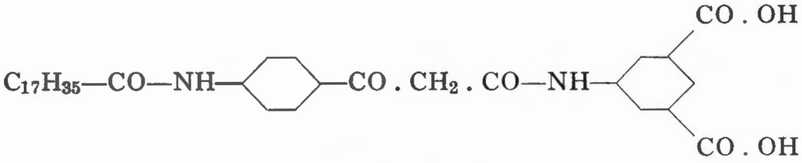
p'-anisylacet-(o-ethyloctadecylamino)-p-carboxy anilide.



(para 511: coupler b)

This is prepared by treating sodium ethyl acetoacetate with anisyl chloride (p-methoxy-benzoylchloride) in dry benzene, then hydrolyzing with sodium methoxide. The anisylacetic ester thus obtained is then condensed with 4-amino-3-methyl-octadecylamino benzoic acid in xylene and precipitated with methanol.

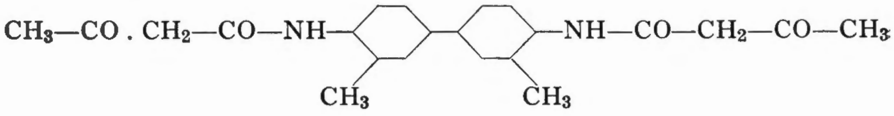
*p'-stearoylamidobenzoylacetamido-*3:5-*isophthalic* acid:



(para 511: coupler a)

p-nitrobenzoylacetic ester is first prepared by condensing o-nitrobenzoyl chloride with acetoacetic ester in alkaline acetone, followed by hydrolysis with an ammoniacal solution of ammonium chloride. The p-nitrobenzoyl-acetic ethyl ester $NO_2.C_6H_4.CO.CH_2.CO—O—C_2H_5$ is then condensed with the dimethyl ester of aminoisophthalic ester in xylene, and the product is hydrolyzed and reduced with iron. The carbon chain is finally attached to the NH_2 group using stearoyl chloride in pyridine. After diluting with acetone, the coupler is precipitated with hydrochloric acid with ice, and is then purified.

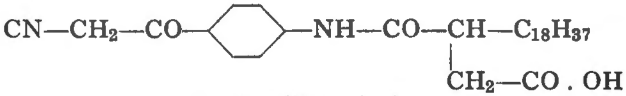
Another yellow coupler:



541c. Magenta non-diffusing couplers

The active coupler is either a ***nitrile*** or a ***pyrazolone*** (para. 538). The anti-diffusion group is ***heptadecyl*** or ***octadecyl***. We have already seen that, with the 1-phenyl-3-amino-5-pyrazolones, the amino group can be substituted by a lauryl or palmityl group; this is done by reacting the amino-pyrazolone with palmityl or lauryl chloride.

Octadecenylsuccino-(p-cyanaceto)-anilide. This is a benzonitrile:

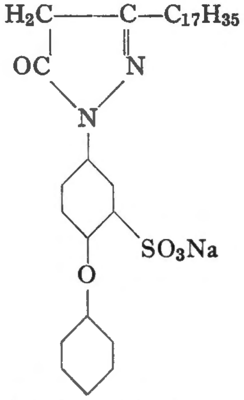


(para 511: coupler e)

p-(ω-chloroacetyl)-acetanilide (M.Pt.2 > 10°C) $Cl—CH_2—CO—C_6H_4—NH—CO—CH_3$ is obtained by the action of chloracetyl chloride on acetanilide in carbon tetrachloride in the presence of $AlCl_3$. Heated with HCl it gives p-chlorocetylaniline (M.Pt. 146°C) $Cl—CH_2—CO—C_6H_4—NH_2$. Potassium cyanide, in aqueous methanol converts it to p-cyanacetylaniline $CN—CH_2—CO—C_6H_4—NH_2$ (M.Pt. 160°C).

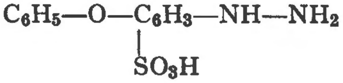
Octadecenylsuccinic anhydride is obtained by treating n-octadecylene with maleic anhydride. The coupler is prepared by condensing this with the cyanacetyl-aniline in dry toluene.

1-(3′*-sulpho-*4′*-phenoxyphenyl*)-3*-heptadecyl-*5*-pyrazolone:*



(para 511: coupler c)

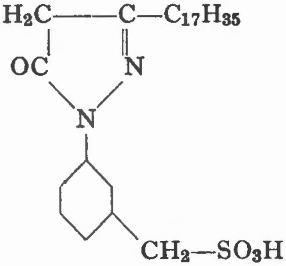
Sodium 1-chloro-4-nitrobenzene-sulphonate reacts with phenol to give sodium 4-nitrophenylphenol-2-sulphonate. By reduction with iron and hydrochloric acid the NO_2 is converted to NH_2. The 4-aminophenylphenol-2-sulphonate is then diazotized and treated with sodium bisulphite. By hydrolysis with HCl at 90°C, the hydrazine



$$C_6H_5—O—\underset{\displaystyle SO_3H}{\underset{|}{C_6H_3}}—NH—NH_2$$

is obtained.

This is merely reacted with stearoylacetic ethyl ester $C_{17}H_{35}$—CO—CH_2—CO.O.C_2H_5 tó produce the pyrazolone (which is extracted with methanol).
1-(3′ *sulphomethylenephenyl*)-3-*heptadecyl*-5-*pyrazolone:*

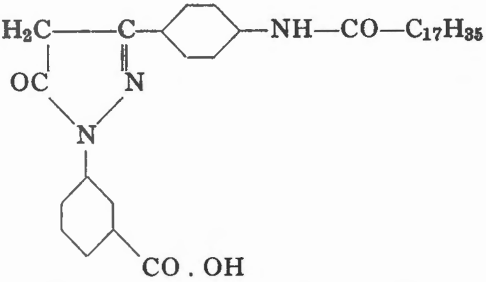


(para 511: coupler d)

m-nitrotoluene is chlorinated to give m-nitrobenzoylchloride NO_2—C_6H_4—CH_2—Cl (M.Pt. 46–48°C after recrystallizing from methanol). This is sulphonated with bisulphite in alkaline solution, then reduced with Fe+HCl, giving m-aminobenzyl-sulphonic acid NH_2—C_6H_4—CH_2—SO_3. The latter is converted to the hydrazine by diazotizing, treating with bisulphite and hydrolyzing (as with the preceding coupler). The hydrazine, SO_3H—CH_2—C_6H_4—NH—NH_2 is condensed with stearoylacetic ester, the product being finally hydrolyzed with sodium methoxide and extracted with benzene. The condensation can also be carried out in a mixture of water and propanol followed by extraction with alcohol.

1-(4′-*carboxyphenyl*)-3-*heptadecyl*-5-*pyrazolone* is prepared by diazotizing p-aminobenzoic acid NH_2—C_6H_4—CO.OH, treating with bisulphite, hydrolyzing with HCl at 90°C and condensing the resulting hydrazine, HO.OC—C_6H_4—NH—NH_2 with stearoylacetic ester.

1-(3′-*carboxyphenyl*)-3-*stearoylanilido*-5-*pyrazolone:*



m-aminobenzoic acid is converted to the hydrazine as above. This is condensed with p-nitrobenzoylacetic ester in acetic acid. This gives the corresponding 3-p-nitrophenylpyrazoline. This is reduced with Fe and HCl to produce the amine, which is then condensed with stearoyl chloride in pyridine. The coupler is precipitated with hydrochloric acid in the presence of ice and is then washed with acetone.

It should be noted that in this preparation the long chain acid chloride is condensed with an amine whereas in the previous preparations a stearoylacetic ester was reacted with a hydrazine.

542. Coupler binders

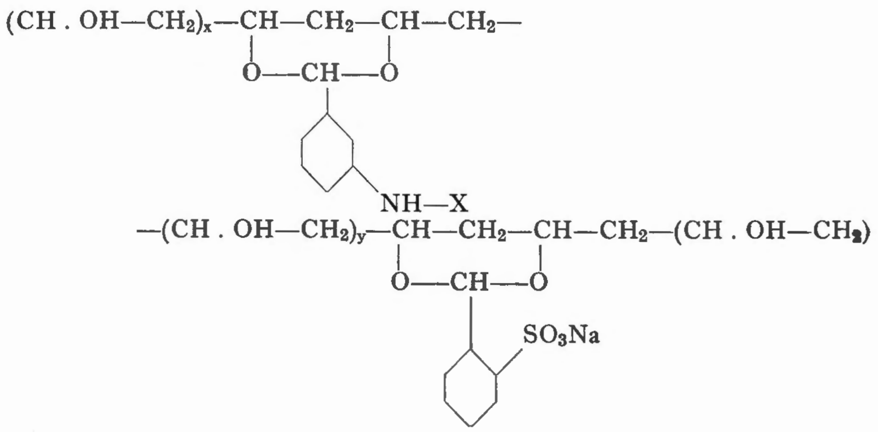
An original method for preventing the diffusion of a coupler is to join the molecule to that of the colloidal binder, thus making it an integral part of the sensitive layer.

The binder which can combine with other chemical groups is polyvinylalcohol which has many hydroxyl groups.

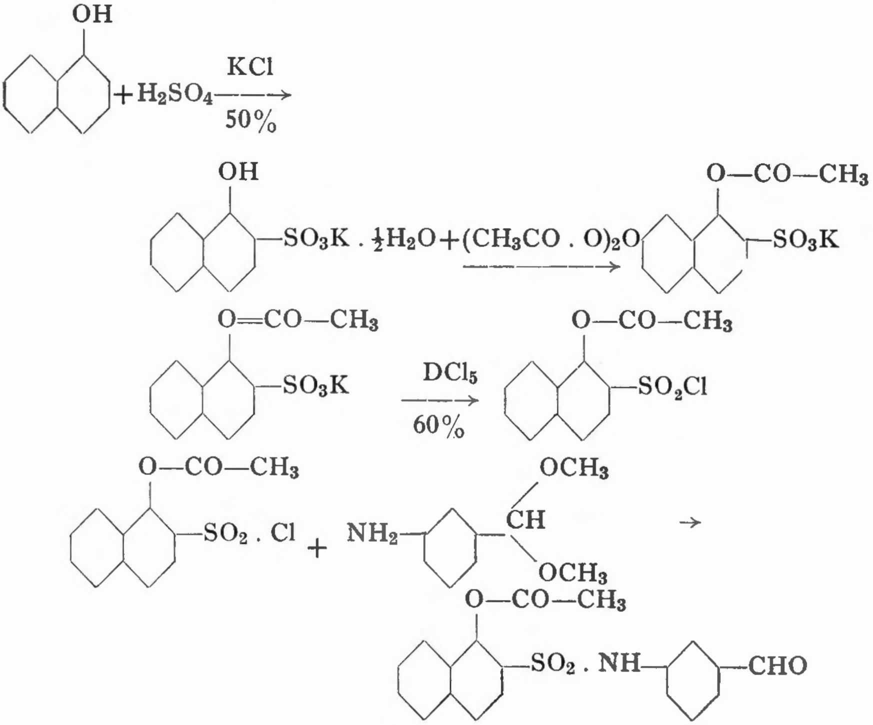
An Agfa patent⁽⁵⁵⁾ has disclosed the possibility of *acetylating* the hydroxyl group of the polyalcoholic polymer chains and combining them with *aldehyde phenols*. For example, polyvinyl alcohol treated with salicylaldehyde, in hot acetic acid, gives a coupler binder for cyan images. The same reaction can be carried out with o-hydroxyphenylacetaldehyde, 1-hydroxy-2-naphthaldehyde, o-hydroxycinnamaldehyde, 2:4:6-trichloro-3-hdyroxybenzaldehyde, etc. By acetalizing polyvinyl alcohol with m-aminobenzaldehyde then with phenylmethyl-pyrazolone-carboxylic acid, a coupler binder for magenta images is obtained. By replacing the pyrazolone with acetoacetanilide carboxylic acid, the coupler gives yellow images.

The coupler binder technique has, in addition, been studied and perfected by Jennings, Murray, White, Woodward and their collaborators in the Du Pont laboratories.⁽⁵⁶⁾ Their work has led to the manufacture of a positive multilayer colour film without gelatin.

As with the Agfa method, polyvinyl alcohol is converted to the acetal with an aldehyde having a colour coupler substituent. Amino-benzaldehyde can be used as the aldehyde, but only a certain number of hydroxyls are condensed with the coupler, to avoid making the binder insoluble. Some alternate hydroxyl groups are linked to aldehyde groups without coupler functions. They are called *modifying groups*. The general structure of a polyvinyl coupler binder is therefore as follows:



The coupler X for cyan is 1-*acetoxynaphthalene-2-sulphonic acid* linked to the amino-benzaldehyde by the NH_2 group as the sulphonamide $—SO_2—NH—$. It is prepared from α-naphthol by the following sequence.⁽⁵⁷⁾



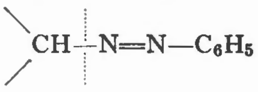
The condensation of the coupler with the polyvinyl alcohol is carried out by dissolving 200 g of coupler, 25 g of sodium benzaldehyde-sulphonate monohydrate (modifier), 500 g polyvinyl alcohol and 25 cc of 85% phosphoric acid in 2 L of dioxane. After 8 hours at 70°C, with continuous agitation, the reaction is complete. The solid obtained is filtered off, washed with acetone and dried. The binder therefore contains 10% of coupler. It is colourless and permeable like gelatin, and its mechanical strength is greater.

The polyvinyl acetal of m-benzoylacetamidobenzaldehyde can be used as the yellow coupler binder, and the *polyvinyl acetal of a m-benzoylaminopyrazolone* for the magenta as indicated at the beginning of the paragraph.

543. Coloured couplers

We have already explained in para. 523 the structure and purpose of coloured couplers.

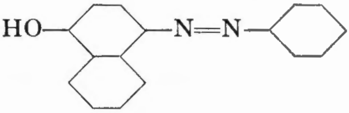
A reactive methylene group, for example, will unite with benzene diazonium chloride⁽⁵⁸⁾ to give a coloured compound of the type



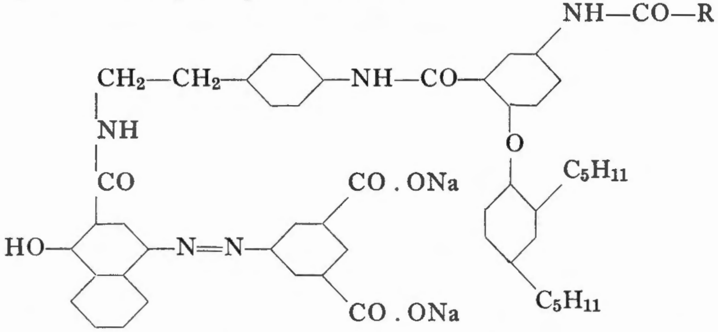
$$>CH—N=N—C_6H_5$$

which readily splits into its starting products. In the presence of a substituted p-phenylenediamine semiquinone, the group —N—N=C_6H_5 is replaced by =N—C_6H_4—NR_2.

With α-naphthol this would give the blue coupler:

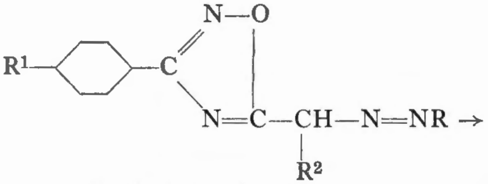


To this basic compound, anti-diffusing groups and solubilizing acid groups can be attached. Kodak have disclosed the use of azo coloured couplers having the following complex structure:(59)

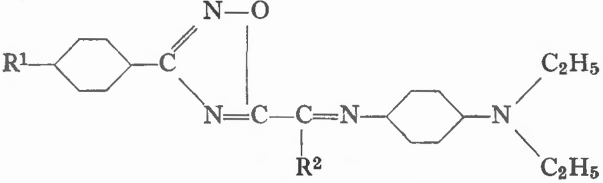


An anti-diffusing chain of the same type can be attached to a pyrazolone in the 3-position (magenta images).

Oxodiazol derivatives. Other coloured couplers for magenta images are obtained with derivatives of 1:2:4-oxodiazol combined with the diazonium compound.(60) Merckx(61) has shown that they are not readily transformed into azamethine dyes unless the radical R^2 next to the reactive methylene group is a nitrile function, quite a normal conclusion for methylene compounds of the type X—CH_2—Y.

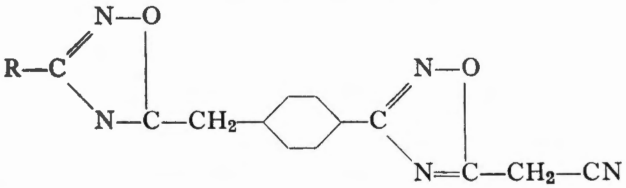


Oxodiazol coloured coupler



Oxodiazol developed dye

Certain oxodiazol magenta couplers which will combine with benzene diazonium chloride have the structure:



They are obtained by condensing p-toluamidozime with cyanacetyl chloride, then heating the cyanacetylamidoxime in the presence of acetic acid.

COLOUR PROCESSES

544. Agfacolor process

The Agfacolor process perfected in 1935 by Schneider, Wilmanns, Frolich and their collaborators was the first to use *non-diffusing couplers*. It is based on the principles disclosed by Rudolf Fischer in 1912.(63) The Agfacolor process has since its appearance been imitated many times. The three fundamental patents(64) were published in 1936–37. The first 24 × 36 mm reversal material was marketed in 1936; the 16 and 35 mm reversal films in 1937 and the 35 mm negative-positive film in 1939.

Details of the manufacture of the different layers were given in paragraphs 511, 512, 513 and 541. For the papers, emulsion of the soft Brovira type are used (para. 323). The amount of silver per sq. m. in each layer is from 0·7 to 1 g. An anti-oxidant such as hydroxylamine chloride is added.

A new positive film 'Type 5' does not contain the colloidal silver yellow filter (which can produce colour fog). The top emulsion, which is not colour sensitized, is coated to twice the normal thickness (12 μ) and is dyed yellow with a dye which is easily washed out.

Treatment of a negative film. Colour development 6–7 mins. at 18°C. Magnesium sulphate bath (4%) 2 min. Wash 15 mins. Bleach 5–8 mins. Wash 5 mins. Fix 5–8 mins.

Variation. *Bleach-fix* 8–10 mins. Wash 20 mins. (see para. 555b).

Negative film developer	*Working soln.*	*Replenisher*
Diethyl-p-phenylenediamine	2·75	4 g
Sulphite anh.	2	2 g
Potassium carbonate anh.	75	75 g
Potassium bromide	1·5	—
Disodium salt of ethylene-diamine-tetraacetic acid (Trilon B)	2	2 g
Nekal BX2 (Alkylnaphthalene sulphoxylate, sodium salt)	1·2	2·5
Water to	1000	1000 cc

15 litres of solution will develop a 100 m of 35 mm film.

Paper developer

Hydroxyethyl-ethyl-p-phenylenediamine	4·5 g
Potassium carbonate anh.	78 g
Hydroxylamine hydrochloride	2 g
Sulphite anh.	2 g
Water to	1000 cc

The hydroxylamine hydrochloride is an anti-oxidant. The sodium salt of ethylene-diamine-tetraacetic acid is a metal sequestering agent whilst the Nekal BX2 is a wetting agent (see end of para. 557).

The processing operations are carried out in very dim green light. The positive has a gap between 570 and 600 mμ and an Osram sodium lamp with an Agfa 165 or 166 filter can be used. For the negative, an ordinary lamp with a number 170 filter is used.

Among the additional formulas which have been published we would mention:

Bleach bath

	Films	Papers
Potassium ferricyanide	100	20 g
Disodium phosphate	4·3	—
Monosodium phosphate	5–8	—
Water to	1000	1000 cc

Hardening fixer for papers

Sodium acetate anh.	60 g
Sodium benzene sulphinate	2 g
Alum	30 g
Hypo	80 g
Water	1000 cc

The latter has recently been replaced by a *bleach fix bath* (see para. 555c).

Important note: The preceding formulas, as well as those which follow, are given solely as illustrations. The different types of colour film actually made are subject to continuous modifications together with the composition of the solutions which quickly become outdated and useless. It is therefore impossible to try to record in a book, which necessarily cannot be altered for several years, the exact methods of treating the various makes.

545. Ansco Color process

The Ansco Color process is derived from Agfacolor with minor modifications. The negative film type 843, on a grey base, has spectral sensitivity maxima at 450, 555 and 655mμ. The absorption maxima of the dyes are 440 mμ for the yellow, 540 mμ for the magenta and 675 mμ for the cyan.(65) Those of the positive dyes are 440, 540 and 660 mμ. Print materials have been manufactured on white opaque acetate (Printon).

Processing of 35 *mm motion picture film at* 20°C (68°F)

	Minutes Treatment		
	Reg. 843	Dupe. 846	Pos. 848
Preliminary alkaline bath(66)	—	—	2
Jet rinse	—	—	30 sec.
Colour developer 608	10–12	6–7	—
Colour developer 609	—	—	11–14
Stop bath 859B	30 sec.	30 sec.	30 sec.
Hardening fixer 804	8	8	8
Wash	4	4	4
Bleach 715A	6	6	6
Wash	4	4	4
Fixer (800)	8	8	
Wash	6	6	
Dry	25	25	

After bleaching and washing, and before final fixing, the positive film is surface dried with an air blast.

Application of viscous developer to the *sound track*: 30 secs.

Wash 2 mins., fix (800) 4 mins., wash 8 mins. Stabilize 2 mins. Rinse 1 sec., dry 25 mins.

Developer 608 *for Ansco color negatives:*	Working solution	Replenisher
Water to	1000 cc	1000 cc
Calgon (hexametaphosphate)	1 g	1 g
Sodium sulphite anh.	3 g	3·75 g
Developer S5	7 g	11 g
Sodium carbonate monohydrate	75 g	75 g
Sodium sulphate anh.	30 g	30 g
Potassium bromide	2 g	1 g
Accelerator DA-1, 5%	5 cc	6 cc
Caustic soda to obtain a pH of 0·45 above that of the fresh working soln.		abt. 2 g

Consumption: about 2½ gals. per 1000 ft. of 35 mm film.

Developer 609 *for Ansco color positive:*	Working solution	Replenisher
Water to	1000 cc	1000 cc
Calgon (hexametaphosphate)	1 g	1 g
Sodium sulphite anh.	2 g	3 g
Developer S5	5 g	7·5 g
Sodium carbonate monohydrate	60 g	60 g
Potassium bromide	1 g	2 g
Potassium iodide	1 mg	—
Caustic soda to obtain a pH of 0·4 above that of the working solution		abt. 2 g

Stop bath 659B (pH = 5·4)

Glacial acetic acid	3 cc	10 cc
Sodium acetate anh.	30 g	20 g
Water to	1000 cc	1000 cc

Hardening fixer 804 (pH = 4)

Water to	1000 cc
Chrome alum	30 g
Potash alum	20 g
Sodium acetate anh.	10 g
Sodium sulphite anh.	10 g
Hypo	200 g

Bleach 715*A* (pH 4·5–4·7)

Water to	1000 cc
Calgon	0·5 g
Potassium ferricyanide	100 g
Sodium acetate anh.	40 g
Glacial acetic acid	2·25 cc

Stabilizer

2% Formalin

Sound track developer

A.	Water to	1000 cc
	D A-5	1 g
	Metol	20 g
	Sodium sulphite anh.	40 g
	Hydroquinone	20 g
	Hypo	3 g
	Formalin (37%)	20 cc
B.	Hydroxyethylcellulose (W.P.40)	45 g.
	Water to	1000 cc

Mix 900 cc A and 100 cc B, then add 200 cc more of stock solution of the thickener.

Reversal films. The following solutions have been given for processing reversal films:

First developer: 14 mins. at 20°C in:

Water to	1000 cc
Calgon 10%	10 cc
Metol	3 g
Sodium sulphite anh.	50 g
Hydroquinone	6 g
Sodium carbonate anh.	34 g
Potassium (or sodium) thiocyanate	2 g
Potassium bromide	1 g

Stop bath: 1–2 mins. in:

Water to	1000 cc
Glacial acetic acid	10 cc
Sodium acetate	20 g

Hardener: 4 mins.

Water to	1000 cc
Chrome alum	30 g

Colour developer: 16 mins. at 20°C in:

Water to	1000 cc
Calgon (10%)	10 cc
Ansco dicolamine	16 cc
Sodium bisulphite	1 g
Sodium carbonate anh.	58 g
Potassium bromide	1 g

Stop bath: 1 min.

Hardener: 4 mins.

Wash: 5 mins.

Bleach: 10 mins. in:

Water to	1000 cc
Potassium ferricyanide	60 g
Potassium bromide	15 g
Disodium phosphate	13 g
Sodium bisulphate	6 g

After washing for 4 mins., fix in 20% hypo. Wash 10 minutes and dry.

546. Gevacolor process

In principle this is similar to the preceding processes (see para. 555).

Negative film. Colour development: 6½ mins. Rinse: 30 sec. Hardening fixer: 5 mins. Wash: 10 mins. Bleach: 6 mins. Wash: 10 mins. Fix: 5 mins. Wash: 5 mins. Stabilize: 10 mins. Final wash: 15 mins.

Reversal film. First development in an M.Q.-thiocyanate bath: 12 mins. at 20°C. An excess of thiocyanate (solvent) gives a blue cast, whilst a lack of it gives a yellow cast. Stop bath: 3 mins. Rinse: 1 min. Re-expose under water at 18 in. from an ordinary 500 W lamp: 2½ mins. Colour development: 13 mins. Clear: 3 mins. Harden: 5 mins. Wash: 15 mins. Bleach: 7–10 mins. Wash: 3 mins. Fix: 5 mins. Wash: 15 mins. Dry.

Gevacolor negative is printed on to paper.

547. Telcolor process

This is the Swiss equivalent of the Agfacolor process. As with the latter, the paper contains no intermediate yellow filter layer of colloidal silver.

Treatment of film (see para. 555b). Colour development at 18°C: 8 mins.

4% magnesium sulphate: 2 mins. Wash: 15 mins. Bleach: 6–8 mins. Wash: 5 mins. Fix: 8–12 mins. Final wash: 15 mins.

The paper is developed with the less toxic hydroxyethylethyl-p-phenylenediamine.

548. Ferraniacolor process

This is the Italian equivalent of Agfacolor and is represented by a reversal transparency film and a negative film for paper prints. For motion picture work, duplicate negatives are made on a reversal duplicate stock.

Reversal processing

1*st developer:* 20 mins. at 18°C. in:

Water to	1000 cc
Sodium sulphite anh.	50 g
Amidol	5 g
Potassium bromide	1 g
Calgon	1 g

Agitation: every 15 secs. for the first two minutes then every minute.

Storage life: 1 week.

Wash: 20 mins.

Exposure: 90 secs. from each side at 3 feet from a 12,000 lux lamp (No. 1 Photoflood)

Colour developer: 9–12 mins. at 18°C. in:

A.	Water	500 cc
	Hydroxylamine hydrochloride	1 g
	Diethyl-p-phenylenediamine sulphate	2·8 g
B.	Water	500 cc
	Sodium sulphite anh.	2·5 g
	Sodium carbonate anh.	65 g
	Benziminazole nitrate (anti-foggant)	17 mg
	Calgon	2 g
	Potassium bromide	1·2 g
	Caustic soda	2 g

pH: 11–11·5.

Life: 2 weeks.

Wash: 20 mins.

Bleach-hardener: 10 mins. at 18°C.

Water to	1000 cc
Potassium ferricyanide	50 g
Potassium bromide	25 g
Sodium acetate cryst.	60 g
Boric acid	5 g
Potash alum	30 g

Rinse: 1 min.

Fix: 5 mins. at 20% hypo.

Wash: 20 mins.

Wipe and dry.

Negative processing

Colour developer: 6½–7 mins. at 18°C. in:

A.	Water	500 cc
	Hydroxyethylethyl-p-phenylenediamine sulphate	4 g
B.	Water	500 cc
	Sodium sulphite anh.	0·5 g
	Sodium carbonate anh.	84 g
	Potassium bromide	2·5 g
	pH 10·8–11.	

Wash: 15 mins.

Bleach: 5 mins. at 18°C in:

Water to	1000 cc
Potassium ferricyanide	100 g
Potassium bromide	50 g

Rinse: 1 min.

Fix: 5 mins. in 20% hypo.

Wash: 20 mins.

Wipe and dry.

Paper processing

Colour developer: 3–5 mins. at 18°C in:

A.	Water	50 cc
	Hydroxyethylethyl-p-phenylenediamine sulphate	4·5 g
B.	Water to	950 cc
	Sodium sulphite anh.	0·5 g
	Potassium carbonate	84 g
	Hydroxylamine hydrochloride	2 g
	Potassium bromide	0·5 g
	Product A.70	2 g

Wash: 15 mins.

Bleach-fix: 10 mins. in product VC.204 containing a complex iron salt and hypo. (See para. 555b and c.)

Wash: 20 mins.

Stabilize in:

Water to	1000 cc
Formalin 40%	90 cc
Sodium carbonate anh.	2 g

Wash: 5 mins.

Dry.

549. Du Pont 'Color Release positive film'

We have seen in para. 542 that the diffusion of couplers can be prevented by combining them with the colloid binder of the layer, in this case, *polyvinyl alcohol.*

Using this system, Du Pont have made a positive colour film(67) made up of three layers of different coupler-binders, each containing a sensitive silver halide, and no gelatin.

This positive, type 275, has the following structure: the base (with a thin cyan anti-halo backing); a bottom layer of yellow coupler binder, which is sensitized to green; a middle layer of cyan coupler binder, red sensitized; a top layer of magenta coupler-binder only sensitive to blue and dyed with a decolorizable yellow dye. Isolating layers separate the emulsions. There is no colloidal silver yellow filter layer. The most noteworthy feature is that the magenta coupler is in the top layer, the cyan coupler is in the middle layer and the yellow coupler is at the bottom, the reverse of normal systems. This enables the sharpness of the magenta and cyan images to be improved. The polyvinyl alcohol emulsions do not normally gel unless the polymer has a very high viscosity. They can, however, be set by the action of borates on the aqueous alcoholic solutions of the binder(68) (para. 338). The presence of inert groups introduced at the same time as the coupler groups prevents the binder from becoming impermeable, enabling the development rate of the three layers to be balanced by controlling their respective content of inert groups.

Printing is carried out with three monochromatic lights, using the filters Corning red 2412, blue 5543 and Du Pont green 60G. The density range of a colour negative developed to γ 0·85–0·9 must not exceed 1·45. If an optical printer is used the negative gamma should be reduced to 0·65–0·7.

Processing. Colour development: 10–12 mins. Rinse 1–2 mins. Fix: 6 mins. Wash: 5 mins. Bleach: 5 mins. Wash: 4 mins. 2nd fix: 4 mins. Wash: 10 mins. Wipe and dry.

After bleaching and washing, the sound track can be sulphided by local application of the reagent.

Colour developer, pH 10·5

Water to	1000 cc
Diethyl-p-phenylenediamine hydrochloride	2·5 g
Sulphite anh.	10 g
Sodium carbonate monohydrate	47 g
Potassium bromide	2 g

1st fixer, pH 4·5. To be diluted with two parts of water just before use.

Water to	1000 cc
Hypo	240 g
Sulphite anh.	15 g
Borax	18 g
Glacial acetic acid	12 g
Potash alum	20 g

Bleach pH 7–7·5:

Water to	1000 cc
Potassium ferricyanide	100 g
Boric acid cryst.	10 g
Borax cryst.	5 g

2nd fixer:

Water to	1000 cc
Hypo	200 g

Sulphiding solution:

Distilled water to	1000 cc
Carboxymethyl cellulose	20 g
Sodium sulphide $9H_2O$	63 g

550. Eastman Color process

In this process, coupler diffusion in the different layers of the material is prevented in a different way, devised by M. Martinez in 1937. *Each coupler is first dissolved in a non-volatile solvent (or in a resin) which is dispersed in minute droplets in the appropriate emulsion.*(69)

The couplers can be protected by tricresyl phosphate, triphenyl phosphate, n-butyl phthalate, n-hexyl benzoate, terpene-maleic resins,(70) etc.

During colour development, the coupler remains in the interior of the globules of protective binder. These are readily permeated by the developer oxidation product which can therefore couple to give the dye.

Couplers were incorporated in this way in the negative *Kodacolor* (1942) and reversal *Ektachrome* films. *Aero Kodacolor*, made during the war, was a reversal film in which one emulsion was infra-red sensitive for camouflage detection.

The Eastman negative colour films were later improved by the adoption of the *coloured coupler* system (paras. 523 and 543) for automatic correction by masking of the magenta and cyan images.

In practice, motion picture negatives are made on *Eastman Color* films, whilst normal negatives are on *Ektacolor*. The two types are made following the same principles.

The colour positives are printed on colour-positive films and paper respectively, containing colourless couplers which are incorporated in the same way.

Ektacolor. Rolls of Ektacolor film are developed in a non-allergenic developer of the sulphonamide type (para. 535). Processing is carried out at 20°C and takes less than an hour. The developed film is treated in a stop bath, fixed in a hardening fixer, bleached, again fixed in a hardening fixer, washed and dried. A U.S. gallon of developer (3·8 L) will develop 9 sq. ft. (0·837 m^2). After one-third of this area has been developed, however, the development time must be increased by 1 minute, and a further minute after two-thirds. With the other baths, a gallon is enough for 12 sq. ft. (1·1 m^2).

After washing, the film appears milky and opaque: this is due to the presence of the globules of coupler-oil in the swollen gelatin. After drying, the refractive indices become practically alike, and the film again becomes transparent.

Due to the presence of coloured couplers, the neutrals appear orange-brown: the whole appearance is of an orange stain. The yellow image is not corrected: it has an unwanted absorption in the green.

Ektacolor film has complementary colour images, and is printed on to a paper with three differentially sensitized layers together with the appropriate dispersed couplers. The colour sensitivity of the paper takes into account the presence of the coloured masks in the negative.

Eastman Color Negative. This motion picture negative is similar to Ektacolor film. The couplers have been improved, and the sensitivity increased. Type 5248 is balanced for 3200°K and has an ASA index of 25 in artificial light and 16 in daylight.

Eastman Color processing follows the sequence:

(1) Removal of the anti-halo coating in a carbonate bath: 1–2 mins.
(2) Colour development in a non-allergenic solution containing 4-amino-N-ethyl-N-methylsulphonamido-ethyl-m-toluidine sulphate(71) and 0·38% of benzyl alcohol. Time: 25–27 mins. at 21°C.
(3) Stop bath: 4 mins.
(4) Wash: 4 mins.
(5) Bleach: 5 mins.
(6) Wash: 4 mins.
(7) Fix: 4 mins.
(8) Wash: 8 mins.
(9) Wetting agent: 1 min.
(10) Dry: 15–20 mins.
(11) Lacquer both sides.

Separation positives are printed from the original colour negative on *panchromatic film* 5216, which is more contrasty than the old 5203. The emulsion of this panchromatic film contains a cyan dye which is not completely removed.

Duplicate negatives. These are printed on '*Internegative*' 5245, which has finer grain and higher contrast than the old type 5243. The Internegative film has the same coloured couplers as the negative film, but the layer order has been changed; the bottom red sensitive layer next to the base contains the yellow coupler; the middle green sensitive layer contains the cyan coupler, whilst the upper blue sensitive layer contains the magenta coupler. The sharpness is increased in this way. The same processing solutions as for the original negative are used.

Eastman Color Positive. The positive film type 5352 is manufactured with a new magenta coupler giving a dye whose blue transmission is improved. The emulsion layers are arranged in the following way: bottom layer, next to the support, blue sensitive, containing yellow coupler; middle layer, red sensitive containing cyan coupler; top layer, green sensitive, containing magenta coupler. A blue filter separates the middle from the bottom layer, whilst a pink dye, intended to absorb the diffused green light (which reduces the sharpness of the magenta image), is incorporated in all three emulsions.(71b) The outer layer is protected with an anti-abrasion gelatin layer.

Printing is done with a 3000°K lamp with three colour filters: Wratten 70 (red), 76+61 (green) and 35+38A (blue), or if three narrow cut bands are required, with Wratten 29 (red), 16+61 (green) and 35+38A (blue).

Laboratory lighting: sodium lamp with Wratten 23A and 57 filters.

Development: 12–15 mins. at 21°C in a solution containing 2-amino-5-diethylaminotoluene hydrochloride (produces dermatitis). The film is fixed in a potash alum hardening fixer. After several days, a gelatinous mud forms, of rubbery consistency, which resists all corrosive agents. It is very difficult to remove, even mechanically. Analysis has shown that this mud is of protein origin. Undoubtedly it results from the dissolving of low molecular weight proteins present in the gelatin, followed by precipitation with alum.

To stabilize the magenta image, the film is treated for 5–10 secs., after processing, in 1:20 formalin, containing a wetting agent.

The sound track is developed after bleaching and air squeegeeing, by roller application of a viscous hydrosulphite solution (10 secs.). Gamma of variable area track: greater than 2.

The positive Eastman Color images are very resistant to acids and alkalis, and even to oxidizing and reducing agents. If the action of the latter is short, the images resume their normal state by the opposite action. However, the colour varies slightly with the pH, and this can be changed by the carbon dioxide in the air. The result of this is that old prints appear somewhat different from fresh ones.

Ektachrome reversal film. Ektachrome is available as roll or sheet film. It is processed as follows:

(1) Development: 15 mins. at 20°C.

(2) Rinse: 1 min.

(3) Harden: 3–10 mins.

(4) Reversal exposure: expose each side for 5 secs. at 1 ft. from a No. 1 photoflood.
(5) Wash: 5 mins.
(6) Colour development: 25 mins. at 20°C.
(7) Wash: 5 mins.
(8) Clear and fix: 5 mins.
(9) Wash: 5 mins.
(10) Bleach: 10 mins.
(11) Wash: 1 min.
(12) Fix, in the clearing bath already used: 5 mins.
(13) Wash: 10 mins.
(14) Blot or wipe.
(15) Dry: do not exceed 43°C.

At 24°C, the 1st development time can be reduced to 10 mins. and colour development to 15 mins. Bleach: 8 mins.

Regular agitation is essential throughout. For sheet film, the racks are removed from the tanks every minute, and drained for 5 secs. from each lower corner.

Paper prints. The structure of the printing paper is similar to that of the positive film. Two types are made: type C for printing from Ektacolor negative and type R, reversible, for prints from Ektachrome transparencies.

551. Kodachrome

In the Kodachrome process, the couplers are not incorporated in the emulsion layers, but each layer is separately developed with the coupler in the developer. The differential treatment of each layer is produced by selective second exposure, each time being followed by a colour development step.(72)

The film has the normal arrangement of three superimposed emulsions, but the emulsion next to the base is sensitized with a red sensitizer which is not destroyed by the first developer.

After exposure, it is developed to γ_∞ then the bottom layer which carries the red record is exposed to light of this colour through the base. By treating in a cyan colour developer this layer alone is developed to a reversed cyan image, whilst the remaining silver bromide in the other two layers is unchanged.

The film is then washed, and the outer layer is exposed to blue light, which is stopped by the intermediate yellow colloidal silver filter layer and does not, therefore, affect the middle layer. A second colour development step produces a yellow image in the top layer.

The third stage is to simultaneously fog and develop the residual bromide in the middle layer with a magenta colour developer containing a fogging agent. All the silver in the film is then rehalogenized and removed by fixing.

Fogging agents:(73) hydrazine sulphate, thiourea, allyl-thiourea, sodium stannite. Compounds which contain the group —CO—CH.OH— have also been proposed.(74)

Kodachrome film, which is a reversal material, is now only used in small sizes (35 mm photo film and 16 mm cine film). It is available in two types: daylight (Regular) and for photoflood light (Type A). 16 mm *Commercial Kodachrome*, for originals which are to be duplicated on *Duplicating Kodachrome* is softer than the normal film. For printing, a 3000°K lamp is used together with an infra-red absorbing filter. For the adjustment of printing speed, a copy can be made on black and white positive stock with a 1·20 neutral density, and developed in D-76, γ 1·2 with D_{max} 1·65. Printers: Debrie, Depue, Art. Reeves. Optical printing for projection of a mask, on the 'Chroma-Tech' printer (Hollywood). For printing tests: Acme tester giving 11 intensities with 5 filters, that is, 55 images.

552. Old, controlled penetration Kodachrome process

The first modern three-colour colour development process was the old Kodachrome process invented by Mannes and Godowsky.(75) Although it is no longer used, due to the lengthy processing, it deserves a fairly detailed description because of its ingenuity.

A film with three emulsion layers separated by gelatin intermediate layers, is exposed and the three images are developed in an ordinary developer—M-Q-thiocyanate for example—and reversed in permanganate. The remaining silver bromide is exposed completely and is developed to *cyan* in a colour developer, giving a positive image which is completely cyan. The film is fixed, washed and *dried* before the next stage: the two outer layers, coloured cyan like the rest, are decolorized with a *controlled penetration bleach* made up of a mixture of glycerin and isopropyl alcohol and a solution of quinone. This decolorizes the dye and converts the silver to silver chloride.

4 mins.	Glycerin	500 cc
	Isopropyl alcohol	1000 cc
	Water	75 cc
	Quinone	5 g
	Hydrochloric acid conc.	20 g

Bleaching is stopped by treatment for 1½ mins. in

Sodium bicarbonate	15 g
Isopropyl alcohol	1000 cc
Glycerin	1000 cc
Water	1000 cc

After washing, the decolorized and rehalogenated upper layers are redeveloped, after exposure, in a *magenta* colour developer. The film is washed and dried. It then has two magenta layers and one cyan.

Third stage: the outer layer is again decolorized in a controlled penetration bleach (about 2 mins.), stopped, washed and redeveloped to *yellow* in a third colour developer.

The silver formed with the dye image is then bleached in ferricyanide and removed by fixing to give a film with three transparent colour images in yellow, magenta and cyan.

The progressive penetration of the bleach is controlled with a microscope on cross-sections cut at regular intervals.

553. Single layer papers

The superimposition of three different emulsions is a disadvantage in the manufacture of colour materials. The idea has naturally been considered, of mixing the three emulsions, differentially sensitized and associated with their respective couplers, to simplify the process. If the mixing is directly carried out in gelatin, however, it becomes impossible to restrict the action of the different silver halides towards their respective couplers.

The difficulty is overcome by dispersing each colour sensitized emulsion, together with its colour coupler, in an appropriate medium. This medium can be a non-volatile liquid or a dispersible polymer.(76) Three silver chloride emulsions, respectively sensitized to blue, green and red, and containing yellow, magenta and cyan couplers can be protected in this way and mixed in a solution of gelatin or other colloid as fine particles. Preferably, each emulsion should be dispersed separately in the colloid before mixing. In addition, to prevent diffusion of developer oxidation products from one particle to another, it is suggested that a grainless silver iodide emulsion containing a non-coupling reducer should be added to the mixture.(77)

These mixtures of emulsion and coupler are used for the manufacture of single layer colour papers.

COLOUR DEVELOPERS

554. Colour developers containing coupler

To develop the latent image of a silver halide emulsion to colour, the developer should contain both a substituted p-phenylenediamine and a coupler (or former). The bath generally contains an alkali carbonate and a relatively small amount of sodium sulphite.

The coupler is usually dissolved first in a water miscible *organic solvent*: methanol, ethanol, isopropyl alcohol, acetone. With the naphthols, the sodium salts can be prepared with caustic soda.

We have seen that the colour produced depends mainly on the choice of coupler and to some extent is influenced by the particular p-phenylenediamine. The formularies advise the following compounds, but many others exist, which are often superior, and which have been given in this chapter.

Cyan couplers: 1-naphthol, 2:4-dichloro-1-naphthol, m-hydroxybiphenyl.

Magenta couplers: p-nitrophenylacetonitrile, 1-phenyl-3-methyl-5-pyrazolone.

Yellow couplers: acetanilide and its derivatives, particularly acetoacet-2:5-dichloranilide.

Colour factor. This is the ratio of dye/silver. It does not have a constant value as it varies with the development time and with the density of the silver image. As we have seen, the reduction of the silver image and the formation of the dye do not take place simultaneously, and consequently do not follow the same curves. The coupler concentration has a considerable influence on the progress of colour development, the greatest consistency occurring when equimolecular proportions of developer and coupler are present (greatest independence of colour factor compared with the silver density).

Tull has shown that the coloration factor decreases as the colour density increases, the variation being more accentuated when development is too rapid. The phenomenon is most apparent when the coupler concentration is too low, or the sulphite too high.

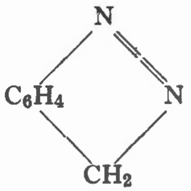
Sulphite concentration. Colour development takes place even in the absence of sulphite. According to Evans and Hanson, the latter's role is played by the coupler. In the absence of sulphite, the colour factor increases greatly. With too high a sulphite concentration, the colour curve falls below that of the silver, whilst the opposite is true with the normal developer.

The pyrazolones are the couplers which are most sensitive to variations in sulphite concentration.

Alkali content. An increase in the amount of alkali increases the activity of the bath and the speed of development, but also increases the tendency to oxidize, and hence the fog. Jelley has recommended the replacement of alkali by an alkylamine such as triethanolamine whose solvent action is less than that of ammonia.(78)

The anilides and the nitriles are susceptible to variations in pH.

Anti-foggants. Development fog can be avoided by adding an organic anti-foggant to the developer. The use of a nitro or amino *indazole*(79) has been particularly recommended, for example 1-*methyl*-5-*nitro*-*indazole* at a concentration of 0·2 per 1000.



554b. Colour developer formulas

These are of the following general type:

Water to	1000 cc
Sodium sulphite anh.	5 g
Diethyl-p-phenylenediamine hydrochloride	3 g
Potassium carbonate	60 g
Potassium bromide	2 g
Coupler	1 g
Acetone or alcohol	50 cc

Other suggested formulas:

Cyan

Diethyl-p-phenylenediamine (HCl)	3 g
Sodium sulphite	5 g
Sodium carbonate	50 g
Potassium thiocyanate	0·5 g
Boiled water to:	1000 cc
m-hydroxybiphenyl	2·5 g
Methanol	100 cc

Magenta

Diethyl-m-toluylenediamine (HCl)	1 g
Sodium sulphite	10 g
Sodium carbonate	30 g
Potassium thiocyanate	0·5 g
Boiled water to:	1000 cc
p-nitrophenylacetonitrile	0·75 g
Acetone	20 cc
Isopropanol	100 cc

Yellow

Dimethyl-p-phenylenediamine (HCl)	1 g
Sodium sulphite	2 g
Sodium carbonate	30 g
Boiled water to	1000 cc
p-nitroacetoacetanilide	2·5 g
Isopropanol	100 cc

Diethyl-p-toluylene diamine hydrochloride is sold under the name *Tolochrome* (May and Baker).

Diethyl-p-phenylenediamine can also be used as the sulphur dioxide compound, known as *Genochrome.*(80) 228 g of this product corresponds to 200·5 g of hydrochloride, 213 g of sulphite or 164 g of base. Example of developer:

Water to	1000 cc
Calgon	4 g
Sodium sulphite anh.	20 g
Sodium carbonate anh.	50 g
Potassium bromide	2 g
Water to	100 cc
Genochrome 10%	7 cc
Coupler solution	100 cc

Coupler solutions in alcohol: 2:4-dichloro-1-naphthol (cyan) 10 g.p.L.,
p-nitrophenylacetonitrile (magenta)(81) 3 g.p.L.
acetoacet-2:5-dichloranilide (yellow) 10 g.p.L.
The developer can be used for 2 hours.

555. Universal developers for coupler-containing emulsions

Each manufacturer of colour papers or films has worked out developer formulas and precise working conditions which it is advisable to follow as carefully as possible. However, in the absence of information it can happen that it is necessary to improvise a processing technique, after a few preliminary tests to determine mainly the development time. Under such conditions it is useful to have a starting point. Gordon has worked out two types of bath, the first is applicable to reversal films of the Ektachrome type and the second to negative films of the Agfacolor type. It is advisable to note that the use of universal formulas for all makes of colour film should be made with care, and that systematic tests should be carried out first, to enable the inevitable correction to be made. It is obvious that all brands of film, and even different batches of the same film cannot, because of their differences, however small, be treated in exactly the same way without giving different results, and without appropriate modifications the colour results may be disastrous.

A. Processing reversal materials of the Ektachrome type.(82)

1. *First developer:* 13½ mins. at 20°C (pH 10·8)

Water to	1000 cc
Metol	3 g
Sodium sulphite anh.	50 g
Hydroquinone	7 g
Sodium carbonate anh.	34 g
Potassium thiocyanate	3·6 g
Potassium bromide	2 g

2. *Hardener:* 5 mins. at 20°C (pH 3·5)

Water to	1000 cc
Chrome alum	50 g
Sodium citrate	20 g
Citric acid	10 g

3. *Colour development:* 25 mins. at 20°C (pH 12·5)

Water to	1000 cc
Diethyl-p-toluylenediamine HCl	12 g
Sodium sulphite anh.	10 g
Disodium phosphate	20 g
Caustic soda	5 g
Potassium bromide	1 g

4. *Fixer:* 4 mins. at 20°C (pH 4·6)

Water to	1000 cc
Hypo	125 g
Sodium acetate	30 g
Sodium sulphite	10 g
Citric acid	20 g

5. *Bleach:* 10 mins. at 20°C (pH 9·3)

Water to	1000 cc
Potassium ferricyanide	80 g
Potassium bromide	60 g
Sodium carbonate anh.	4 g
Benzyl alcohol	16 g

Between the different baths it is, of course, necessary to wash in running water. For comparison, refer to the table at the end of para. 550, relative to Ektachrome.

If the first development is unduly protracted, warmer tones are produced whilst prolonged colour development or too high a temperature gives a yellowish fog. If colour development is shortened (or carried out too cold) the colours appear cooler. Too much metol in the first developer results in a greenish cast; too much hydroquinone, a reddish cast.

A litre of colour developer will develop twenty 9 × 12 cm films. After 10 days' keeping a green cast is produced.

If the pH of the bleach bath is too low (acid) the magenta image may be reduced. A careful wash must precede bleaching or the developer present in the film may be oxidized giving a coloured fog. The benzyl alcohol introduced into the above formula has the purpose of reducing this oxidation.

Reversal exposure comes before colour development: 5 secs. at 1 ft. from a No. 1 photoflood on each side of the film.

Pilkington(83) has given the following experimental formula for the colour developer:

Stock solution:

Water to	1000 cc
Potassium metabisulphite	75 g
Genochrome (para. 554)	190 g
Potassium bromide	50 g

For use take:

Water to	1000 cc
Sodium carbonate anh.	55 cc
Stock solution	20 cc

The first developer, according to this worker, contains 2·5 times the amount of thiocyanate for development of Ektachrome compared with Ansco film. A lack of thiocyanate gives yellowish highlights with Ektachrome and conversely (optimum concentration 0·5%). Fixing in a neutral bath gave a red fog with Ektachrome but is advisable with Ansco Color. Conversely the bleach bath must be basic for Ektachrome and acid for Ansco film.

555b. Universal developers for processing negative films

(Agfacolor, Gevacolor, Ferraniacolor, Telcolor, Pakolor, etc.) according to Gordon's formula(84) (see paras. 544, 546, 547, 548).

Colour development in:

Water to	1000 cc
Hydroxyethylethyl-p-phenylenediamine (sulphate)	4 g
Potassium carbonate	75 g
Potassium bromide	2·5 g (0·5 for Gevaert)
Sodium sulphite anh.	2 g
Ethylene diamine tetraacetic acid	1·5 g
Trisodium phosphate	10 g

The developer does not give severe dermatitis. It is the constituent of *Droxychrome* (May and Baker).

Ethylene diamine tetraacetic acid is a metal ion sequestering agent.

Development times: Agfa 7 mins., Ferrania 9 mins., Gavaert 10 mins., Telco 9 mins., Pakolor 9 mins.

Exhaustion of the developer: after 10 rolls of 3½ × 2¼ or seven 20-exposure rolls of 35 mm. Will keep for 10 days (oxidation).

A ***magnesium sulphate solution*** containing 3% $MgSO_4$ (assumed anhydrous) is used between development and washing in order to prevent softening of the gelatin.

Bleach-fix bath (Agfa: D.B.P. 866,605—1953)(84b):

Water to	1000 cc
Ferric salt of ethylenediamine-tetraacetic acid	60 g
Sodium carbonate anh.	5 g
Potassium bromide	30 g
Sodium or potassium thiocyanate	10 g
Hypo	140 g

Can be used for eighteen 120-rolls or twenty-one 20-exposure rolls of 35 mm.

Other formulas for Agfacolor, Gevacolor and Ferraniacolor have been worked out by Thomson.(85)

555c. Gordon's formulas for papers (prints from negatives)(85b)

Developer

Water to	1000 cc
Hydroxy ethylethyl-p-phenylenediamine sulphate	4·5 g
Potassium carbonate	75 g
Potassium bromide	2·5 g
Sodium sulphite anh.	2 g
Ethylenediamine-tetraacetic acid	1·5 g
Tripotassium phosphate	10 g
Hydroxylamine hydrochloride	2 g

(On the incompatability of hydroxylamine and ethylenediamine-tetraacetic acid see para. 557.)

Development times at 18°C:

Agfacolor	3–6 mins.	Pakolor	6 mins. (at 20°C)
Ferraniacolor	3–5 mins.		
Gevacolor	4 mins.	Synthacolor	8 mins.
		Telcolor	3 mins.

Stop fixer (Gevaert G55)

Hypo	170 g
Sodium sulphite anh.	10 g
Sodium bisulphite (dry)	15 g
Water to	1000 cc

Bleach fix bath

Water to	1000 cc
Ferric salt of ethylenediamine-tetraacetic acid	60 g
Sodium carbonate anh.	5 g
Potassium bromide	30 g
Hypo	150 g
Sodium citrate	30 g
Potassium thiocyanate	10 g
Tinopal BV (Geigy)	3·5 g

The *ferric salt of ethylenediamine-tetraacetic acid* is marketed as Ferric Sequestrol CP2 by Geigy. In its absence, mix 35 g of ferric chloride hexahydrate, 40 g of ethylenediamine-tetraacetic acid and 40 g of sodium carbonate anh.

Bleach-fix time 8 mins., pH 6·4. The bath is exhausted when the pH reaches 6·6. Life: 2–3 weeks, in darkness. The ferric ethylenediamine-tetracetate bleach bath is of the Belitzki type (see para. 172b).

556. Working method for colour developing

Twenty-four hours after preparation, the activity of a colour developer increases and remains so for 48 hours. This is why a new developer is not used immediately. It is first 'ripened'. Each batch of 1000 litres is analysed, corrected if necessary and again analysed 24 hours later. In use, the bath is analysed twice daily. Its temperature is maintained at ±0·1°C. The tolerance in contrast must not exceed 0·05. An output of 1200 ft. of 35 mm film per hour requires a total volume of 4000 litres in circulation. The machine is usually constructed of vinyl resin material. A bath for continuous film development is kept up to strength by frequent addition of replenisher and if protected against oxidation fog (see following paragraph) may last a month.

Meyer and Roth(86) have stated that 3 ft. of Agfacolor film carries over 26 mg of diamine of which 17 mg is absorbed by the gelatin and the couplers, and 9 by mechanical action. This shows the necessity of a stop bath or a prolonged wash.

The *agitation* must be uniform and constant, whether it is continuous or intermittent, for the duration of development depends (to the extent of 20%) on the method of agitation used. Instead of agitating the film, it is frequently recommended that the liquid should be circulated by means of a pump. It is, however, preferable to use some form of mechanical agitation as well. Sheet films are developed by hand, being removed from the tank at frequent intervals and allowed to drain from alternate bottom corners.

Any variation in the composition of the first or the colour developer can result in an undesirable colour cast. The amount of metol, hydroquinone, alkali, bromide, thiocyanate, or p-diamine must be determined frequently.

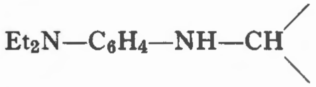
The *bleaching* operation is also important. The rate is proportional to the ferricyanide concentration, and therefore diminishes as the bath is used. Flannery(87) determined the concentration of ferrocyanide potentiometrically using ceric sulphate and regenerated the ferricyanide with bromine (dissolved in methanol) acting on the ferrocyanide.

$$2K_4Fe(CN)_6+Br_2 \rightarrow 2K_3Fe(CN)_6+2KBr$$

To maintain the pH of the bleach bath constant at pH = 6, buffer of phosphate plus sodium bisulphate is added. Three feet of 35 mm film result in the formation of 0·66 g of ferrocyanide.

557. Oxidation of colour developers

Colour developers are readily oxidized by the air as the sulphite does not protect the developing agent effectively: for 1 molecule of the latter, 2 molecules of sulphite are used. In the absence of coupler, the ratio of developer/sulphite destroyed starts by being only 1/1·5.(88) The mechanism of the first phase of oxidation is uncertain: either a quinoneimine is formed together with hydrogen peroxide which converts the sulphite to sulphate, or a peroxide which in the presence of sulphite produces the quinoneimine and sulphate. Second phase: part of the quinoneimine forms a non-developing sulphonate with the sulphite whilst another part reacts with the couplers to produce a leuco derivative



$$\mathrm{Et_2N{-}C_6H_4{-}NH{-}CH}<$$

which, oxidized by the air, produces dye and hydrogen peroxide as a *colour fog*.

Couplers like 1-naphthol and p-nitrobenzylcyanide protect the developer against oxidation. The redox potential is reduced as the tendency of the coupler to couple increases.

The colour fog is reduced by the addition to the developer of a reducing agent such as *hydroxylamine hydrochloride*, which is more easily oxidized than the developer itself.(89) Concentration 1–2 g per litre.

Traces of *copper* accelerate developer oxidation. This explains why developers prepared with distilled water often change more quickly than those prepared with ordinary water, as the distilled water frequently contains copper from the still. In addition sulphite itself contains 0·5 mg of copper per kg, which catalyses the oxidation reaction.

It is possible to prevent the copper from reacting with the developer by sequestering it with a complex forming agent. The best results are obtained with ethylenediamine-tetraacetic acid (disodium salt) (Trilon B) at a concentration of 2 g per litre. The amount of sulphite oxidized is then reduced to one-half. Unfortunately, *this sequestering agent is incompatible with hydroxylamine sulphate which it decomposes with the evolution of nitrogen.*(90)

558. Faults in the multilayer system

The superimposition of three emulsions differentially colour sensitized necessitates the *diffusion* of colour sensitizers and couplers being practically nil.

If the *colour sensitizers* diffuse from one layer to another the separating action of the system is partially destroyed. The diffusion of sensitizer may be even more pronounced if its molecule contains a shorter chain and if it is smaller. To increase this, other more complex nuclei must be attached to the benzene rings of the dye, such as fluorene groups. *The diffusion of sensitizers is always greatly reduced by the couplers dispersed in the emulsions.* In addition, their thinness enables drying to be rapid which still further limits the time in which diffusion is possible.

The *couplers* are, in principle, made non-diffusing by joining long chain groups to their molecules. However, Meyer and Ulbricht(91) have shown that a coupler although non-diffusing in gelatin (gel form) diffuses when it is in a solution of gelatin (sol form). Thus gelatin containing a non-diffusing coupler, coated on to an emulsion layer produces to some extent a coloured image in the latter by development.

559. Colour development faults

The colour developing agent, oxidized by the latent image, is converted to a *semi-quinone* which *diffuses* towards the neighbouring particles of coupler.

This diffusion is limited by the concentration of coupler. In actual films this concentration is generally adequate. If the coupler concentration is low, there will be a loss of sharpness. In addition, the diffusion of the oxidized developing agent is slowed down by sulphite which converts it to sulphonate.

The vertical *Eberhand effect* (para. 226c) due to local variations in the concentration of developer, its oxidation product, and the bromide by-product, can effect the regions neighbouring high densities. In other words the image in a layer is to a greater or less extent influenced by the images in the other two layers, with possible reduction in the γ.

A multilayer system is subject to many possibilities of colour fog:(92)

1. *Emulsion fog*. Each of the 3 emulsions has its own fog level which results in a slight coloration if the 3-fog densities are not equal. This fault

occurs in many ways from old material, for the speed of increase of fog for the three emulsions is rarely the same.

2. *Development fog*. Due to a lack of bromide, to protracted development, too high a temperature or the presence of an impurity in the solution.

3. *Oxidation fog* from the air (see para. 557).

4. *Oxidation fog by the bleach bath* of developer which has not been removed by washing, particularly in the lower (cyan) layer. By reaction of the oxidized developer and the coupler, a bluish fog is formed. This fog is lower around the perforations which are washed more efficiently than the rest of the film.

5. *Contact fog*. At the interface between the yellow filter, which contains colloidal silver (acting as development centres) a colour image is formed by the same mechanism as diffusion transfer (para. 406). The yellow and magenta layers may be stained in this way.

6. *Background stain* due to incomplete elimination of the colour sensitizers, the filter layer or the anti-halo layer.

560. Correction of colour casts

A colour cast of a developed film may be due to a negative defect, a printing error, an exposure error, unequal development in the three layers or fog either from processing or age.

Whatever its cause, it is frequently desirable to introduce some correction, even partial, although the manufacturers do not approve of the user taking too many liberties when handling their films.

The correction of a colour cast can sometimes be carried out by slight *local staining* but this destroys the purity of the whites for there are no dyes available which fix themselves only on the image dyes.

Only *chemical reduction* can give results which are of interest. Tests should first be made on scraps of film to determine the action of *weak acids* such as citric acid and *strong acids* such as dilute sulphuric or hydrochloric acid, of weak bases (borax) or strong ones (carbonate or caustic soda), of *oxidizing agents* (hydrogen peroxide, persulphates, sodium peroxide, acid dichromate), of reducing agents like sodium hydrosulphite at various pH values; of *sulphiding agents* such as sodium monosulphide and of *metallic salts* such as copper sulphate in acid, neutral, and ammoniacal solution. For each test note the concentration, the pH and the treatment time. Sometimes rinsing must be brief to leave, in the layers of the film, part of the correcting product (borax for example).

By way of example, several formulas will be given which have been disclosed for certain types of film. In view of the continual changes made by manufacturers in the constitution of their colour couplers, the information below has not an absolute value.

The resulting colours may vary with the type of film.

(The treatment time in all these solutions is 1–4 minutes.)

Cyan reducers

1% hydrosulphite. The action of this bath is increased as the pH is reduced. With Kodachrome images the magenta layer is reduced more rapidly than the others.

1% sulphite + a few drops of HCl until the pH is 7.

3% hydrogen peroxide: 10 cc + ·4% caustic soda 60 cc.

0·2% sodium peroxide.

Acetanilide 0·4 + sodium carbonate 0·2 + water 100.

Acetoacet-sulphanilide 0·1 + ammonia 10 + water 100.(93)

Reduction of blue and magenta by formation of greyer dyes.

Copper sulphate 1 + water 100 + ammonia 1·5. The action of this bath is less energetic in neutral solution. With some films, copper sulphate reduces the yellow.

Magenta reducers

Dry bisulphite 5 + sulphite 18 + water 1000 (pH 6·9).

m-aminobenzoic acid (hydrochloride) at a concentration of 0·75%, then 3% borax.

0·2% hydrazine sulphate. If the cyan and magenta images fade at the same time the cyan can be restored by immersion in 5% carbonate.

18% tartaric acid or 2% hydrochloric acid, then an alkali bath. With some films a magenta image is, on the contrary, intensified in an acid bath.

Yellow reducers

Caustic soda 3 + ferricyanide 20 + boric acid 1·5 + water 1000 (pH 11·8).

Cholic acid 5% (or sodium cholate).

Oxidation by chloramine (sodium salt of p-toluene sulphochloramine) 10 cc 1% + 1 cc 0·4% HCl. Does not keep.

Formalin 80 cc + 5% caustic soda 20 cc.

1% dichromate + 2 cc sulphuric acid then 5% bisulphite (oxidation).

Reduction of yellow and cyan

First treat in: potassium iodide 2 + iodine 1 + water 100, then in 40% hypo.

Yellow intensifier

10% hypo 100 cc + nitric acid 10 cc + 500 cc water. Wipe off the sulphur which has deposited, if necessary, then immerse in a solution of 3% hydrogen peroxide made alkaline with ammonia (which does not keep).

Magenta intensification (with some films)

2% sulphuric acid.

Cyan intensification (with some films)

5% borax, rinse very briefly.

561. Alteration of images

The three colour images obtained by colour development can be altered in three ways.

1. *Bleaching* by sunlight or electric arc. The prints should be kept in an album. To some extent they can be protected against ultra-violet radiation with a cellulose acetate sheet.(94) The magenta is the most stable of the colours.

2. *Acidification* by the carbon dioxide in the air gives a change of hue. This can be brought back to its original state by immersion in 1% borax without washing.

3. *Oxidation* accompanied by heat and high humidity. This results in a yellow-brown fog and reduction of the image; particularly when the layers still contain some slightly soluble developer. The magenta and yellow azamethines hydrolize to colourless ketones which are turned brown by reoxidation.

The formalin stabilizing has the effect of tanning the gelatin and thereby reducing the humidity in the layer.

Varnishing reduces the risk of acidification and oxidation.

562. Colour developer analysis

The analysis of colour developers consists of determining the substituted p-phenylenediamine on one hand and on the other the auxiliary constituents. The estimation of the latter is carried out by the usual methods considered in Chapter X. The p-phenylenediamine can be estimated as metol (para. 126). Spectrophotometric estimation can give good results (cf. para. 125). The two following methods were studied by Meyer and Roth in the Agfa laboratories.(95)

Potentiometric titration with nitrite in acid solution. When the p-phenylenediamine is all diazotized, nitric acid is formed which quickly raises the potential.

$$R_2N—C_6H_4—NH_2+2HCl+NaNO_2 \rightarrow R_2N—C_6H_4—NCl\equiv N+NaCl+H_2O$$

The developing agent must first be separated from its sulphonate in *alkaline solution* with a solvent which is not miscible with water. The sulphonate is estimated by the difference between the total estimation after extraction in *acid solution* and heating to remove the SO_2.

50 cc of developer together with 9 g of anhydrous potassium carbonate and 12–15 g of sodium chloride are shaken with 40 cc benzene. The aqueous layer is separated and again extracted with 20 cc of benzene. The benzene solutions which contain the developing agent base are mixed. This base is extracted from the benzene with 20% hydrochloric acid and it is with this acid solution that the potentiometric estimation with a 0·04N solution of

sodium nitrite is made. The end point is marked by an increase of potential from 50 to 90 mV: 1 cc of nitrite solution is equivalent to 10·4 mg of diethyl-p-phenylenediamine sulphate. Time for the analysis: 20 mins.

If the developer contains hydroxylamine or a coupler, this method of estimation cannot be used. If there is a coupler, add some calcium chloride before treating with the solvent.

Colorimetric determination.

The p-phenylenediamine contained in the developer is converted to an indophenol blue dye using 1-naphthol-2-sulphonic acid in the presence of an oxidizing agent. This reaction can be used to determine the amount of sulphonate: 50 cc of used developer is diluted to 2% and 1 cc of 3% naphthol-sulphonic acid is added (plus a little caustic soda) then 1 cc of 5% ferri-cyanide. Make up to 100 cc. The intensity of the blue colour is measured with a photometer.

Estimation of hydroxylamine. Hydroxylamine salts are anti-oxidants as we have already seen (para. 557). They can be estimated in colour developers using the colorimetric method of Brune and Rieger:(96) hydroxylamine, in the presence of a fatty acid ester in alkaline solution, is converted to hydroxamic acid, and the addition of nitric acid and a ferric salt forms a red complex.

Another method worked out by Birr(97) is to estimate the acid liberated by formalin, either with a bromophenol blue indicator or potentiometrically: 50 cc of developer is acidified to pH 3·9 with sulphuric acid, first 2N, then N/10. Add 100 cc of 6% formalin at the same pH. If hydroxylamine is present, the solution will become more acid. After leaving for 2 mins., this is back-titrated to pH 3·9 with N/20 caustic soda, needing x cc. The amount of hydroxylamine sulphate present is $0{\cdot}08207x$.

Sulphite determination, in the presence of a coupler. To avoid iodine adsorption by the coupler and the precipitated dye, SO_2 is liberated and extracted by distillation.(98)

1. Weissberger A.: *J.A.C.S.*, 1951, 3100–3125.
2. Jordanski and Arbusoff: *Sci. et Ind. Phot.*, **23,** 22; *Zh. Rikl. Khimii,* 1951, 337.
3. *Sci. et Ind. Phot.*, **17,** 282.
4. Meyer K., Brune W. and Siebenlist H.: *Zeits. Wiss. Phot.*, Oct. 1952, 129–136.
5. Peterson W. D. and Kodak: F.P. 860,363 (1939).
6. F.P. 866,339 (1941); U.S.P., 2,193,015 (1939).
7. B.P., 691,815 (1951).
8. Raasch M. S. (Dupont), *J.A.C.S.*, 1953, 2956.
9. Kodak: F.P. 856,392 (1939).
10. Vittum P. W. and Brown G. H.: *Sci. et Ind. Phot.*, 1949, 428.
11. Eastman Kodak: U.S.P. 2,039,730.
12. Kodak Pathé: E.P. 1,070,666, (1954).
13. Weissberger A. and Kodak: F.P. 870,142 (1941).
14. Jennen J.: 27th Cong. de Chemie Ind., Brussels, 1954, No. 345.
15. F.P. 911, 801—Van Dormael: *Chim. et Ind.*, June 1954.—1-hydroxy-4-sulpho-2-naphthoyl-N-methyloctadecylamide and -N-methylcetylamide have been disclosed by ICI: F.P. 1,087,166 (1954), Brit. prior., 1952.

15b. Several acetoacetanilides are manufactured by British Industrial Solvents (Devonshire House, Mayfair Place, Piccadilly, London, W.1) and by Carbide and Carbon Chemicals Company (New York).

16. Kumnine N.: *Jl. Soc. Sci. Phot. Japan*, 1952, 88–95 (in Japanese) details of preparation.

17. Bruylants P. and Mercx P. (Gevaert): U.S.P. 2,375,344; B.P. 615,218; F.P. 870,771; Seymour (Kodak) U.S.P. 1,969,479; See also Blanksma: *Rec. Trav. Chim. P. Bas.*, 1938, 2; 1939, 498.

18. Thiers and Van Dormael: *Sci. et Ind. Phot.*, 1952, 173.

19. Curtius: *Jl. Prakt. Chem.*, 1930, 218.

20. I.G.F.: U.S.P. 2,186,735—Ilford B.P. 518,017, (1938); Dupont U.S.P. 2,140,540, (1937) have patented malonic monoamides.

21. Thiers and Van Dormael: *Sci. et Ind. Phot.*, 1952, 386.

22. F.P. 869,169 and B.P. 540,760 (1939).

23. B.P. 674,103 (1949); Van Dormael: *Chim. et Ind.*, June 1954.

24. B.P. 689,023 (Belg. prior. 1950).

25. Schultze: *Zeits. Naturforschung*, 1947, 400–404.

26. F.P. 897,483 (1940–43).

27. B.P. 615,218 (Ger. prior., 1941); Gerbaux: *Bull. Soc. Chim. Belge*, 1949, 498.

28. Patented by W. Seymour (Kodak) in 1934.

29. I.G.F.: F.P. 860,984 (1941) (Ger. prio., 1938).

30. Kuminine N. and Itano K.: Konishiroku Rev., June 1954, 34–41, (in Japanese); Kuminine N.: *Jl. Soc. Sci. Phot. Japan*, Nov. 1951, 37–43; Kodak: F.P. 1,099,911 (1955), U.S. prior., 1949.

31. Kodak: F.P. 1,077,534 (1954) (U.S. prior., 1951).

32. U.S.P. 2,294,909 (1939).

33. F.P. 1,067,680 (1954) (U.S. prior., 1951).

34. Sawden, Ruoff and Vittum: *J.A.C.S.*, 1950, 4947.

35. Jennen J. (Gevaert): *Ind. Chim. Belge.*, 1951, 472–476.

36. Gevaert: B.P. 663,190 (1948); Baker W.: *J.C.S.*, 1949, 307.

37. Homolka, in *Jarbuch*, 1914, **28**, 22; see also *Ber.*, **33**, 985.

38. Cie Thomson-Houston: F.P. 910,105.

39. K. and L. Schinzel: *Phot. Ind.*, 1936, 942.

40. Henn R. W.: *P.S.A. Jl.*, Nov. 1953, 149.

41. Henn R. W. and Fasset D. W.: *P.S.A. Jl.*, 1953, 146.

42. *Ind. Eng. Chem.*, 1953, 1726.

43. Rzymkowski: *Sci. et Ind. Phot.*, 1950, 86.

44. I.G.F.: F.P. 873,984 and 876,033.

45. I.G.F.: F.P. 876,814 and 876,815.

46. For further details see the following French patents: 803,566, 807,792, 810,401, 818,388, 844,637, 825,233, 825,878, 826,602, 827,625, 827,626, 828,579, 828,603, 830,878, 830,926, 834,402, 839,998, 840,880, 841,425, 844,928, 849,861, 852,803, 852,842.

47. I.G.F.: F.P. 872,440.

48. I.G.F.: F.P. 873,702 and U.S.P. 2,145,369.

49. I.G.F.: F.P. 871,598.

50. F.P. 912,572; Other antidiffusing groups, Gevaert: U.S.P. app. 383,387 (30th Sept. 1953).

51. G.P. 745,046.

52. Kodak: F.P. 846,463 (1941).

53. B.I.O.S. Report 1355, H.M. Stat. Off., London, 1945.

54. Incorrectly called stearylamine.

55. F.P. 870,795.

56. Jennings A. B., Murray O. W. and White C. F. A.: F.P. 927,414 (1946); Woodward D. W.: F.P. 927,616 (1946).

57. McQueen D. M. and Woodward D. W.: *J.A.C.S.*, 1951, 4930–4934.
58. Kodak: F.P. 1,070,244 (1954) (U.S. prior., 1952).
59. Kodak: F.P. 1,077,535 (1954) (U.S. prior., 1951).
60. Vittum, Weissberger and Wilder (Kodak): U.S.P. 2,435,616; Glass, Vittum and Weissberger (Kodak): U.S.P. 2,453,661 and B.P. 598,657; U.S.P. 2,455,170 and B.P. 598,174; Heimback and Morreall (Ansco): F.P. 927,604.
61. Mercx R.: *Sci. et Ind. Phot.*, 1950, 45–48.
62. Mercx R.: *Bull. Soc. Belge.*, 1947, 339–348.
63. U.S.P. 1,055,155 and 1,102,028.
64. F.P. 803,566, 807,792 and 810,401 (1936–7).
65. Duerr H. H.: *J.S.M.P.T.E.*, 1952, 465–479.
66. To remove the antihalo layer with a jet rinse.
67. Jennings, Stanton and Weiss: *Jl. Soc. Mot. Pic. Tel. Eng.*, 1950, 455–476.
68. Chu, Nottorf and Vinton (Du Pont): *P.S.A. Jl.*, 1953, 43–47.
69. U.S.P. Re. 18,680, 2,262,987, 2,150,695, 2,322,027, 2,169,004, 2,336,327, F.P. 867,331.
70. Brusilovskii A. M.: *Trudy Inst. Kinoinzhenerov*, 1949, 125–136.
71. Hanson W. T. and Kisner W. I., *Jl. Soc. Mot. Pic. Tel. Eng.*, 1953, 667–701.
71b. Such a system can be used with a bromide emulsion next to the base, the two upper emulsions being chloride. These are not normally blue sensitive. They are not therefore affected during the printing of the lowest image.
72. The first disclosure of this process was in Seymour's patents (Kodak): U.S.P. 1,900,869 and 1,900,870 (1931).
73. A slightly alkaline solution of hydrosulphite will develop without exposure to light.
74. F.P. 815,342.
75. U.S.P. 2,113,329, 2,059,884.
76. Kodak: F.P. 1,069,614 (1954) (U.S. prior., 1950).
77. Kodak: F.P. 1,055,778 (1953) (U.S. prior., 1949).
78. F.P. 858,210.
79. F.P. 868,067.
80. May and Baker Ltd. (London), *Brit. Jour. Phot.*, 1948, 492.
81. Also called p-nitrobenzyl cyanide.
82. Gordon H.: *Camera*, 1948, 209–212.
83. Pilkington W. J.: *Brit. Jour. Phot.*, 1948, 487.
84. Gordon H.: *Brit. Jour. Phot.*, 1954, 558–559.
84b. Heilmann: *Mitt. Forshungslabv. Agfa*, 1955, 256–261; *Sci. et Ind. Phot.*, 1956, 210.
85. Thomson C. L.: *Brit. Jour. Phot.*, 1953, 409 and 518.
85b. Gordon H.: *Brit. Jour. Phot.*, 1955, 440–443 and 449.
86. Meyer K. and Roth L.: *Zeits. Wiss. Phot.*, Dec. 1953, 232–242.
87. Flannery, F. E. (Ilford): *Phot. Jour.*, 1951, 121–122.
88. Brune W. and Kronacher V.: *Zeits. Wiss. Phot.*, April 1953, 1–6, 6–15.
89. Weyde and Trabert: F.P. 860,020; Jelley E.: B.P. 462,140.
90. Meyer K., Brune W. and Siebenlist: *Sci. et Ind. Phot.*, 1952, 317; Meyer K.: *Bild. und Ton.*, March 1954, 69–72.
91. Meyer K. and Ulbricht H.: *Zeits. Wiss. Phot.*, Aug. 1951, 72.
92. See a study by K. Meyer (Agfa): *Bild und Ton.*, 1954, 198 and 228.
93. Acetoacetsulphanilide is prepared by heating an equimolecular mixture of sulphanilic acid and acetoacetic ester at 180°C. The compound crystallises on cooling.
94. Mackey E. S. (Ansco): *P.S.A. Jl.*, 1949, 682–684.
95. Meyer and Roth: *Bild und Ton.*, 1955, 75; 1956, 143.
96. Brune W. and Rieger E.: *Zeits. Wiss. Phot.*, 1952, 179–181.
97. Birr E. J. (Agfa): *Zeits. Wiss. Phot.*, 1952, 122–124.
98. Meyer K. and Roth L.: *Sci. et Ind. Phot.*, 1956, 143.

Chapter XXXI

PRODUCTION OF COLOURED IMAGES AFTER DEVELOPMENT

563. Colour coupling development

Colour coupling development, as we have seen, gives coloured images automatically, and therefore enables several individual primary images to be produced together. This process, which is very popular, has its advantages and its disadvantages; beneath its apparent simplicity a complicated chemistry is hidden. In addition, the fact that several coloured images are produced simultaneously is not, as one would think, a simplification, but an obstacle to consistent quality.

Colour development is not the only way to obtain coloured images. There are others whose application to colour photography and cinematography has been proposed, although they are greatly handicapped by the difficulty of forming the different monochromatic images in a reduced number of layers. The colouring of each image is carried out *after* development.

As this work is not solely reserved for current processes, but also to those which are instructive to the photographic chemist, we consider it desirable to devote a chapter to these colouring methods which, although sometimes old, are not necessarily without interest.

LOCAL DESTRUCTION OF DYES IN CONTACT WITH SILVER IMAGES

564. Principle of the method

Emulsion layers corresponding to the three primary colours are respectively dyed with cyan, yellow and magenta non-diffusing dyes. As these layers are generally used to obtain positive images, the originals are *separation positives* which are printed on to a film having, on one side, a cyan dyed layer, and on the other, two superimposed layers dyed magenta and yellow respectively.

The cyan layer is printed by white light from the red separation. The magenta-dyed layer on the other side is printed with blue light from the green separation. Finally the third layer, dyed yellow, situated under the magenta layer, is printed from the blue separation with red light; to do this, the emulsion used for this layer must be red sensitive.

On developing, three superimposed silver negative images are formed simultaneously, dispersed in the dyed layers. The film is fixed and washed.

It is now that the image-forming process is used. The silver image is dissolved as a complex, and the dye is destroyed, at the same time, by oxidation or reduction in proportion to the amount of metal present at each point. The principle of this method was disclosed in 1905 by K. Schinzel under the name *Katachrome.*

565. Gasparcolor

Sulphur compounds give a complex which can bleach dyes: thiourea, allylthiourea, thiosemicarbazide, thiodiglycolic acid, cystein salts, thiocyanates, alkali sulphides, etc. *They are activated by reducing agents* such as phenols, aminophenols, substituted aldehydes, sugars, etc. The reaction takes place in acid media.⁽¹⁾

The following systems have been disclosed in the quoted patents:

Thiourea 10 g + citric acid 5 g + water 200 cc.
Thiosemicarbazide 5 g + sulphuric acid 1 g + water 100 cc.
Thiodiglycolic acid 5 g + glucose 5 g + water 100 cc.
Sodium sulphide 5 g + metol + water 100 cc.
2-hydroxy-3-aminophenazine sulphonic acid 0·002% + hydrobromic acid 5%.⁽²⁾

These are, however, only indicative of the possible reactions for, when applied in practice, they are all very slow and the degradation of the gelatin frequently interrupts the reaction. Bleaching with 1·8% sodium sulphide, even without a reducer, has, however, been verified.⁽³⁾

Another solution disclosed by Geigy⁽⁴⁾ contains potassium iodide, pyridine, sodium hypophosphite and sulphuric acid. The silver is finally converted to the chloride with cupric chloride, and the silver chloride is removed with hypo.

Burt⁽⁵⁾ used a triple image transfer of coloured images, each obtained by immersing a silver image in a dye solution containing thiourea or thioacetanilide, potassium chloride and monosodium phosphate. The silver is converted to chloride.

The following dyes can be used: *substantive* and *acid azo dyestuffs, vat dyestuffs, alizarin dyes, etc.*: heliotrope BB, chloramine red 7LB, diamine fast pink G or BBF, diamine pure blue FF, naphthamine clear blue 4B. For three-colour work the preferred dyes are diamine pure blue FF, mordant yellow GG (or beizen gelb GG) and diamine fast pink BBF, or chrysophenine G, diamine pure blue and supranol brilliant red 3B, in a concentration of 0·6 to 0·8 g per m^2.

Geigy⁽⁴⁾ has disclosed, for the blue-green, a disazo-naphthol derivative.

The diffusion of the dyes is prevented by precipitation of the dyes with a nitrogenous organic base such as 2-phenyl-4-aminoquinoline (as hydrochloride) or guanidine (sulphate).

To increase the speed of the films, the dyes can be replaced by colourless couplers which are converted to dyes after printing.

For this procedure, Gaspar has disclosed the following methods.(6)

The emulsion contains a diazotizable compound such as primuline sulphonic acid. After printing and development, it is diazotized in a bath containing a small amount of copper sulphate, then after rinsing, it is treated in an alkaline coupler solution. In the presence of the copper salt, the azo dye is only formed in the absence of the silver image. Complete diazotization can also be carried out followed by treatment in cupric chloride which destroys the dye in contact with the silver image.

The *Gasparcolor* process was used several years ago for the production of colour motion picture prints. More recently, tests have been made for its application to the printing of colour postcards.

566. Christensen process

In an old process (1919) the bleaching agent was hydrosulphite or stannous chloride, strong reducers.(7

Seymour disclosed the use of the indigo and vat dyes: indigo blue, algol pink BBK, and algosol golden yellow 1BK for example. After development the film was bleached in the following bleaching solution which bleached the layer around the silver image:

Stannous chloride	80 g
Caustic soda	100 g
Triethanolamine	100 g
Anthraquinone	0·025 g
Water to	1000 cc

The triethanolamine and anthraquinone appear to behave as solvents for the leuco derivatives produced.

The stannous chloride can be substituted by potassium thiocyanate or a mixture of pyridine and potassium cyanide.

Carrol and Chechak used sodium stannite in a similar way for destroying the dye.(8) The dyes used were ortho substituted diamines tetrazotized and coupled with β-naphthols.

567. Destruction of a dye by oxidation

Many formulas have been disclosed for the local destruction of dyes by oxidation. We reproduce them without comment as examples. Thus Schweitzer converted the image into an oxidizing salt with vanadium ferricyanide, then treated the layer with chromic or hydrochromic acid to bring about the bleaching.(9)

The oxidizing agent can be a cobalt, lead or manganese salt whose action is followed by that of an acid bath. A silver image in dyed gelatin which is converted to silver chromate behaves similarly; in the presence of acid the dye is bleached in proportion to the amount of silver. A similar result is produced with sulphuric acid and water reacting on the silver image.

The dye is only destroyed in the areas *without a silver image* when the layer is treated with calcium hypochlorite or sodium bromate in sulphuric acid solution.

Examples:

Potassium bromate, 4 g + sodium chlorate, 10 g + 20% hydrochloric acid, 5 g + water, 200 cc.

Potassium bromate, 5 g + sulphuric acid, 2 g + copper sulphate, 0·2 g + water, 200 cc (to which can be added vanadium chloride, 0·1 g and 1% potassium iodide, 1 cc).

568. Coloured images by local oxidation of organic compounds

A silver image can be bleached to an oxidizing compound which can pass from a higher to a lower valency: during this change the compound can oxidize an organic compound to a dye.

The image is first bleached in a ferri-cyanide-permanganate or ferricyanide-chromic acid bath.(10)

	10% Ferricyanide	800 cc
	1% Permanganate	200 cc
or	10% Ferricyanide	1000 cc
	10% Chromic acid	400 cc

The bleaching can be carried out in two steps: the image is treated in ferricyanide, and then in manganese bromide $MnBr_2$ which converts it to silver bromide and manganic ferrocyanide. This manganic ferroycanide by being reduced to manganous ferrocyanide can oxidize organic compounds

$$Mn^{+++} + e \rightarrow Mn^{++}$$

After bleaching the photograph is cleared in 5% oxalic acid before being treated with a solution of an organic compound which can be oxidized.

With *benzidine* a blue colour is obtained, with *α-naphthylamine*, purple; with *p-phenylenediamine*, pink; and with *o-toluidine* and *dianisidine*, green. These compounds are used as the soluble hydrochlorides.

The silver salt is dissolved in hypo containing 1% potassium dichromate which prevents the reduction of the images.

In actual fact the colours obtained are weak, and it would be better to use other oxidizable substances such as the leuco bases(11) or the leuco sulpho esters (indigosols).(12)

Ozotype. Instead of a silver image, at one time a sensitive layer of gelatin dichromated in the presence of manganese or cobalt sulphate or potassium metavanadate, was used. After a few minutes' exposure and washing in cold water the image could oxidize colour forming amines.

COLOUR TONING

569. Principle of ferrocyanide toning

We have already shown in paragraphs 68 and 397 the chemical constitution of the ferr*i*cyanides and ferr*o*cyanides and their oxidizing and reducing properties.

The silver image, treated in a solution containing *potassium ferricyanide* and a *metal salt*, is oxidized and converted to silver ferrocyanide and at the same time a coloured metal ferrocyanide is precipitated. Thus with a ferric salt it is as if the ferric ferricyanide produced oxidizes the silver to silver ferrocyanide with the simultaneous formation of blue ferric ferrocyanide.

$$\underset{\text{Ferric ferri-cyanide}}{4\mathrm{Fe[Fe(CN)_6]}} + \underset{\text{Silver}}{4\mathrm{Ag}} \rightarrow \underset{\text{Silver ferro-cyanide}}{\mathrm{Ag_4[Fe(CN)_6]}} + \underset{\text{Ferric ferro-cyanide}}{\mathrm{Fe_4[Fe(CN)_6]_3}}$$

In practice, a mixture of ferricyanide and a metallic salt soon precipitate: this disadvantage is overcome by acidifying, or better, by converting the salt to a complex, with an organic acid, generally oxalic or citric. Ferrioxalic acid, for example, is stable in the presence of ferricyanide and reacts like ferric ferricyanide: oxalic acid is considered as a solvent.

Whilst the ferric and uranium salts are relatively stable in the presence of ferricyanide it is not so with *nickel* and *copper* salts. The former give, with potassium ferricyanide, a yellow precipitate of nickel ferr*i*cyanide and the latter a dirty green precipitate of copper ferr*i*cyanide. However, if the pH is raised by adding *neutral sodium* (or potassium) *citrate* no ferricyanides are precipitated. The copper solution can then tone a silver image. The pH of the neutral citrate is, however, too high for the nickel which cannot give a ferr*o*cyanide. To activate the nickel bath without precipitating ferr*i*cyanide an intermediate pH is necessary, that of *disodium citrate.*

It is therefore important to know the optimum pH for keeping and using the toning bath.

Two baths can also be used for toning: the silver is converted to ferrocyanide in a slightly ammoniacal solution of potassium ferricyanide, then, after washing, it is treated in an acid solution of a metallic salt such as ferric chloride. The amount of coloured ferricyanide produced by this method is much lower than by single bath toning. It is not therefore advantageous.

Alkalis decompose the toned image to hydroxide which remains in the gelatin, and soluble alkali ferrocyanide.

$$\underset{\text{Ferric ferro-cyanide}}{\mathrm{Fe_4[Fe(CN)_6]_3}} + \underset{\text{Caustic soda}}{12\mathrm{NaOH}} = \underset{\text{Sodium ferro-cyanide}}{3\mathrm{Na_4[Fe(CN)_6]}} + \underset{\text{Ferric hydroxide}}{4\mathrm{Fe(OH)_3}}$$

To avoid rapid decomposition of the baths:

1. *Keep in the dark*, as ferricyanide is very sensitive to light.

2. *Add traces of an oxidizing agent* which is more powerful than ferricyanide, for example, 1:100,000 dichromate. A higher concentration of oxidizing agent considerably reduces the rate of toning.

570. Iron blue toning

The solvent in this case is oxalic acid, and the iron salt ferric oxalate or ferric ammonium alum. Ferric oxalate is not crystalline and must be analysed if a constant concentration of iron is necessary.

Author's formula:

Ferric Soln.	Water	100 cc
	Ferric oxalate	1 g
	Water	40 cc
	Oxalic acid	2·4 g
	Water	3 cc
	Hydrochloric acid	0·3 cc
	Water	100 cc
	Potassium ferricyanide	10 g

The ferric oxalate is ground and dissolved hot. The ferricyanide must be freshly prepared and kept in the dark. Immediately before use take:

Ferric solution	140 cc
Ferricyanide solution	8 cc
Water	140 cc

0· 5% of ordinary alum can be added optionally.

The image is toned in 6½ minutes. It is then rinsed and fixed for 30 seconds in 2% hypo which removes the silver ferrocyanide and makes the image transparent. Finally wash for a few minutes in running water, the last wash being acidulated with a drop of hydrochloric acid.

As the image is intensified two or three times, it must consequently be developed to a much lower gamma.

The bath keeps in a tray for an hour without precipitating. For continuous processing only a very small quantity need be used at a time so that it can be renewed frequently, and thus maintain the composition substantially constant. If the HCl is reduced, the fog increases and the γ drops. If the oxalic acid is reduced the solution turns blue more quickly: if it is increased, toning slows down. By reducing the ferricyanide, fog is formed; by increasing it, the contrast drops.

We include several other formulas used by different workers:

J. B. Harris's formula

Ferric ammonium oxalate	6 g
Potassium ferricyanide	6 g
Citric acid	6 g
Water	1000 cc

Sedlaczek's formula

Ferric alum 10%	25 cc
Ferricyanide 10%	20 cc
Oxalic acid 10%	60 cc
Potash alum 10%	100 cc
Hydrochloric acid 10%	5 cc
Water to	1000 cc

The ferric alum can be doubled; the potash alum is optional.

F. E. Ives formula

Oxalic acid	4·2 g
Potassium ferricyanide	1·75 g
Sodium chloride	4·2 g
Potassium bromide	0·35 g
Ferric chloride (pharmaceutical)	1 cc
Water to	1000 cc

*Kodak formula T*12

Ferric ammonium citrate	4 g
Oxalic acid	4 g
Potassium ferricyanide	4 g
Water to	1000 cc

Milbauer(13) replaced the organic acid by fluosilicic acid to give improved keeping properties and to avoid blue-stained highlights.

Ferric alum 10%	30 cc
Fluosilicic acid 10%	30 cc
Potassium ferricyanide 10%	20 cc
Water to	1200 cc

In addition, the writer has prepared a self-toning paper by adding ferric phosphate precipitated in gelatin to a photographic emulsion. The paper is developed, bleached in ferricyanide, washed and treated in water which has been acidified with a little hydrochloric acid. Toning to blue is instantaneous and the image is very sharp.

Ferric ferrocyanide blue images are sensitive to pH variations which change the hue: greenish-blue in acid medium and violet-blue in alkaline medium.

571. Nickel toning

Nickel toning is carried out, as we have seen (para. 569) in the presence of disodium or potassium citrate. Yellowish white nickel ferrocyanide is obtained

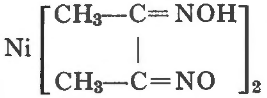
Nickel chloride	5 g	2 vol.
Citric acid	5 g	
Potassium citrate (neutral)	30 g	
Water	300 cc	
Potassium ferricyanide	5 g	1 vol.
Water	100 cc	

A bath which is too acid is unstable; if it is too alkaline it does not tone.

Nickel ferrocyanide is also obtained by treating the ferricyanide bleached image with a solution of nickel chloride or nickel sulphate and hydrochloric acid.

Nickel ferrocyanide is not itself suitable for toning. It combines, however, with certain organic substances to give *coloured complexes* which are used for single images in three-colour processes. The nickel ferrocyanide image is well washed to remove all traces of the salt, fixed in hypo and treated, after rinsing in an alkaline solution of the organic compound.

To obtain a *magenta image*, the reaction which Tschugaeff discovered in 1905 is suitable: a nickel salt combines with *dimethylglyoxime* in soda or ammonia solution to give a characteristic deep red insoluble complex with the formula



$$\mathrm{Ni}\left[\begin{array}{l}\mathrm{CH_3{-}C{=}NOH}\\ \qquad\;|\\ \mathrm{CH_3{-}C{=}NO}\end{array}\right]_2$$

For toning, an alcoholic solution of the reagent is added to ammonia water, for example:

Dimethylglyoxime	8 g
Alcohol	25 cc
Water	950 cc
Ammonia	25 cc

Glyoxime itself gives a brown complex. $\mathrm{Ni(ON{=}CN{-}CH{=}NOH)_2}$, *aminoglyoxime* a yellow colloidal compound $\mathrm{Ni(ON{-}CH{-}C(NH_2){=}NOH)_2}$, *methylisobutyldioxime* a red-orange precipitate, *β-methyl-p-anisylglyoxime*, a scarlet complex, *α-benzyldioxime* a red image. *Trihydroxyaminopropane* gives an orange-red trioxime.(14)

The writer has used *dicyanodiamidine* sulphate (Grossmann's reagent) in ammoniacal solution for a yellow image and 1:2-*diaminoanthraquinone*-3-*sulphonic acid* for a blue image.

Nickel forms a *yellow* fer*ri*cyanide. According to F.P. 898,431 and 2 (1941) a nickel fer*ro*cyanide image can be oxidized to nickel fer*ri*cyanide with potassium ferricyanide itself.

572. Complex toning in acid media

It is possible to bring about colour toning by a second method starting with *nickel*, *cobalt* or *uranium* ferrocyanides, but this time the reaction is carried out in acid solution. The ferrocyanide is fixed in hypo, then *decomposed by caustic soda*. Only a hydroxide precipitate remains, and this can be treated with an *acetic acid solution containing the organic reagent*: the acid dissolves the hydroxide, and the resulting soluble nickel cobalt or uranium salt is immediately precipitated by the organic substance which then forms a coloured complex.

With α-nitroso-β-naphthol and a cobalt ferrocyanide image, orange-brown toning is produced.

With α-nitroso-β-naphthol and uranium ferrocyanide, the image is toned yellow.

With the nitroso-β-naphthols, the nitroso-α-naphthols and the phenylazo-β-naphthols combined with nickel, cobalt or uranium salts a wide range of colours is obtained.

The cobalt ferrocyanide toning bath is similar to the nickel bath.

573. Titanium yellow toning

The titanic salts (and not the titanous) give a beautiful yellow image (slightly orange) in oxalic acid solution. The titanium is in the tetravalent state.

Titanic sulphate 10%	100 cc
Oxalic acid, saturated solution	25 cc
Glycerin	50 cc
Potash alum, saturated solution	50 cc
Water to	1000 cc
Potassium ferricyanide 10%	10 cc

By combining an iron salt with the titanic salt, a green image is produced, as with iron and vanadium.

574. Vanadium yellow toning

Vanadium ferrocyanide is greenish yellow. To prepare a toning bath, take:

Vanadium chloride, liquid	4 cc
Oxalic acid	10 g
Water to	1000 cc
Potassium ferricyanide 10%	65 cc

575. Uranium toning

There are two uranium ferrocyanides. The first, red-brown, has the formula $[K_2(UO_2)]_3[Fe(CN)_6]_2 . 6H_2O$. The second, red and slightly soluble, has the formula $K_6(UO_2)[Fe(CN)_6] . 12H_2O$. In the presence of excess uranium salt, sepia images are obtained due to the production of the former, whilst with an excess of ferricyanide, orange-red images are obtained. The bath itself is made from a uranium salt, nitrate $UO_2(NO_3)_2 . 6H_2O$ or acetate $UO_2(CH_3COO)_2 . 2H_2O$, potassium oxalate or oxalic acid, and potassium ferricyanide.

Red-brown toner (Kodak formula T 17)

Uranium nitrate	8 g
Oxalic acid	4 g
Potassium ferricyanide	4 g
Water to	1000 cc

The three ingredients are each dissolved separately in part of the water, the acid is added to the uranium solution, then the ferricyanide to the mixture, and the total volume is made up to 1 litre. Before use, dilute with two parts of water. The silver image first turns to a chocolate colour, then brown and finally red. Wash 10 minutes.

Red toner

Uranium nitrate 10%	100 cc
Potassium oxalate, neutral, 10%	100 cc
Hydrochloric acid	5 cc
Water to	1000cc
Potassium ferricyanide 10%	100 cc

100 cc of 10% alum can be added to harden the gelatin.

576. Yellow toning with lead chromate

A silver image is first converted to *lead ferrocyanide* in the following bath:

Distilled water	800 cc
Lead nitrate	8 g
Potassium ferricyanide	12 g
Distilled water	200 cc

The lead nitrate can be replaced by neutral lead acetate together with 10% acetic acid.

After toning and thorough washing with distilled water, the silver ferrocyanide is dissolved in hypo. After washing treat in a solution of *potassium chromate* to obtain a *yellow-orange* lead chromate image.

As lead chromate is opaque this method of toning is only suitable for prints on paper. In addition, to avoid yellow fog the photograph should be well washed in distilled water before treating in the lead solution.

577. Yellow toning with mercury

Yellow toning with mercury was disclosed by Hamburger in 1911(15) who formed mercurous iodide on a previously bleached image. The image is somewhat unstable and can be phototropic (para. 14). A new formula by Schreiber gives better results:

Potassium ferricyanide	1 g
Water	50 cc
Potassium iodide solution, 166 g.p.L.	45 cc

If used on a diapositive, the quantity of potassium iodide must be increased until the bleached image becomes perfectly transparent. This is determined with prior tests. The iodide concentration depends in fact on the initial grain of the silver image. Treatment time, about 5 minutes.

The image is washed and dipped in a 2% solution of *mercuric chloride* for 30 minutes. It is immediately toned to a beautiful yellow.

It should be remembered that mercuric chloride is very poisonous. Care must therefore be taken not to dip the fingers in the bath, nor to touch the photograph which must be carefully washed to eliminate all traces of poisonous mercury salt.

578. Yellow cadmium toning

Cadmium ferrocyanide treated with sodium sulphide produces yellow *cadmium sulphide* CdS. With sodium selenide, cadmium selenide is formed with a purplish shade. Before toning, the silver ferrocyanide must be removed with hypo followed by washing, otherwise the image will be brown. Like lead chromate, cadmium sulphide is opaque and is suitable only for papers.

The first stage, to cadmium ferrocyanide, can, according to Swahn, be carried out in a bath similar to

Water to 1000 cc + sodium citrate 60 g + cadmium chloride anh. 10 g + potassium ferricyanide 10 g + ammonia 100 cc.

579. Toning by precipitating metallic salts of organic compounds

Organic compounds, containing the groups —SH or =NH, readily form insoluble metallic salts in which the metal replaces the hydrogen atom.(16)

To obtain a coloured image, the silver image is bleached in a ferricyanide-bromide bleach, and after washing, is treated in a solution containing 20% sodium carbonate and 5% of the organic reagent.

As the silver ferrocyanide is rather more soluble than the organic silver salt, there is a double exchange of ions with precipitation of the organic silver salt and formation of a soluble ferrocyanide.

This organic silver salt is hypo soluble. Also it must be made stable to light by conversion to another salt, copper or nickel for example, with elimination of the silver.

o-carboxyphenylazothiobarbituric acid gives a yellow image (treatment time—6 minutes).

Rhodanine gives a brown image.

o-hydroxyphenylthiourea gives a chocolate-brown image.

Potassium dithiooxalate gives a maroon image.

Thionine gives a violet image.

o-hydroxybenzyl rhodanine gives a yellow-brown image.

Partial treatment enables slightly toned images to be obtained.

MORDANTING AND DYEING

580. Principle of mordanting and dyeing

A photographic image can be converted to a chemical compound having a great affinity for dyes, in the same way that alumina retains dyes by converting them to lakes. It is then said that the image is mordanted.

A mordanted image, bathed in an acidified solution of a basic dye, adsorbs the dye strongly, but only where the mordant is present. By washing, the excess dye which stains the gelatin is removed and the coloured image appears.

In principle, it is simple to colour images by mordanting and dyeing. In practice, it is a critical process if absolutely consistent results are to be obtained, with carefully controlled contrast, freedom from stain, fog and patches, and with perfect transparency without image spread.

For a dyed image to be useful, the opacity of the mordant must be negligible as with copper thiocyanate. It can also be of the same colour as the dye: example titanium ferrocyanide. If the mordant is opaque it must be removed without allowing the free dye to diffuse from the correct location. Two methods can be used for this:

(*a*) For silver iodide, precipitation of the dye with a salt such as concentrated potassium iodide which, at the same time, serves as a solvent for the mordant.

(*b*) Precipitation of the dye as the carbonate or hydroxide, when the chemical constitution of the dye permits, with simultaneous solution or decomposition of the mordant (copper ferrocyanide).

The dyes used for these images are basic ones; they do not stain ordinary gelatin permanently.

We would finally note that dye toning is difficult to apply to papers, which are permanently stained by the dye.

581. Silver iodide mordants

Disclosed by Traube in 1907, this mordant process can be used in several ways.

A. The image is first iodized in:

Potassium ferricyanide	2 g
Potassium iodide	1·5 g
Water	100 cc

After 1½ minutes, it is washed then dyed to *magenta* for example by treating for 3 minutes in:

Water	100 cc
Rhodamine B	0·5 g
Acetic acid	0·5 cc

The dyed image is then washed until the whites are clear. It can be made transparent by fixing in concentrated potassium iodide solution to which alum or formalin must be added (as potassium iodide attacks gelatin). The image becomes violet in the presence of potassium iodide. The colour can be restored by treating for 30 seconds in 1% borax, or better, by treating with ammonia vapour after drying.

For yellow and blue, *auramine O* and *methylene blue* are suitable, and in principle many other basic dyes can be used.

B. Iodizing with a solution of iodine in potassium iodide

Water	100 cc	2 cc
Potassium iodide	20 g	
Iodine	10 g	
Water		100 cc

The gelatin is stained brown. It is decolorized in 3% bisulphite.

The potassium iodide is a solvent for the iodine, which is only slightly soluble in water. If the amount of iodide is increased, the silver iodide produced has a finer grain, and can even give a transparent image (cf. para. 577) but, in the author's experiments, the mordanting power was less, although several writers state the contrary.*

582. Mordanting with cuprous thiocyanate

This mordanting method, discovered by Christensen, is one of the most useful, and consists of converting the image to silver and copper thiocyanate with a solution containing copper sulphate, potassium thiocyanate and disodium citrate. The latter can be replaced by a mixture of neutral citrate and acetic acid.

As there is considerable intensification, only soft low density images must be used, which are completely bleached (5–10 minutes) in:

Sodium citrate (neutral)	56 g
Copper sulphate	12 g
Potassium thiocyanate	10 g
Acetic acid	20 cc
Water to	1000 cc

After washing for 10 minutes, the bleached image is dyed in a bath containing 0·3–0·5% of dye and 1–2% acetic acid. The dyeing time must be controlled. The excess dye is washed out.

Cyan dyes: Nile blue, Capri blue, methylene blue.

Magenta dyes: Fuschine, rhodamine, safranines.

Yellow dyes: Thioflavine, auramine, phosphine.

A mixture of rhodamine S, methylene blue and thioflavine T or phosphine M gives a black image (Lumière's intensifier).

583. Mordanting with copper ferrocyanide

Copper ferrocyanide is a very strong mordant. It adsorbs the fuschines, rhodamine 6G, thioflavine T, auramine O, pyranine G, methylene blue, and Nile blue, strongly. Von Barsy(17) has recommended Astrofloxine FF 0·1% (magenta), Citroflavine 8G 0·2% (yellow) and methylene blue 0·05%, with 1% acetic acid.

---

* *Translator's note.* The transparent or translucent AgI. xKI complex is, due to the finer dispersion, claimed to have a much more efficient mordant than the opaque Traube mordant (see Hoyt Miller, B.P. 100,098; Friedmann, *History of Colour Photography*, p. 340).

The following method has given us yellow and magenta images of high purity:

Copper solution	Potassium citrate	26 g	100 cc
	Water	100 cc	
	Copper sulphate	3 g	30 cc
	Water	30 cc	
	Ammonium carbonate, 10%		
	Potassium ferricyanide 10% (freshly made)		

For use take:

Copper solution	100 cc
Ammonium carbonate solution	1 cc
Ferricyanide solution	16 cc

The image is treated for 3–8 minutes at 22°C, with frequent agitation, in this bath. It is then rinsed and fixed in 2% hypo for 30 seconds and washed for 4 minutes. Dyeing is in the following solutions:

Yellow image

3–6 minutes	Water	600 cc
	Auramine O	1 g
	Acetic acid	3 cc

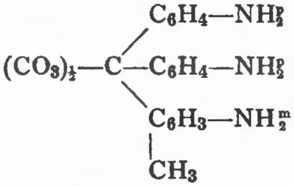
Magenta image

6 minutes	Water	100 cc
	Rosaniline acetate pure	0·1 g
	Acetic acid	1 cc

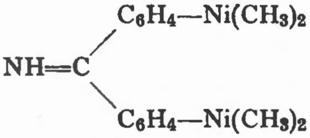
The images are washed for 10 minutes in running water, then fixed for 3 minutes in:

Water	100 cc
Sodium carbonate	10 g
Formalin	3 cc

which decomposes the copper ferrocyanide, and precipitates the dyes as carbonates and insoluble bases. The images are then transparent.



Rosaniline Carbonate



Auramine base

Auramine base is almost colourless. It is reconverted to the hydrochloride, by exposing *dry* for 10 seconds to hydrochloric acid vapour, then left in a current of air.

Contrast factors: 3 for magenta, 2 for yellow. The magenta can be reduced to 2 by less powerful mordanting.

584. Mordanting with the ferrocyanides of titanium and other metals

Many ferrocyanides are mordants for dyes. These include the ferrocyanides of *titanium* and *uranium*. Their characteristic yellow and red-brown colours restrict their use to dyes of similar hue. *Lead* gives a colourless ferrocyanide, but its use necessitates distilled water for solutions and washing.

Silver ferrocyanide was tried as a mordant by Crabtree and Ives using a single bath containing both mordanting agent and dye. To avoid precipitation of the dye, the solution contains 10% acetone:(18)

Water to	1000 cc
Acetone	100 cc
Ferricyanide	1 g
Acetic acid	5 cc
Dye	according to type used

Average dye concentration 0·02–0·04%. It is dissolved in a little water before being added to the acetone.

585. Formation of mordants by development

The *ferrous oxalate* developer deposits an intense yellow image of *ferric hydroxide* when the amount of oxalate is reduced to 0·2 mol. per litre in an alkaline solution pH = 8·7.(19)

With the *titanous oxalate* developer, Rzymkowski obtained a deposit of colloidal TiO_2 which can mordant basic dyes.(20) The developer had the composition:

Potassium oxalate 25%	13 cc
Potassium bromide 10%	2 cc
Dye solution 1:2000 (auramine for example)	80 cc

Just before use add

Titanium trichloride (10–15% commerical solution)	5 cc

This developer gives a coloured image of the dye and mordant directly, at a very low pH of 0·5–1, and is rapidly oxidized. It can be regenerated electrolytically.

Development is stopped in 1% hydrochloric acid. After fixing, the silver is removed in Farmer's reducer.

Developing in the presence of a mixture of auramine, rhodamine and methyl violet, a black image with a gamma greater than 4 is obtained.

COLOUR PROCESSES USING SUCCESSIVE TREATMENTS

586. Two-colour processes

Although they cannot rival three-colour processes, two-colour (cyan and orange-red) processes have been produced for a long time, particularly in the U.S.A., because of the relative simplicity of their treatment.

The positive film is either a *duplitized* stock, coated on both sides with yellow dyed emulsion to restrict penetration of the light, or an ordinary single-coated stock.

Printing on duplitized stock. The red and blue separation negatives are printed on each side of the positive material. The sound track is printed on the side corresponding to the red separation. The two images are developed simultaneously, fixed and then toned, with or without intermediate drying. The image from the red filter negative is toned cyan, and that from the blue negative is toned orange-red. As toning intensifies the images considerably (about 3 times), these must be developed to a very low gamma. The image can be toned by several processes:

Cyan toning with iron, and *orange-red* with uranium as in the old *Multicolor* process (U.S.A.).

Cyan toning with iron, and *orange dyeing* after mordanting with *copper ferrocyanide* or *thiocyanate.*

Cyan and orange-red dyeing after mordanting both sides of the film. The sound track is sulphided.

To process by individual toning or dyeing, the film must be *floated* or the solution applied by *roller*. Another method is to *lacquer one side* with cellulose phthalate (soluble in sodium carbonate) in a thickness of 5 μ.$^{(22)}$ The unprotected face is mordanted and coloured, and then the lacquer layer is dissolved and the image the other side is iron toned.

The individual images can obviously be *colour developed*. The *Trucolor* (U.S.A.) process uses incorporated couplers on each side of the film, with excellent results.

587. Two-colour processes using ordinary film

The double-coated film has the disadvantage of being easily damaged, not only during processing, but also during projection, which give it a shorter life than ordinary film. Also, the two images are not both in focus at the same time, during projection. Practice has shown that the second fault is the minor one for normal size screens.

It is, however, desirable for economic reasons to print two-colour films on ordinary positive stock. A large number of patents have been taken out on this subject over the last forty years despite the many difficulties.

The operating method is generally as follows: incorporation of a yellow dye in the emulsion by bathing, which restricts penetration of the light. This pre-treatment also shrinks the base before printing. The red record is then printed on the emulsion face, developed, and iron toned without fixing, and the emulsion is then *resensitized* with a bromine acceptor such as sulphite. The blue record is then printed through the base on the inner part of the emulsion layer, and developed, fixed, mordanted and dyed orange-red. The practical realization of such a process requires many extra steps without which the results would be very bad.

Pohlmann(23) improved the colour range by double dyeing the orange-red image with a red and a yellow dye applied successively. The dense areas then appear red and the highlights yellow with the whites remaining clear.

The best recent practical production of two-colour prints on ordinary film is by the Spanish *Realcolor* process.

Simultaneous printing on ordinary film. The usual process for two-colour printing on ordinary film comprises the printing and treatment of each image separately; and this causes difficulties due to registration and control of the baths.

The application of controlled penetration bleaching, once used for Kodachrome film (para. 552) enables the two images to be printed and developed together.

The ordinary film is first dyed yellow. The images are then printed, one on the front and the other through the base. They are developed together in a magenta colour developer, fixed and dried. The film is then treated in a controlled penetration bleach such as:

Water	15,000 cc	5500 cc
Hydrochloric acid	4000 cc	
Quinone	1000 g	
Isopropyl alcohol		30,000 cc
Glycerin		8000 cc
Hydrochloric acid		250 cc

Treatment time is of the order of 3 minutes. Stop bath—sodium carbonate solution. To slow down bleaching, reduce the glycerin, the hydrochloric acid or the quinone solution.

With this treatment, only the surface image is affected. If treatment is prolonged the bath attacks the deep image. Silver chloride is formed at the surface. This is exposed and developed in a cyan colour developer, or developed in an ordinary developer, then toned in an iron toner. The complete system has been tried by the writer and presents no serious difficulties.

588. Three-colour processes with separate printings

The relative simplicity and cheapness of two-colour films has resulted in many attempts to apply a *third colour*—yellow—to obtain complete three-colour prints. The application of the third colour is not, however, simple, and the solutions which have been proposed are all the result of ingenious and patient research. Some of these processes have been abandoned, but others are exploited or are being developed.

The problem is different depending on whether the original film is duplitized, ordinary or of a special type.

In each case three separation negatives are used. The red record is printed on one side; its image will be toned cyan. The green record is printed on the other side for magenta toning. The blue record provides the yellow image. It cannot be printed until the others have been developed. Lack of register due to shrinkage must not be forgotten. Fortunately, slight differences are hardly visible, in this case.

The following *methods for applying the yellow* have been, or are, used:

1. *Recoating* a duplex film with emulsion, using a roller, and printing the yellow on this new layer. This was used on the *Bonneau-Thomson* process, now abandoned.

2. *Imbibition printing* on a double-coated film already having cyan and magenta image. Used principally in U.S.A. and France.

3. *Dichromate sensitizing* of a film having cyan and magenta images, and dyeing yellow after exposure and washing. Old *Chimicolor* process.

4. *Regeneration of silver bromide* in the original *unfixed* emulsion after toning. *Supercinecolor* process (U.S.A.).

5. Two images are printed on the two sides of duplitized stock, then toned magenta and cyan after development. *Only the silver ferrocyanide is removed.* The blue record is printed on the cyan image (using a mask also toned cyan and carrying the negative of this image). *The residual silver bromide* is used for the third image.

6. *Formation of a sensitive silver halide* in the fixed layer already containing the cyan and magenta images. Recent process of the writer (para. 590).

7. *Successive development of two mixed or superimposed emulsions of silver bromide and chloride respectively*, and of different colour sensitivity. This method has been worked on by many people and does not seem to have been applied. A special film is required.⁽²⁴⁾

589. Supercinecolor process⁽²⁵⁾

The red and green separation negatives are printed on either side of double-coated stock, frame by frame. The film is developed, but not fixed, and dried. The side printed from the red record is toned cyan with iron. *The silver ferrocyanide is then reconverted to bromide*, washed and again dried. The blue record is then printed on the regenerated layer. It is developed by floating to avoid developing the same image printed on to the rear emulsion in the absence of yellow dye.

The film is fixed, washed and mordanted by *iodizing* (para. 586, note 21 and para. 581). The rear face bearing the green filter image is dried with an air squeegee. The side bearing the third (blue record) image is dyed yellow, washed and dried, then the rear face (green record) is dyed magenta. After washing and drying, the film has three component images with absorption maxima at 445 mμ for the yellow, 540 mμ for the magenta and 700 mμ for the cyan.

The sound track is printed cyan.

590. Process using formation of silver halide

Cold precipitation of a silver halide in a gelatin layer from solutions of alkali halides and silver nitrate is not generally usable in practice owing to the irregular layer obtained and the very low contrast.

The writer has recently perfected a method of sensitizing by forming silver halides which is sufficiently simple and consistent, and gives images of good contrast (see para. 340). The development and toning of layers thus prepared is similar to that of ordinary emulsions.

This method of sensitizing can be used on a plain gelatin-coated film as well as a film already bearing one or more coloured images.

Among the different ways of using this resensitizing method for printing three-colour films is the following:

An ordinary positive film is first dyed yellow to limit the penetration of the printing light and to pre-shrink the base. The red and green separations are printed from one side and the other and are both developed in a magenta colour developer, fixed and dried.

The film is then treated in a controlled bleach bath (see end of para. 587), redeveloped cyan, and the silver eliminated in a reducer. It is then washed, resensitized and dried.

The blue record is then printed using a mask of the red negative toned cyan (to cancel out the cyan positive image in the film). It is developed in a yellow colour developer. The silver is bleached to halide and the film is finally fixed, washed and dried.

591. Miscellaneous processes

Among the various processes intended to *imitate* the trichromatic synthesis, we would mention the two following ones:

Danlos process(26) using duplitized stock. Two positives and one mask are used: the red separation positive—the separation positives of red and green printed *successively*—a positive *mask* made by printing the green and blue negatives *superimposed*. The two positives are printed on one side and the other of the film, which is developed, *reversed*, washed and dried. The side having the print from the green/blue separations is again exposed, through the mask this time. The print of the mask is then developed. The residual bromide is converted to iodide to be dyed magenta whilst the metallic silver is converted to a mordant which is dyed yellow.

Alfacolor process(27) of K. Jacobson. Two bipack separations are printed on a double-coated stock containing three colour couplers.

Three-colour prints on paper. These can be obtained by superimposing three-toned monochrome images on thin collodion supports. Paper is coated with a stripping layer of nitrocellulose itself coated with emulsion. The old American Chromotone process was based on this principle.

Three-colour reproduction on aluminium oxide. We have already seen (para. 404) anodized aluminium can adsorb many photosensitive substances. For three-colour reproduction, a Siemens process was as follows:

Magenta: sensitization with silver, and toning with gold.

Yellow: Ferroprussiate sensitizing and heating to obtain yellowish ferric hydroxide.

Cyan: Ferroprussiate sensitizing.

1. F.P. 727,168; 746,644; 746,645; 747,252 (1931–1932).
2. F.P. 863,507 (1941).
3. Arbuzov G. I. and Gilman L. I.: *Zh. Obs. Khimii*, 1950, 1786–1789.
4. Geigy J. R.: F. P. 1,074,560—Swiss priority 1951.
5. Burt G. H. (True Colour Film); F. P. 1,074,576 (1952), Br. priority 1951.
6. F.P. 862,418 and 862,419.
7. F.P. 503,954.
8. F.P. 914,840 and 914,841 (1945).
9. F.P. 476,213 and 607,638.
10. Bullock: U.S.P. 1,279,248 (1918).
11. F.P. 712,472.
12. F.P. 715,203.
13. Milbauer J.: *Phot. Korr.*, 1926, 124–127.
14. Nickel also reacts with cyclohexanedioxime, α-furyldioxime, oxalendiuramidoxime, rubeanic acid, ammonium thiocarbamate, o-hydroxyquinoline, orange II, etc.
15. B.P. 20,880.
16. Kodak—Pathe: F.P. 864,463 (1941).
17. Von Barsy A.: *Fotographie*, 1951, 299–301. He disclosed the treatment of copper ferrocyanide with a 0·5–1 % solution of titanium trichloride $TiCl_3$ for 30 seconds, washing 10 minutes then drying.
18. *Amer. Phot.*, 1928, 656–665.
19. James T. H.: *J.A.C.S.*, 1945, 1908–11.
20. Rzymkowski J.: *Fotographie*, 1948, 63; *Arhiv. Kemiju*, 1948, 26–45; *Sci. Ind. Phot.*, 1950, 139.
21. U.S.P. 2,141,354.
22. U.S.P. 2,331,746; Stott J.G.: *Jl. Soc. Mot. Pic. Tel. Eng.*, 1947, 306–315.
23. G.P. 682,673 (1937).
24. A. and L. Lumière showed in 1911 that silver chloride is more easily developed than silver bromide. This enables the silver chloride to be developed first, then the bromide, in two different colours. K. and L. Schinzel, R. Fischer and others have again claimed the invention of this method.
25. Gundelfinger A. M.: *Jl. Soc. Mot. Pic. Tel. Eng.*, 1950, 74–86.
26. Danlos P.: *Bull. Ass. Fr. Ing. Techn. Cine.*, 1951, 810.
27. Frerk. W.: *Kinotechnik*, Feb. 1951, 24.

Chapter XXXII

PHOTOGRAPHIC IMAGES BY MODIFYING GELATIN AND OTHER COLLOIDS

592. Photographic methods of modifying gelatin

Certain compounds such as the *alums* (para. 139), the *aldehydes* (para. 355), the *tannins* and the p-*quinones* have the property of hardening gelatin, and making it insoluble in warm water. Gelatin hardened in this way only swells slightly in water (para. 256).

$$\underset{\text{Polypeptide}}{Y{-}NH_2} + \underset{\text{Aldehyde}}{H\,.\,CHO} \rightarrow \underset{\text{Insolubilized polypeptide}}{Y{-}N{=}CH_2} + H_2O$$

$$\underset{\substack{\text{Poly-}\\\text{peptide}}}{Y{-}NH_2} + \underset{\text{p-quinone}}{2(O{=}C_6H_4{=}O)} + H_2N{-}Y \rightarrow \underset{\text{Insolubilized polypeptide}}{Y{-}NH{-}O{-}C_6H_4{-}O{-}NH{-}Y}$$

$$+ \underset{\text{hydroquinone}}{C_6H_4(OH)_2}$$

In the case of hardening with quinone, it is possible that the latter, oxidized by the silver halide is first converted to *hydroxyquinone* which in turn reacts on the amino groups of the gelatin.

The production of *quinone* in a gelatin layer can be localized, by the action of the developed silver salt on the developing agent in solution. Result: the gelatin is only made insoluble *in situ* with the image.

Another method of locally insolubilizing gelatin is to use the tanning action of *chromium oxides* resulting from the decomposition of *dichromates* either in contact with the silver of an image, or by the action of light.

Instead of forming an image by hardening gelatin it is, on the contrary, possible to *soften* it locally, in the presence of silver, with *hydrogen peroxide*.

To sum up, the production of images by photographic modification of gelatin can be achieved by one of the following methods:

A. (1) Developing a silver image with a tanning developer.
  (2) Bleaching a silver image with a dichromate hardening bleach.
  (3) Dichromate hardening in *contact* with a silver image (Carbro).
  (4) Local softening of gelatin with hydrogen peroxide in the presence of silver.

B. Action of light on dichromated gelatin.

C. Dichromated gelatin can be replaced by other dichromated colloids: *gum arabic*, *albumen*, *polyvinyl alcohol*, *cellulose*, *shellac*.

D. Softening, by light, of gum arabic insolubilized with *ferric chloride*.

E. Direct *hardening* by light (without the use of dichromate) of various substances: *bitumen*, *rubber hydrochloride*, *synthetic polymers*.

All these processes for obtaining photographic images can be *applied* in four different ways:

(*a*) incorporation of *coloured pigments* in the colloids (carbon process);

(*b*) superficial application of greasy inks (bromoil, collotype);

(*c*) chemical attack on the support, using the image as a resist (graticules, photomechanical plates).

(*d*) dyeing the image with *organic dyes* (direct dyeing or imbibition transfer).

593. Tanning developers

Some phenolic developing agents, particularly *pyrogallol*, *pyrocatechin* and *hydroquinone*, will harden gelatin in the neighbourhood of a developed silver image. The hardening action is only complete when the quantity of sulphite is small: 2 g.p.L. at the most, when the alkali is carbonate, and 4 g.p.L. when it is caustic, with hydroquinone. Up to 16 g can be used with pyrogallol in carbonate solution and 6 g with pyrocatechin in soda solution.

Under these conditions, hydroquinone readily gives fog from aerial oxidation. Of the other developers, p-aminophenol, metol and amidol tan only slightly, glycin and p-phenylene diamine have no hardening power.

Tanning does not appear to be complete until after washing.(1) Only pyrogallol tans in a completely local way. With pyrocatechin there is some diffusion around each point.

The hardening agent is, as we have seen, the oxidation product of the polyhydroxybenzene, that is, a quinone, which is only freely formed in the absence of sulphite. The quinone compound which is formed produces, with the gelatin, a slightly coloured insoluble compound which is called the *residual image*.

Thus, to obtain an image of hardened gelatin, development can be carried out in one of the following solutions (preferably with one of the first two):

A	Pyrogallol	2 g
	Sulphite anh.	8 g
	Carbonate anh.	7 g
	Potassium bromide	0·5 g
	Water to	1000 cc

B	Pyrocatechin	3 g
	Sulphite anh.	6 g
	Caustic soda	6 g
	Potassium bromide	1 g
	Water to	1000 cc

C	Metol	1·5 g
	Hydroquinone	1·5 g
	Sulphite anh.	2 g
	Carbonate anh.	15 g
	Potassium bromide	1·5 g
	Water to	1000 cc

By adding *metol* to the pyrogallol, the tanning effect is doubled.(2) Proportions 2-3.

Ascorbic acid is an effective preservative. Concentration 1 part to 2·5 parts of tanning developer (by weight).

An image printed through the base, developed in a tanning developer and then washed off in hot water gives a gelatin relief. Stripping can also be carried out by treating for at least 10 minutes in a solution of sodium salicylate at normal temperatures.

If an iodobromide emulsion is prepared in an albumen such as gliadine, soluble in aqueous alcohol, stripping can be carried out in that solvent.(3)

The *diffusion* of local tanning by the exhausted developer can be used, in so far as it is a mordant, to intensify an underexposed image: Rzymkowski(4) dyed with 1% nigrosine (threshold shifted by 0·7 log E).

For the same reason, the complete hardening of the gelatin is achieved with a relatively small number of developed grains. It is therefore possible to *greatly increase* the contrast of images by sulphiding the remaining grains(5) in a warm basic solution of thiourea: expose through the base, develop for 6 minutes at 20°C (68°F) in: hydroquinone 4 g, sulphite anh. 15·5 g, carbonate anh. 2 g, bromide 1 g, water to 1000 cc. Rinse for 30 seconds then strip by gentle rubbing for 5 minutes at 35°C (95°F), in

Thiourea	2 g
Caustic soda	16 g
Water to	1000 cc

Wash for 1 minute and dry.

Development in a pyrocatechin-caustic bath suppresses the shoulder and toe of the characteristic curve:(6) pyrocatechin 12 g, caustic soda 30–60 g, water to 1000 cc. Time 6 minutes at 23°C (73°F).

Photographic stencils. Tissue paper, strengthend by impregnation with a synthetic resin, is coated on one side with a gelatin-silver chloride emulsion to give 4·5 g AgCl and 15 g gelatin per m^2. The very contrasty ortho emulsion is of the reflex type. Exposure behind the document: 5–10 seconds at 50 cm from a 250 W photoflood lamp.

The tanning developer is prepared by mixing two stock solutions containing the developing agent and the carbonate. By developing, the gelatin is tanned in proportion to the amount of silver. Stripping in water at 40–50°C (104–122°F), for one minute, dissolves the unhardened gelatin leaving the sheet perforated. The apparatus comprises three dishes and a roller around which the stencil is fixed.

594. Tanning bleaches

A silver image, developed and fixed normally, can be simultaneously bleached and tanned in proportion to the silver deposit.

The bleach bath must contain *dichromate or chromic acid* and an *alkali halide. Potassium ferricyanide* can be added advantageously.

The silver image is converted to silver chloride or bromide. Chromic chromate is also formed and is adsorbed by the silver salt. This chromate is hydrolyzed to chromic hydroxide which tans the gelatin by forming an addition product with both the basic and acidic functions of the polypeptide molecule. The complete reaction:

$$\underset{\text{Silver}}{6Ag} + \underset{\text{Chromic acid}}{6CrO_3} + \underset{\text{Potassium bromide}}{6KBr} = \underset{\text{Silver bromide}}{6AgBr} + \underset{\text{Chromic chromate}}{Cr_2CrO_6} + \underset{\text{Potassium chromate}}{3K_2CrO_4}$$

does not, however, tell the whole story, as only half the amount of chromium indicated is found in the residual image.

The reaction is accelerated by potassium ferricyanide which acts as a catalyst.

Tanning bleach formula (Bullock)

Potassium dichromate	19 g
Potassium bromide	28 g
Potassium ferricyanide	19 g
Acetic acid	5 cc
Alum (optional)	25 g
Water to	1000 cc

The bleached image is fixed in hypo which dissolves the silver bromide.

Other formulas:

A	Potassium dichromate	30 g
	Potassium bromide	120 g
	Acetic acid	35 cc
	Water to	1000 cc
B	Chromic acid	20 g
	Sodium chloride	50 g
	Sodium sulphite	1 g
	Water to	1000 cc

C	Copper sulphate 20%	42·5 cc
	Potassium bromide 20%	42·5 cc
	Potassium dichromate, saturated solution	15 cc
	Hydrochloric acid	10 drops
	Water	300 cc

The sulphite, in formula B, slows down the bath but produces a better modelled and sharper relief. A bath containing ammonium dichromate, sodium chloride and sulphuric acid has also been disclosed.(7) The image is stripped in a 20% solution of ammonium thiocyanate for two minutes.

Before bleaching the image, it is advisable to soak it in water to swell the gelatin layer.

595. Contact hardening

The indirect hardening of gelatin by contact with a silver image, discovered by Manly, is known under the names *ozobrom* and *carbro*. Instead of bleaching and tanning the image itself, as above, an independent gelatin layer is impregnated with bleaching solution, and pressed into contact with the previously swollen image bearing layer.

The same reaction between the silver and chromic acid in the presence of ferricyanide takes place with the difference that it is the gelatin of the auxiliary layer which is hardened in proportion to the amount of metal: the chromic hydroxide is formed deep in this auxiliary layer which enables a relief image to be obtained by simple contact with an ordinary silver image.

The image to be reproduced, generally printed on paper, is developed, fixed in plain hypo, and washed in water. Before pressing in contact with the auxiliary layer it is soaked for 15–30 minutes.

The auxiliary gelatin layer is treated for 3 minutes in a bath such as:

Potassium dichromate	12 g
Potassium ferricyanide	12 g
Potassium bromide	12 g
Water to	1000 cc

which must be kept in the dark.

Another stable formula was given by Symmes:(8)

Potassium dichromate	11 g
Potassium bromide	7·5 g
Potassium ferricyanide	7·5 g
Potassium bisulphate	0·6 g
Chrome alum	1·6 g

The pigmented paper is treated in this bath without previous wetting.

The British Vivex three-colour process used the following sensitizing bath (keeps for several weeks):(9)

Potassium dichromate	3·5 g
Potassium bromide	10 g
Potassium ferricyanide	10 g
Sulphuric acid, concentrated	1·16 cc

The dichromate and sulphuric acid can be replaced by 1·8 g chromic acid crystals.

The silver image is squeegeed to the sensitized layer and kept in perfect contact for 5–10 minutes. The separated gelatin layer then has an insoluble image which must be washed to remove excess sensitizer.

The bleached image used to make the insoluble image can be redeveloped after washing, as it is formed of silver bromide. In this way a large number of insoluble gelatin images can be prepared by alternate bleaching and developing.

In a variation of the process, the sensitized layer is treated with a 'control' bath before placing in contact. After draining for 15 seconds it is treated in the control bath for 5–90 seconds which reduces the resulting image. The longer the sensitized layer is treated, the lower the resulting contrast. P. L. Anderson recommends the following formula:

Formalin	650 cc
Acetic acid	30 g
Hydrochloric acid	30 g
Distilled water	45 g

which is used at a dilution of 30 cc per litre of water. The effect of the bath varies with the number of layers treated. Time of contact of the layer with the image: at least 15 minutes.

596. Relief images by local softening of the gelatin

A relief gelatin image is obtained by decomposing the gelatin surrounding the silver of a photographic image in proportion to the different densities. The soluble decomposed gelatin is removed together with the metallic particles: it leaves a *reversed relief*. If the layer has not been fixed, the residual halide can be developed to produce a positive image from a positive original.

The gelatin is destroyed by hydrogen peroxide in the presence of a silver halogenizing agent in acid solution.

Wall and Smith's formula

Copper sulphate cryst.	100 g	250 cc
Potassium bromide	10 g	
Nitric acid	15 cc	
Water to	1000 cc	
Hydrogen peroxide, 4 vols.		250 cc
Water		500 cc

Marriage's formula(10)

Cupric chloride	12 g
Acetic acid	55 cc
Water to	1000 cc
Hydrogen peroxide 21 vol.	40–80 cc

Take only enough solution to cover the image as the liquid is blackened with silver mud and must be discarded after use.

To remove the softened gelatin, it is helpful to rub the surface lightly with the finger, a wad of cotton wool or a very soft brush. If the layer has been hardened with alum or formalin, the action takes place slowly, or not at all.

Speck(11) has shown that it is better to only soften the gelatin in the bath, acidified to pH = 2·6–3 for 90 seconds at 18°C, and then to etch in warm water.

Silk-screens with water impervious resist. Gresham(12) has perfected a method of preparing silk screens for water-inks in which a *temporary support* is covered with a cellulose lacquer, then with a photographic emulsion. After exposure and development, the image is attached as above, and after drying, the lacquer is dissolved in the areas where it is exposed. The residual gelatin is eliminated with hypochlorite, and the lacquer stencil is transferred on to silk fabric.

DICHROMATED COLLOIDS

597. Dichromated gelatin

Gelatin, impregnated with potassium dichromate, constitutes a photosensitive system.(12b) Under the action of light it appears to produce a chromic compound which *locally hardens* the gelatin. The amount of this chromic compound retained is 3·5% at the most. The chromium can be estimated, after dissolving in 1% sulphuric acid, by oxidation with persulphate and iodometric titration.

Eggert and Biltz have expressed the reaction schematically as:(13)

$$6h_\nu + 3(NH_4)_2CrO_4 + 6H(\text{from the gelatin}) \rightarrow (CrO)_2CO_4 + 6NH_4OH$$

$$(CrO)_2CrO_4 + 2(\text{gelatin}) \rightarrow \text{tanned gelatin}$$

Smethurst has remarked that such a reaction would hardly be possible with other colloids such as methylcellulose. He suggested that the hardening is more likely to be due to polymerization resulting from the formation of cross-linkages between the molecular chains.(14)

The same writer(15) proposed a possible reaction:

$$H^+ + HCrO_4^- + h_\nu \rightarrow CrO_3 + H_2O$$

The energy necessary for the reaction being about 60 Cal per gram-mol. Another scheme was put forward by Asperger(16)

$$Cr_2O_7^{--}+H_2O+h_\nu \rightarrow OH^-+HCrO_4^-+CrO_3$$

$$CrO_3+HCrO_4^-+OH^- \rightarrow Cr_2O_7^{--}+H_2O+Q$$

$$CrO_3+\text{gelatin} \rightarrow (\text{gelatin—}CrO_2\text{ complex})+O$$

The *hardening* of gelatin by dichromates is a process which *proceeds slowly in the dark.* According to Smethurst, the reaction in the dark is not the same as the reaction brought about by light.

The sensitivity to light of a dichromated substance requires the presence of polar groups —OH or —COOH.

The *effectiveness of the radiations* is at a maximum at 210 mμ in the far ultra-violet; the sensitivity decreases to 325 mμ then again increases to a second, weaker, maximum at 355 mμ in the near ultra-violet, then again drops to 580 mμ in the yellow-green. The zone of photographic activity is, in practice, situated between 355 and 425 mμ. The characteristic curve has a long straight line.

The maximum sensitivity is obtained at the isoelectric point of the gelatin. This is why the reaction is normally carried out in the presence of an organic acid or its salt, to maintain a sufficiently low pH. In ammoniacal alkaline medium an increase in contrast is obtained due to the disappearance of the low densities.

The *addition of certain* salts has often been disclosed: cobalt, copper, nickel, cerous and various rare earth chlorides. The results do not, however, seem conclusive. Asperger has even disclosed a slowing down in the presence of Mn^{++}, NH_4^+, Cr^{+++}, Co^{++}, Cu^{++}, Ni^{++}. The cyanides, then the bromides, the thiocyanates and the chlorides slow down or stop the reaction at a concentration of 10^{-5} Mol/cm^2.

G. Maillot has claimed an increase in sensitivity of 2–4 times by replacing the potassium dichromate by the dichromates of *pyridine* or *quinoline.*(17) These compounds are prepared by mixing chromic acid CrO_3 with the base (pyridine or quinoline) in concentrated solution. The dichromate crystallizes immediately. There are several possible combinations with each base.

Dichromate gelatin can be *hypersensitized with mercury vapour* (Gorodnitzky).(18) The exposure is reduced to one-fifth after 30 minutes' hypersensitizing and one-tenth after one hour. After 2 hours the gelatin becomes insoluble.

Humidity plays an important part: if it is too high, sensitivity and keeping properties are decreased; too low makes the layer brittle. A 14% moisture content is normal, and this is obtained by leaving at 21° in an atmosphere of 60% R.H.

In practice, sensitization is carried out by 2-3 minutes' immersion in sodium, potassium or ammonium dichromate solution, to which 0·5–1% alkali citrate has been added.

A sensitized paper hardens completely in the dark after 17 days. It is useless after 7 days. It can, however, be kept almost unchanged at *low temperatures*. Heinrici⁽¹⁹⁾ states that there is a small drop in γ with Autotype photo-gravure paper after 46 days at 6·5°C (43°F).

When the *sensitized gelatin is coated* on glass plates, the photosensitive solution is made up of a mixture of gelatin, dichromate, citrate, and occasionally a dye to restrict light penetration. For example:

Soft gelatin	150 g
Ammonium dichromate	30 g
Potassium citrate	10 g
Cochineal red	0·5 g
Water	1000 c
Alcohol	50 cc

To avoid crystallization of the dichromate the plates are dried in a warm atmosphere.

An image printed on dichromated gelatin appears brown and full of detail, except when a dye has been incorporated in the layer. After exposure, the excess sensitizer is removed by washing, and the soft gelatin can be removed with hot water.

The dichromate sensitizer can be combined with a ferrioxalate:⁽²⁰⁾

Ammonium dichromate	15 g
Ferrioxalate (potassium)	8 g
Water	100 cc

Swelling. We know that the dichromated gelatin layer, exposed and then washed, leaves the hardened gelatin as a relief image. It is sometimes useful to have the maximum relief, that is, the greatest difference between the hardened and the unhardened gelatin. The degree of swelling here depends not only on the nature of the gelatin, but on the time and temperature of bathing, and also on the pH. An acid bath, after several hours gives the maximum swelling.

The permeability of the hardened gelatin can be restored, according to La Mantia⁽²¹⁾ by 30 minutes' immersion in 5% sodium perborate at 10°C, which removes the chromium oxide.

Wet dichromated gelatin. Dichromated gelatin is only slightly sensitive in the wet state. It can, however, be activated by rare earth salts. In this way, images can be obtained with 2–5 minutes' exposure to a high pressure mercury vapour lamp. These images are very contrasty. They can be softened by increasing the concentration of dichromate or by dilution of the dye bath in the staining operation which follows. The sensitivity is at a maximum below 15°C (59°F).

598. Dichromated gum (gum bichromate)

Gum arabic differs from gelatin as it is soluble cold. Its varying sensitizing properties make consistent results difficult to obtain. In particular, the viscosity of the solutions varies not only from batch to batch but with age. Constant results can be obtained with *arabic acid*, the active constituent of the gum, prepared by passing the solution over the ion exchange resin I.R. 100 (Rohm and Haas) which replaces the calcium and magnesium ions with hydrogen ions.(22) The viscosity of arabic acid is lower than that of the gum, pH 2 instead of 4·5. A way of avoiding variations in solutions of the crude gum is to make them alkaline, pH $\geqslant 8$, with ammonia.

The preparation of perfectly clear solutions of the gum is slow: several days' soaking are necessary to disperse the lumps, and still more to decant the colloidal impurities.(23) Proportions—equal quantities of gum and water.

The '*gum-dichromate*' process was widely used at one time. It consisted of coating, with a roller, shrunk paper (wet and dried twice) with a very thin layer of coloured gum containing ammonium dichromate:

Gum arabic solution 1:1	20 cc
Ammonium dichromate 6·5%	60 cc
Pigment	5–10 g

or

Gum arabic solution 1:4	40 cc
Potassium dichromate 9%	24 cc
Pigment (pure water colour)	4–8 g

Quantity used: 3 cc for 18 × 24 cm.

Normal stripping time in cold water: 90 minutes.

Today, gum-bichromate is used for printing on metal and for graticules. In the case of prints on metal, an acid calcium chloride solution is used for stripping, sometimes with a final alcohol rinse.

599. Dichromated albumen

Dichromated albumen is prepared by grinding together 10 g of dry albumen with 10 g of pumice stone (to prevent coagulation) then adding water slowly, the resulting solution being filtered. If fresh egg-whites are used, the beaten solution is also filtered. Add 5 g of ammonium dichromate in 100 cc water to the albumen solution and then ammonia, drop by drop, until the solution is pale yellow. Make up to 500 cc. This mixture will keep for several days. With fresh egg-whites, use 100 cc for 16 g dichromate in 1 litre of water.

Sensitization of zinc for line blocks(23b)

Egg-white	64 cc
Fish glue	15 g
Ammonium dichromate	15 g
Water to	1000 cc

Add a few drops of ammonia.

Koch and Rossell(24) have stated that the spectral sensitivity of dichromated albumen varies greatly with the pH. In the ultra-violet at 300 mμ the sensitivity diminishes with the pH. Towards 380 mμ it is at a maximum for neutral solution and minimum for a high pH, whilst at 440 mμ in the blue it is a maximum for basic materials and minimum for neutral.

The determination of sensitivity figures is of value only at constant humidity.

600. Dichromated polyvinyl alcohol

Dichromated polyvinyl alcohol is used for printing matrices for photolithography and photogravure in place of dichromated gum, as it is more sensitive and does not show the great variations in properties brought about by the variations of atmospheric humidity. A typical formula is:

Polyvinyl alcohol (high viscosity)	11·5 g
Potassium dichromate (saturated solution)	5 g
Water	83·5 g
Dye	Q.S.

Development is in cold water after swelling. The residue is baked, but less so than glue.

Polyvinyl alcohol can also be used in the preparation of screens.

601. Dichromated cellulose

The use of dichromated cellulose has been known for a very long time. However, instead of using a solution of cellulose which is coated on to a support, then coagulated, it is now preferable to use a superficially hydrolyzed cellulose acetate film. This enables *photolithographic matrices* to be prepared as cellulose is wetted by water and repels greasy inks whereas acetate accepts greasy ink.

The film is hydrolyzed by treating for 5 minutes in a 5% caustic soda solution in 40% alcohol,(25) followed by washing. The thickness of the hydrolyzed layer must be determined accurately, as the quality of the image and the printing life depend on it.

To avoid shrinkage of the support and to make it resistant to the mechanical stress of the printing machine, the acetate film is strengthened by aluminium foil, on the back for thin films, and in the middle for thick ones. An orange anti-halo layer is used in each case. The Kodak Ektalith films are made in this way.(26)

Sensitization is in a 5% dichromate solution containing 3% ammonia and 0·3% of a wetting agent preferably using a roller nip and two sheets of blotting paper.

Sensitivity is equal to that of dichromated gelatin.

Stripping involves rubbing the surface with a solution of zinc chloride for 3 minutes, or with an alkali containing an oxidizing agent for 1–2 minutes. In the second case, neutralization in acid is followed by a water rinse. Before neutralizing it is best to impregnate the layer with a dye.

In the light-affected areas, the *cellulose is oxidized and made removable*, leaving the acetate exposed.

Number of prints—75,000 for line subjects or 50,000 half-tone. The prints are sharper than with grained zinc.

602. Dichromated glue (or enamel process)

Fish-glue has the property of *vitrifying* under the action of heat, at about 300°C, to form resists which are not attacked by acids or normal organic solvents. This valuable property at one time enabled it to be advantageously substituted for albumen, for printing on metal. Nowadays hot *fish-glue* is rivalled, for zinc sensitizing, by shellac which is a *cold enamel* (para. 603).

Photogravure fish-glue is a pasty liquid which is clarified fish-glue.(26b) It is diluted several hours before use with one or two parts of water.

The thickness of the glue layer must be greater than a similar albumen layer. After drying there must be no iridescence.

The glue is *sensitized* with ammonium dichromate, but the proportion must not be excessive. The following is an optimum formula (A. J. Newton):

Fish-glue	100 g
Water	200 cc
Ammonium dichromate	5 g

The dichromate is dissolved in the water first.

This mixture requires an exposure of 5 minutes at 65 cm from a 10 amp arc.

Stripping is carried out in water. The baring of the metal can be seen if the layer is dyed with methyl violet. The plate is rinsed in alcohol and dried.

The insoluble gum layer is then baked at about 300°C until it is tinted brown. Some authorities, however, recommend baking only until it is pale yellow.

Formula recommended for sensitizing copper for half-tone blocks:(27)

Fish-glue	360 g
Dry albumen	7·5 g
Ammonium dichromate	52·5 g
Water to	1000 cc

603. Dichromated shellac

The composition of shellac varies widely with its origin.(28) For photographic use, it must be *modified by hydrolysis*. Even after this treatment the product polymerizes slowly and its properties are altered. The preparation of large quantities must therefore be avoided.

Preparation.(29) Soak 100 g of shellac in 250 cc alcohol, preferably anhydrous, until it is dissolved. Cool to 15°C and slowly pour in a solution of 16 g caustic soda in 800 cc water, and again cool to 15°C. The heat of reaction must not raise the temperature above 23°C.

The shellac hydrolyses. Note carefully the time for this change which varies with each batch. An average of 30–40 minutes is needed. The reaction is stopped in 5 minutes by adding enough ice to lower the temperature to 5°C.

The hydrolyzed lac is then precipitated with 122 cc of sulphuric acid, previously dissolved in 800 cc water, and cooled to 5°C. Excess acid must be present. After decanting, the precipitate is washed with water until neutral to methyl orange. It is strained off with muslin and *used immediately*, without drying, to prepare the solution.

The *extent of hydrolysis* is extremely important, as it determines the ultimate solubility in alcohol during stripping. It is checked by determining its *acid number*, the number of mg of KOH necessary to neutralize 1 g of the dry resin. 10 cc samples taken at regular intervals are titrated with decinormal sulphuric acid in the presence of phenolphthalein. The amount of H_2SO_4 needed decreases as hydrolysis progresses.

If the hydrolysis is insufficient, the shellac will not strip in alcohol, but if it is excessive, even the exposed areas are removed. Generally, hydrolysis should be stopped at *an acid number of* 122–127.

Dissolving the hydrolyzed shellac. The resinous mass obtained as above is mixed with 15 cc of ·920 ammonia and then dissolved on the waterbath. It is then made up to 750 cc (or other suitable amount).

Sensitization. For each 100 cc of the above solution, take 2–5 cc of 20% ammonium dichromate. The sensitized solution keeps for several weeks, but the layer, coated on metal and dried, polymerizes rapidly in the dark. The rate of polymerization depends on the relative humidity.

The coated layer dries in two minutes if the drier is heated to 35–40°C.

Exposure. Do not leave the plate until it is cold and has taken up moisture. Expose and strip immediately after.

Stripping is done with a 0·2% alcoholic solution of methyl violet. Do not exceed this concentration of dye or the shellac will be insolubilized by a secondary reaction between the dichromate and the dye. Check the water content of the alcohol and avoid any which is diluted. Keep the temperature constant. After stripping, rinse in clean alcohol, rinse with a jet of cold water and dry.

Although shellac gives an enamel cold, photoengravers prefer to bake at about 95°C to strengthen the resist.

604. Ferric chloride process

Ferric chloride, $FeCl_3$, *insolubilizes* gelatin and gum arabic *in the absence of light*, but when exposed, the colloid again becomes soluble. Also suggested are cellulose glycollate and sodium cellulosehydroxyethane sulphonate.(30)

Smethurst prepared a photosensitive solution without coagulation by pouring a fine stream of the gum into the ferric chloride, agitating vigorously. Any coagulum dissolves in excess ferric chloride. The product is used without further addition of water. Hardening is greatest at pH 2·2. Sensitivity is four times lower than dichromated gum.

605. Insolubilizing with diazonium compounds

Insolubilizing colloids in the presence of diazo compounds was disclosed by A. and L. Lumière in 1899 and studied by Zahn. *The reaction product acts as a hardener and can serve as a coupler*. In this way casein, sensitized with a diazo compound in the presence of copper nitrate and chrome alum gives positive images with warm water development.

Neuroth and Ostwald disclosed the nitrides and other aromatic nitro compounds.

Acetate films, coated with a dyed or pigmented gelatin layer, and sensitized with diazo compounds (see para. 650) can be used, after exposing and treating in warm water, to make screens. A silk cloth is squeezed on the wet gelatin. After drying it is stripped off with the gelatin from the support.(30b)

A gelatin-coated metal plate can be sensitized in the same way. After exposing, it is treated with a diluted acid which disaggregates the exposed areas, by formation of very fine nitrogen bubbles (Kodak).(30c)

DIRECTLY PHOTOSENSITIVE LAYERS

606. Bitumen

Natural bitumen, which seeps from rock masses, and particularly *Judea bitumen*, is sensitive to light, which makes it insoluble in its normal solvents. Bitumen was used by Nicephore Niepce in his historic experiments. It is said to be one of the oldest substances used in photography. It was widely used in the last century for the preparation of photomechanical plates. Its extremely low sensitivity has led to its abandonment in favour of the dichromated colloids. Nevertheless, the bitumen process is of interest because of its originality.

Bitumen is made up of three varieties, α, β and γ. The insensitive α type is soluble in alcohol; the slightly sensitive β type is soluble in ether. The γ type is the only truly sensitive one. It is obtained by extracting dry, powdered Judea bitumen with ether for 24 hours, then extracting the residue with chloroform. The chloroform solution is evaporated to leave γ bitumen.

The α, β and γ varieties contain, respectively, 7, 10 and 13% sulphur. The first two can be converted to the third by reacting sulphur with bitumen in boiling cumene for one hour. Judea bitumen contains 4% α, 44% β and 52% γ. Trinity bitumen contains 5% α, 60% β and 35% γ. Bitumen is in the form of hard brittle brown-black masses. M.Pt. 100°C, soluble in benzene, toluene, chloroform, petrol, turpentine, etc.

The light sensitivity of bitumen can be increased by the action of sulphur as shown above. Valenta at one time disclosed boiling with 10% sulphur in carbon disulphide, evaporating the solution and heating the solid for 5 hours at 180°C.

Sensitive solution: bitumen (crushed) 120 g, benzene 100 cc. When dissolved add 15 drops of lavender essence, then benzene to 1 litre. Filter after standing for 12 hours.

Exposure time: about 2 hours in sunlight from a tracing.

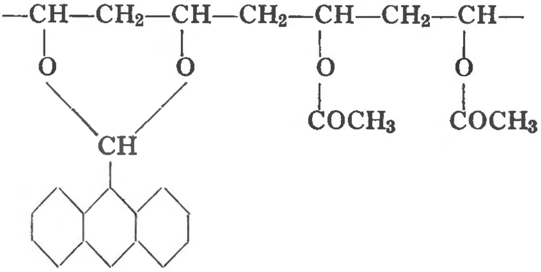
Stripping with turpentine, using a wad of cotton wool.

607. Photosensitive resins

Valenta disclosed, long ago, that *natural resins* fused with sulphur are light sensitive, particularly colophony. The sulphided resin is dissolved in benzene and coated on paper.

Beebe and Murray(31) have suggested *rubber hydriodide* for the preparation of sensitive layers; it is prepared by the action of HI gas on a chloroform solution of rubber cooled in ice.

More recently, Schröter and Rieger(32) have described *polymerized* polyvinyl alcohol derivatives whose light sensitivity is provided by the association of iso or heterocyclic groups, having at least 3 linearly joined benzene rings. *Anthracene-aldehyde acetal* of polyvinyl alcohol is an interesting example of this:



It has two absorption bands—at 250 and 400 mμ. Coated from a chlorinated solvent, it becomes insoluble in benzene by polymerizing under the action of light. Exposure: 1 minute at 50 cm from a 12 amp arc.

Kodak *Photo-resist*(33) is a solution in an organic solvent of a straight-chain unsaturated polymer, and under the action of light, cross-linkages are formed which make it insoluble. It is as sensitive as dichromated gelatin between 360 and 430 mμ, and in the dark it keeps indefinitely in solution. It is stripped in a solvent such as trichlorethylene. The hardened resin is a good acceptor of greasy inks.

APPLICATIONS

608. The carbon process

The carbon process uses a gelatin relief, made with a pigmented layer sensitized with dichromate. This process, which is now relatively unimportant, was, until recently, practised using *Autotype* papers. The images obtained have straight characteristic curves and are very stable. They produce excellent artistic effects.

The starting material is made from a gelatin solution containing a plasticizer, such as sugar or glycerin, soap and a pigment. For example:

Hard gelatin	200 g
Sugar	30 g
Soap	25 g
Pigment	30–50 g
Water to	1000 cc

This amount covers 30 sq. ft.

The pigment must be very finely divided, in a mill, after having been pasted with the glycerin and water. Otherwise, water-colour pigments can be used. The principal pigments are:

Carbon black, red ochre, yellow ochre, raw sienna, cobalt blue, Egyptian blue, ultramarine, Prussian blue, chrome green, chrome yellow, cadmium yellow, Cassius purple, etc., which can be mixed in various proportions, and shaded with insoluble organic dyes such as indigo, thioindigo (purple), sodium alizarinate, indian yellow.

There are actually many organic pigments formed from dyes laked with alumina or phosphotungstic acid, the I.C.I. 'Toners' for example. Blues and greens which are very fast to light are obtained from the phthalocyanines.

Blacks are necessarily obtained with carbon black (preferably Peerless or Dixie brands).

Three-colour prints are not often made by the carbon process; but if they are, transparent organic pigments or substantive dyes (para. 565 and 621) must be used. The simplest way is to use the Autotype tissues.

Sensitizing is carried out in a potassium dichromate solution whose concentration can vary from 1 to 6%. The weaker the bath, the more contrasty the print (see para. 597). The sensitized paper keeps for only a few days. Exposure is controlled with printing-out paper.

The exposed layer is washed to remove the dichromate, and is transferred wet to a hardened gelatin-coated paper before hot water development (35–40°C) (95–104°F). It is the rear of the layer, originally in contact with the paper, which is treated with hot water. In the case of a single image, the transferred image need only be hardened with alum; but if the image is to be turned round again, or if three monochrome images are to be registered, *double transfer* must be used. The first is on to a temporary waxed transparent support, and the second on to a slightly hardened gel-coated paper.

The temporary support can be glass, thick celluloid, then cellulose acetate or gel-coated cellophane. The latter is easily stretched in the wet state and enables inaccuracies in registration to be corrected.(34) The cellophane is removed after the second transfer in warm water (40°C) (104°F).

The removal of the unhardened gelatin can be accelerated, or carried out cold with *weak hypochlorite*, *ammonium thiocyanate*, *concentrated potassium bromide*, *concentrated potassium iodide*, or the diastase enzyme *photobiase*.

If the gelatin layer is very thin, hardening takes place through to the support, and transfer is useless. This is the principle of the old Artigue *velours* *paper*, in which a 1·5% gelatin solution was coated at the rate of 35 cc per sq. ft., and powdered with pigment. A variation was to powder a solution of pigmented gelatin (Fresson paper).

For *dichromate gum*, see para. 598.

609. Carbro or ozobrom process

The carbro process uses indirect hardening which we have described in para. 595. The sensitized pigmented layer (as in the carbon process) is pressed in contact with a silver image, and is hardened in proportion to the densities of this image. The gelatin layer is washed and applied to a transparent temporary support (waxed celluloid) and 'developed' in hot water, which also removes the paper base. It is dried, wet in cold water, and squeegeed to a sheet of damp gel-coated paper. On drying, the paper contracts, taking the image with it. The paper is again wetted, and the second monochrome image is applied in the same way, and then the third to complete the colour image. The most opaque pigmented layer is always applied first.

The three separation positives must be printed on special photographic paper, which is not supercoated. They are preferably developed in a low bromide amidol developer, fixed and washed. The pigment papers are sensitized as described in para. 598.

In the old *Vivex* process(35) the pigment papers were sensitized for 10 minutes at 18°C (64·4°F), and left in contact with the corresponding positives for 10–15 minutes. The pigment papers, carried on a metal plate, were then bathed in 50% alcohol, and applied in this liquid to cellophane, previously washed to remove the glycerin. They were then stripped at 41–43°C (106–109°F), with the cellophane mounted on celluloid, and fixed to a drum. The three images were then transferred to paper, starting with the yellow, and were stuck with an aqueous-alcoholic solution of gelatin in acetic acid.

A variation is to stick together three primary images, mounted on very thin cellulose films, using an albumen adhesive.

We would also mention the *gum-ozobrome* process in which the gelatin is replaced by gum arabic.

610. Greasy ink processes

Instead of incorporating the pigment in the gelatin, the hardened gelatin image can be made visible by surface application of a *greasy ink* which only takes on the hardened parts.

In the *bromoil* process, a positive image is hardened by bleaching (para. 594), fixed, washed and swollen to obtain a relief which is blotted and then inked with a brush. The quality of the result depends on the skill and artistic sense of the operator.

The paper on which the positive image is printed must neither be strongly hardened nor supercoated. It is developed in amidol.

Oleotype is similar to bromoil except that the relief is obtained on dichromated gelatin.

We would put *resinotype* in this category. A negative image in dichromated gelatin is made visible by sprinkling resin pigments on it: the pigment only sticks to the *unhardened* parts. If the sensitive layer is a photographic paper, the hardening is carried out in a bleach bath.(36)

611. Collotype

If a greasy ink is spread over the surface of a gelatin image-bearing layer, *it will adhere to the hardened parts, but be repelled by the unhardened areas.* This happens in bromoil. If, however, the inked image is pressed in contact with a sheet of paper the image is printed on the latter, a process which can be repeated many times. The collotype process is based on this principle. Thick ground plate-glass is coated with dichromated gelatin and dried. After exposure it is washed, swollen with glycerin-water and inked.

The sensitizing solution contains 10% gelatin and 2% dichromate (previously dissolved in a little water). Drying temperature 38–40°C (100–104°F). If a lower temperature is used, the dichromate will crystallize. In exposing, a brown image on a yellow background is obtained. It must not be too dense. The gelatin layer can also be sensitized just before use, by immersing in 3% dichromate, then drying with hot air. The exposed plate is washed to remove excess sensitizer. It is then *damped* by immersing for 30 minutes in a mixture of 750 cc glycerin and 250 cc water. In this bath the relief is reduced and the surface becomes flat. If the image is overexposed, reduce the amount of glycerin. If it is underexposed it is the water which should be reduced. The glycerin reduces the contrast. If the plate has been insufficiently damped, the highlights retain the ink. If it remains too long in the bath, the whites and the half-tones do not accept ink.

The plate is blotted with fine calico before inking. Then the greasy printing ink is applied with a gelatin roller. If the ink is too thin, the whites become grey; if too thick, the half-tones are lost. If the gelatin layer is misted over in cold weather, it does not accept the ink. When a hard press is used, place a rubber blanket between the upper platten and the paper. With a machine, 1500 prints can be obtained from one plate. The plate is cleaned with a rag dipped in water and turpentine.

Coated paper gives the best prints, but if the surface is not insoluble, it may stick to the plate. Sized paper is necessary for printing, as non-sized paper, which absorbs the ink well, requires frequent damping of the plate.

Dichromated gelatin plates have now been replaced by *superficially hydrolyzed cellulose acetate matrices*, which were described in para. 601. These matrices enable 30–40 times the above number of prints to be made.

With both types of plate, *three impressions* can be made with yellow, cyan and magenta inks to give three-colour copies.

Ferrogelatinography. This was the old Dorel process: a thick gelatin layer containing ferrous sulphate, a hygroscopic compound (glycerin) and a wetting agent (sodium taurocholate or ox-gall) is pressed on to an exposed *ferroprussiate* image which is unwashed. The excess ferricyanide forms a ferrous ferricyanide which tans the gelatin locally, enabling it to accept greasy ink, as in collotype. Spencer used a green iron citrate paper containing oxalic acid and potassium ferricyanide.

RESIST PROCESSES

The *resist processes* consist of forming an image in a photosensitive colloid coated on a permanent support, stripping the colloid layer and *etching the support chemically* in the areas left bare. The colloid is removed to leave a relief or block which can be used for mechanical printing.

612. Half-tone

Half-tone consists, in principle, of inking a *plate with a sharp relief*, and applying this plate to the paper. In this way, only whites and blacks are produced, with no intermediate tones.

The modelling of the image—that is the rendering of half-tones—is achieved by dividing the printing surface into dots: a large number of black dots close together having the appearance of a dark region, whilst a smaller number of dots widely spaced gives the illusion of a light grey.

To obtain a dotted plate, *cross-ruled screens* printed on glass are used. The image to be reproduced is photographed on to a plate placed behind a screen. The developed image consists of a large number of dots whose number and diameter is dependent on the density of each part of the image.(37)

The *half-tone plate* is made of copper or zinc. The surface of the plate is covered with fish glue or shellac, sensitized with dichromate and dried (see paras. 602 and 603). The screen negative film, removed from its support, is fixed to this layer. After exposure to a lamp whose light hardens the sensitive layer, the negative film is detached. The glue or shellac is stripped to leave a relief design. The remaining glue (not the shellac) is heated to 300°C to convert it to a protective enamel.

As heating has a detrimental effect on the mechanical properties of zinc, it is better to use shellac for which baking is unnecessary.

The metal is then etched in the areas left unprotected. Copper is treated with *ferric chloride* and zinc with *nitric acid*. The back of the plate is of course protected with a layer of varnish. The etching, however, does not take place in only a vertical direction, it also works laterally destroying the dots. Etching must therefore be carried out in several stages by protecting the parts which have had sufficient treatment, and this is a very critical process.

For *three-colour half-tone*, three impressions are made corresponding to the three separation negatives. The *loss of saturation* produced by dividing the image into dots is compensated by a *supplementary black printing* which fills in the empty spaces. Furthermore to avoid moiré patterns, each screen must be oriented differently. To this should be added the many retouching stages which are often necessary, and the difficulties of precise *registration* of the four images. The first image which is printed is generally the yellow, followed by the magenta, the cyan and the black.

The inks have been standardized by the British Standards Institute. Some magazines print without intermediate drying of the inks, in a high-speed machine (200 prints per minute).

Protection of metal plates against oxidation. The oxidation of metal plates for photomechanical processes after graining is prevented by replacing the water in the grainer by 2% dichromate, after treating the metal with a detergent such as trisodium phosphate.(38) Zinc and aluminium are adequately protected in this way. A more complete solution is to treat the grained metal in a solution of: Water 1000 cc, ammonium dichromate 29 g, sulphuric acid, concentrated 3 cc. Bruno and Hartsuch(39) prefer, for aluminium, a hydrofluoric acid solution: Water to 1000 cc, ammonium dichromate 70 g, hydrofluoric acid (S.G. 1·14) 9 cc.(40) Treatment time, 1½–3 minutes. In addition, it is as well to wrap zinc or steel blocks in paper impregnated with sodium benzoate.

Magnesium alloy plates require special treatment before coating with resist, to avoid losing the resist during etching: 30 seconds immersion in: Water to 1000 cc, ammonium dichromate 16 g, sodium selenite 8 g, phosphoric acid 4 cc, followed by washing.

Etching zinc. If the resist is glue, an alcohol base bath is preferable:(41) anhydrous alcohol 1000 cc, concentrated hydrochloric acid 40 cc (or nitric 25 cc). After 1–2 minutes replace the liquid with anhydrous alcohol containing castor oil or oleic acid.

If the resist is shellac, an aqueous mordant can also be used: calcium chloride (41° Bé solution) 1000 cc, dry ferric chloride 25 g (or zinc chloride 250 g), hydrochloric acid 25 cc (or 20 cc with zinc chloride): time 1–2 minutes.

Etching aluminium protected with a glue resist, use: anhydrous alcohol 1000 cc, hydrated ferric chloride 1000 g, hydrochloric acid 25 cc, phosphoric acid 12 cc. Use a wad. Time — several minutes.

With a shellac resist, Haigh and Cartwright recommend: calcium chloride (41° Bé solution) 1000 cc, ferric chloride 200 g, zinc chloride 200 g, hydrochloric acid 20 cc. Etching time 2–3 minutes.

Etching copper is carried out with 40° Bé ferric chloride at 32°C. The etching rate increases with dilution. The concentration of cupric chloride in the used bath affects the rate and the quality. This effect is slight, however, for a concentration of between 4 and 16 g.p.L. Cu in 40° Bé ferric chloride.(42)

Electrolytic etching. The metal plate is the anode (+) of an electrolytic cell containing a solution of 5 parts of sodium chloride and one part of ammonium chloride using a voltage of 10. A higher voltage gives contrasty images. The cathode is a stainless steel grid. The cell is agitated with compressed air.(43)

613. Bimetallic plates

The use of bimetallic plates is based upon the *different affinity for greasy ink of two metals*. The first metal, which makes up the image, accepts the ink, whilst the second repels it, as with hardened and unhardened gelatin. The idea of bimetallic matrices dates back over a hundred years, and many systems have been disclosed since then. At the moment, more than a million prints can be made with this type of plate.

There are two ways of obtaining a metallic image on the background of another metal:

(*a*) By covering a metal plate with a resist, preferably obtained photographically, then to deposit the other metal on the exposed areas by electroplating or by the inferior method of amalgamating.

(*b*) By locally attacking the exposed areas of a very thin metallic layer carried on another metal. The resist image is obtained photographically as with all the preceding methods.

The metal chosen for the print image is generally copper. The backing metal is *chromium* or *stainless steel.* Some processes use a lead base (Boekelman), and others nickel or zinc with brass (Hansleiter, Blau). The Alkaprint process uses aluminium.(44) The first bimetallic systems used an amalgam (which repels the ink), but mercury has the disadvantage that it is gradually removed by inking).

The state of the metallic surface is extremely important as it affects the repelling properties in the *wet state*, which is the way it is used (as all these metals accept ink to some extent). The graining of the plate must therefore be carefully controlled.

Other heterogeneous systems. Stainless steel, or chromium containing about 10–12% nickel, is superficially oxidized by electrolysis. This layer of oxide, covered with a photographic resist image, can be removed locally, also by electrolysis. The remaining *chromium oxide* image, slightly moistened, retains ink perfectly.(45)

Another heterogeneous printing system uses a *cellulose* ground (which repels the ink) and an image of *cellulose acetate* (which takes ink). A superficially hydrolyzed cellulose acetate sheet is the starting material, and it is coated with a photographic emulsion. The image, exposed from the rear, is developed in a tanning developer and stripped in warm water. In the bared parts, the cellulose is dissolved in 58% zinc chloride. The gelatin is removed with hypochlorite to leave an image of cellulose acetate on a cellulose background.(46)

614. Photogravure

The image is lightly engraved on a metal plate or cylinder (at least several hundred millimetres diameter). Contrary to half-tone, in which the ink is on the raised parts of the block, it is in this case applied to the cavities, whose variable depth alters the thickness of the ink. Under pressure, the ink is transferred to the paper.

To avoid losing the ink from the cavities, these are divided into minute squared cells which enable the plate to be wiped with a squeegee without removing the ink from the cavities.

Photogravure plates are made in the following way: the image to be reproduced is photographed as a negative, from which a diapositive is printed. *A sheet of gelatin-coated paper is sensitized in* 2·5% *dichromate.*(47) It is then successively printed with a *grid pattern* (to form the cells) with clear lines, and the *positive image*. The gelatin surface is damped and the paper is rolled around a *copper cylinder*. It is then carefully stripped with warm water at 35–40°C (95–104°F). The paper comes away to leave an image with the honeycomb pattern in the cavities. It is dried at 18–20°C (64–68°F) at a R.H. of 55–60%. The thickness of the dried image varies from 8 to 28 μ.

The copper cylinder is then etched in *ferric chloride* in several stages at various concentrations (41 to 30° Bé). The permeability of the gelatin is, in fact, unequal in the shadows and highlights, because of the differences of exposure, and therefore tanning. Ferric chloride of one strength will only attack certain parts of the image effectively: very concentrated, it only penetrates the slightly hardened shadows, but dilute, it effects the whole image.

In printing, the cylinder carrying the cavity image is inked by immersion rather than by using a roller. The excess ink is removed with a steel doctor, and the roller is pressed into contact with paper, being rolled under pressure.

As the ink is spread on the paper, there is *no loss of saturation* due to the presence of white areas. Three impressions in yellow, magenta and cyan inks are enough for a colour print; the black printer is unnecessary.

Intaglio half-tone is a variation of photogravure in which a sensitized paper is not used, but a directly sensitized metal plate or cylinder as in normal half-tone. In Henderson's very critical technique, disclosed in 1940, and taken up again in 1949,(48) the print is made directly on to a cylinder covered with dichromated shellac. The sensitized layer is coated with a special turntable rotating on two perpendicular axes, one of which is that of the cylinder. In printing, the positive moves tangentially to the cylinder, which turns at a peripheral speed equal to the linear film speed. Stripping and etching are carried out mechanically by spraying on a solution of ferric chloride and removing the excess liquid with compressed air.

The positive used in intalgio half-tone must have a screen, the dense areas being divided by a grid of fine transparent lines.

615. Off-set

In the off-set process a cylindrical plate of zinc bimetal or hydrolyzed cellulose acetate, deposits ink on a rubber roller which in turn transfers it to the paper. Printing is therefore indirect and can be made on any type of paper, smooth or rough.

616. Photomechanical printing inks

Photomechanical printing inks are made up of a *binder* and a *pigment*. The binder generally has a linseed oil base brought up to the required consistency with a mixture of oil and a resin or with a resin alone. The inorganic or organic pigment can be mixed with a dye soluble in the binder. It must of course be perfectly blended.

For half-tone, boiled linseed oil is used whose viscosity is increased by a resin such as Albertol 209L. For off-set, thin binders are selected, whilst for photogravure the principle base of the binder is a resin. *Photogravure inks* are virtually solutions in an organic solvent of resin-pigment mixtures. Being very thin, they are rapidly absorbed by the paper pores which makes rapid drying possible: 9 seconds for rotary printing. For colour printing, the inks are matted by the addition of alumina, for example. The resins giving the best binders are gum dammar, and processed copals of the Albertol type which are soluble in hot oil. The binder can be made up for example, from 3 parts of Albertol 116Q or 826 and 2 parts of toluene or xylene. The ink is then made up of: binder 250 g, magnesia 90 g, Hansa yellow G 45 g, linseed oil standolie 2 g, sangajol (white spirit) 10, xylene 10. The Hansa yellow can be replaced by lacquer red pigment or reflex blue.

617. Photoceramics

Porcelain is coated with dichromated gelatin which is exposed under a negative. Coloured powders such as cobalt, manganese or chromium oxides, damped or mixed with borax, are applied after washing. The powder does not take on the hardened areas. The object is then fired. A vitreous print can also be obtained by transferring a carbon print and fixing in the presence of aluminium borate.

618. Manufacture of graticules by photographic means

The method is to etch a support (of glass or plastic material) through the spaces left bare in a photographic resist. Glass is only attacked by hydrofluoric acid. The use of this acid, whose action is unreliable, can be avoided using Smethurst's lead sulphide method:(49) a mirror of *lead sulphide* is deposited on the glass, and a thin layer of dichromated shellac is coated over the lead sulphide. After exposure, the layer is stripped with alcohol on a turntable revolving at 3000 r.p.m., which is also used for coating. The resist is baked at 125°C, and the PbS mirror is etched with a solution of 10% dichromate in 10% hydrochloric acid.

A process using the attack of glass by hydrofluoric acid was perfected by Loening.(50) It consists of first coating the glass with a layer of *bakelite* resin, which is very resistant to this acid even in a thin layer. This bakelite layer is then re-coated with dichromated gum arabic. After exposure, the gum is stripped in water for one minute, dried, and then treated in *lactic acid* diluted with an equal volume of *ethyl lactate*, for two minutes to dissolve the bakelite. The solvent action is stopped by mopping with a mixture of equal volumes of lactic acid and water which absorbs the remaining acid. After rinsing and drying, the glass is attacked by immersing in a mixture of hydrofluoric acid and glycerin.

The bakelite solution is made from: ethyl acetate 100 cc, bakelite 5362 40 g, waxoline red (I.C.I.) 1 g, oil soluble yellow 1 g. coated on a turntable at 660–700 r.p.m. The gum solution contains: water 100 cc, gum senegal 25 g, chloroform 0·25 cc. An equal volume of 20% ammonium dichromate is added, and then the viscosity of the gum solution is brought to 27·5 c.s. by adding water.

For other graticule manufacturing methods, see the references.(51)

619. Manufacture of metallic grids by photographic means

Loening and Gresham(52) have established a technique for the photographic preparation of copper grids with a cloth-like appearance with 80 strands per cm and without unevenness.

A nickelled copper plate is coated with bakelite, then with dichromated shellac. Printing time: 2 minutes at 38 cm from a 12 amp arc. After stripping, the plates (whose edges and back are protected with bitumen varnish) are suspended in a 20% copper sulphate solution containing 0·1% sulphuric acid at 18°C. Then electrolysis is started at 40 mA per 100 sq. in.: for one minute the plate is the anode, and for 10 minutes, the cathode. The grid is varnished, and plating is continued for 20 minutes to strengthen the surround. The bitumen is dissolved in xylene, the bakelite in ethyl acetate, and the grid is removed. Thickness of copper: 5–10 μ for the grid and 75 μ for the frame.

620. Silk-screens

Photosensitive colloids have found a further application in the production of silk screens. A silk fabric, covered with gelatin and sensitized with dichromate readily gives screens after exposure and stripping.

An easier method is to use a stripping paper or film *independent of the silk*. The necessary materials are available commercially—Autotype 1045 and 104 Fast, which are not sensitized; Autotype Films R.S.50 and Kodak Ektagraph which are sensitized by the manufacturer. After exposure, the gelatin from the paper is transferred to a waxed temporary support; the film is exposed through the base. After stripping, the image is transferred to silk to which it adheres completely when dry. The temporary support is finally pulled off.

1. Evans W. H.: R.P.S. Cent. Conf., London, 1953.
2. Pontius R. B.: *P.S.A. Jl.*, 1951, 76.
3. Heidenhain J.: F.P. 831,199 (1937).
4. Rzymkowski J.: *Photo-techn. u. Wirsch.*, 1951, 105.
5. Levenson G. I. P.: *Brit. Jour. Phot.*, 1952, 4.

6. Rzymkowski J.: *Sci. et Ind. Phot.*, 1951, 17.
7. Stevens G. W. W. and Kodak Ltd.: B.P. 548,672 (1941).
8. Symmes E. M.: *Amer. Phot.*, 1947, 13.
9. Coppin F. W. and D. A. Spencer: *Phot. Jour.*, 1948, 78–83.
10. Marriage A.: *Brit. Jour. Phot.*, 1944, 142.
11. Speck R. P. and Kodak: U.S.P. 2,494,068 (1946).
12. Gresham D. C. and Kodak: F.P. 933,966 (1945).
12b. The action of dichromate on colloids in the presence of light was observed by Ponton in 1839 then by Fox Talbot in 1852. Poitevin made a systematic study of it.
13. Eggert J. and Biltz M.: *Sci. et Ind. Phot.*, **5**, 80.
14. Smethhurst P. C.: *Sci. et Ind. Phot.*, **18**, 23.
15. Smethhurst P. C.: *Phot. Jour.*, 1952, 115–123.
16. Asperger S.: *Arhiv. Kemiju*, 1948, 46–60; *Sci. et Ind. Phot.*, 1950, 140.
17. *IX Int. Cong. Phot.*, Paris 1935.
18. *Polygraftscheskaje Proiswodstwo*. Quoted by O. Watter, in: *Die Lechtgerbung in Theorie und Praxis der Druckformherstellung*, and *Sci. et Ind. Phot.*, 1954, 40.
19. Heinrici F.: Fachefte F. *Chemigraphie*, 1949, 26.
20. F.P. 874,015.
21. La Mantia L.: *Bull. Tech. Union Suisse Litho.*, 1949, 35; *Sci. et Ind. Phot.*, 1950, 332.
22. Miesse C. B.: *Modern Litho and Off-set Printer*, 1949, 102–106.
23. Place the pieces of gum in muslin before dipping in water.
23b. Kodak Materials for Graphic Arts, 1937.
24. Koch W. and Rossell R. F.: *Penrose Ann.*, 1953, 122.
25. Colt R. S. and Kodak: U.S.P. 2,448,861 (1948).
26. Clark W.: *Le Procédé*, 1950, Nos. 9 and 10.
26b. It must contain 50% soluble protein. Sometimes a gummy product is formed.
27. Kodak Materials for the Graphic Arts, 1937.
28. Gardner and Whitmore: *Ind. and Eng. Chem.*, 1929, 226–229.
29. Knott E. B.: *J.S.C.I.*, 1940, 252; Loening E. E.: *Process Engravers Monthly*, 1948, 209 and 241.
30. Bohm: Fettchemic G.m.b.H.: F.P. 897,220 (1943).
30b. *Der Polygraph*, 1955, 527.
30c. Hepher M.: *Penrose Annual*, 1955, 122; B.P. 711,702.
31. U.S.P. 1,587,271 (1926).
32. Schröter G. A. and Rieger P.: *Kunstoff*, 1954, 278.
33. Martinson L. E.: *Proc. Tech. Ass. Graphic Arts*, May 1954 and *Le Procédé*, 1954, 70.
34. For operational details see Pilkington W.: *Brit. Jour. Phot.*, 1941, 114.
35. Coppin F. W. and Spencer D. A.: *Phot. Jour.*, 1948, 78–83.
36. For operational details of all these special processes see Henney and Dudley: *Handbook of Photography* (McGraw-Hill, N.Y.).
37. (A) There are coloured screens, especially magenta, whose contrast can pass through all gamma values by merely inserting coloured filters. There are also *degraded screens* obtained by colour development (Yule J. A. C.: F.P. 917,589 and 917,590 (1943)).
    (B) *Kodalith Autoscreen* enables a screen to be dispensed with, as it is pre-exposed with a dot pattern of 53 cycles per cm. The contrast is always too high for half tone.
    (C) Several machines are capable of photoelectrically analysing and producing screen negatives automatically, with masking.
38. N———: *Lithographer's Jl.*, 1949, 12.
39. *Modern Lithographer*, 1948, 51–53.
40. Hydrofluoric acid is dangerous to use.
41. Haigh A. and Cartwright H. M.: *Process Eng. Monthly*, 1944, 218 and 246.

42. N———: *Photoengravers Bull.*, 1947, 19–24.
43. Hislop W. J. C.: *Proc. Eng. Monthly*, Oct., 1948.
44. Cartwright H. M.: *Process Engr. Monthly*, 1951, 115.
45. Batcheller C.: *Mod. Lithog.*, May 1945, 59; June, 1945, 51.
46. Loening, Mitson and Kodak B.P.: 565,752 (1943).
47. The resulting contrast drops with the potassium dichromate concentration. The acidity works in the same way. The more concentrated the bath, the less time the sensitised paper keeps: 4 days with 2%, 2 days at the most with 4%.
48. de Goeij H.: *Fachhefte f. Chemigraphie*, 1950, 73–87.
49. Smethurst P. C.: *Phot. Jour.*, 1944, 147–151.
50. Loening E. E.: B.P. 573,798; *Proc. Eng. Monthly*, Sept. and Oct., 1950.
51. *B.I.O.S. Report* 1552 (1946), H.M. Stat. Off., London (Albumen Process with silver image transferred to glass); Badger R. M. and Strand W.: *U.S. Nat. Def. Res. Comm. Report No.* 34 (1943).
52. Loening and Gresham: *Process Eng. Monthly*, 1950; 358 and 361; U.S.P. 2,459,129 and B.P. 523,798.

Chapter XXXIII

PHOTOGRAPHIC PROCESSES INVOLVING THE DYEING OF GELATIN

621. Dyeing of gelatin

Organic dyes are either *acid* or *basic*. The acid dyes are anions (−) due to their sulphonic or carboxylic groups; they are attracted to the $NH_2(+)$ groups of the gelatin. The basic dyes are cations (+) because of their amino groups; they are attracted to the COOH (−) groups of the gelatin. In practice, the behaviour of dyes, particularly the azo dyes, depends on the predominance of the acid or basic groups. Their adsorption by gelatin can be considered as an electrostatic phenomenon.

The colour of dyed gelatin is not identical with that of the dye in solution. With acid dyes a bathochromic effect is produced and with the basic dyes a hypsochromic effect is produced. The absorption bands are shifted about 20 $m\mu$ due to the topographical modification of the electrical charges in the dye molecule. The conjugated double bonds can be destroyed, and a second absorption maximum can appear.(1) If the sulphonic groups are symmetrically placed the colour does not change.

In the study of the behaviour of a soluble dye towards gelatin, one must make a distinction between the two cases:

1. The gelatin is not hardened.
2. The gelatin is hardened (photographic image).

The action of the dyes can then be divided up in the following way:

(*a*) The dye stains in a permanent manner only unhardened gelatin. *It differentiates between the two gelatins.*

(*b*) The dye stains in a permanent manner both unhardened and hardened gelatin.

(*c*) The dye does not stain gelatin permanently. By simple washing it diffuses rapidly out in water.

In general, *the adsorption of a dye depends on the pH.* Usually, dyeing is carried out in acid medium for acid dyes or in alkaline medium for the basic dyes; but in the special cases which we shall be dealing with, the opposite conditions are used. It is notable *that no dye becomes attached exclusively to hardened gelatin.* It is therefore necessary to incorporate a mordant. We then come into the technique of *dyeing by mordanting* (para. 580) in which a basic dye does not dye the gelatin in acid medium but becomes attached to the mordant.

A. Dyes which only stain unhardened gelatin, leaving the hardened gelatin perfectly clear. Among those which the author has used, the most interesting are:

Heliogen soluble blue, induline B, benzo fast blue BN, benzochrome blue black, acid violet.

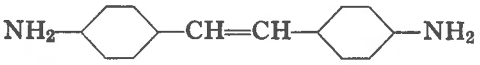
Dianil red, Congo red.

Thiazol yellow, primuline yellow, chromiun G.S.

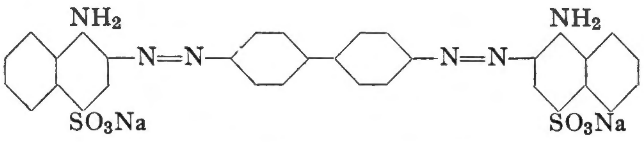
In all these cases, *dyeing must be carried out in a basic medium,* for in acid medium either the action is general and there is no differentiation or the dye precipitates.

Other dyes for unhardened gelatin exclusively, belong to the class of *substantive dyes.* The substantive dyes have the property of dyeing cotton directly without prior mordanting in tannin. The fundamental reason of this affinity for cotton (and also for gelatin) is not at the moment clear. However, we know that a large number of substantive dyes are disazo dyes containing certain diamine nuclei such as *benzidine* or *diaminostilbene* and their derivatives, or even *diaminodiphenylamine* and *diaminodiphenylthiourea.*

benzidine



diaminostilbene



Substantive disazo dye (Congo Red)

Among these dyes the principle ones are:(1b)

Diamine blue, direct sky blue (St. D), dianil blue, Chicago blue.

Congo red, Corinth Congo (By), diamine scarlet, benzopurpurine (By), Hesse purple, anthracene red (By), direct pink (St. D), direct red (St. D).

Chrysophenine G (By), direct chrysophenine J (St. D.), brilliant yellow (By), chloramine yellow (St. D.), curcumin S, Mikado golden yellow (By & L), Mikado orange (By & L), direct golden yellow (St. D), direct orange (St. D).

The substantivity is also conferred by introducing into the azo dye molecule, *J acid* (2:5-aminonaphthol-7-sulphonic acid) or one of its derivatives. In this way rosanthrene O (Ciba), benzo fast scarlet (By), and various oranges are obtained.

B. Dyes staining gelatin in the general way. Among the many dyes which stain the gelatin, with no pronounced discrimination between the hardened and unhardened regions, we would note:

In acid solution:

Neutral wool blue R, Azura blue II, soluble blue C6B, acid brilliant blue VS.

Soluble nigrosine (purplish black)

Toluidine green, naphthol green

Xylidine ponceau, wool scarlet, naphthionic red A, acetophenylene red J.

Naphthol orange, orange II, metanil yellow, aurophenine.

In alkaline solution:

Toluidine blue, methylene blue, methyl violet, ethyl violet

Erythrosine, eosine

Phosphine.

In neutral solution:

Acridine orange, acridine yellow, benzoflavine.

A mixture of dyes which rapidly stains hardened gelatin protective leader films to an *intense black*, is made up according to the author of:

Neutral wool blue R (St D.)	5 g
Naphthol green	5 g
Naphthionic red A (St. D)	6·2 g
Metanil yellow N extra	0·5 g
Acetic acid	100 cc
Water	1000 cc

C. Diffusing Dyes. A large number of dyes stain gelatin and bleed more or less rapidly when they are immersed in water. The best known and most widely used is *tartrazine* which has no resistance to washing. We know that tartrazine is used to limit the penetration of light in photographic emulsion layers. *New coccine* and *Pure yellow F4G* also are suitable. The other normal yellow dyes are more difficult to eliminate completely although they do diffuse: acid yellow SS, chrysoine, flavine, naphthol yellow S, pyrazole yellow, quinoline yellow, orange I. In addition we have already seen that the *basic dyes* in acid solution do not dye gelatin permanently: auramine, fuchsine, rhodamine, safranine, Nile blue, methylene blue, etc.

622. Applications of selected dyeing of unhardened gelatin

Selective adsorption of dyes by unhardened gelatin was once used for the manufacture of coloured reseaus or mosaics for additive colour reproduction.

An old *two-colour motion picture* process called Kodachrome (1923) used a dupletized positive film in which the two images printed on either side of the support were hardened in a dichromate-bromide ferricyanide solution then dyed using blue and orange-red dyes respectively which dye the unhardened gelatin.

More recently the adsorption of acid dyes has been used in *three-colour cinematography*: the green and red separation images are printed on a double-coated film, mordanted and dyed magenta and cyan respectively, with basic dyes. One of the two sides of the film is resensitized with dichromate and dried. The blue separation *positive* is printed in this dichromated layer using a high intensity source. The film is washed and bathed in a yellow acid dyestuff which, by remaining in the unexposed parts, provides a yellow image.

The dyes used must not react between themselves, for it frequently happens that the acid dye could precipitate itself on the basic dye used in the earlier stage. Furthermore the basic dyes must not be destroyed by the dichromate. Lessertisseux(2) has disclosed as suitable basic blues, *Capri blue* (tetramethylbenzotoluoxazine hydrochloride) and Rhoduline 5B (MLB) and, as yellow dyes which can be used with these blues, Hoechst yellow F (azo dye from sulphoxylidine and methylphenylpyrazolone), Mikado golden yellow, and thiazole yellow (azo dye from dehydrothiotoluidine). If the acid dye is a magenta one, *pinatype red R* (MLB) can be used. The other side of the film which must only have a magenta image, can be dyed with *rhodamine S* (tetramethyl-m-aminophenol succinate).

The *Chimicolor process* perfected by Didier and Valette was similar to the one we have just described. The separation negatives were obtained with a special camera using several films. Two separation negatives and one positive were needed for printing.

623. Dyed reliefs

In principle, obtaining coloured gelatin reliefs is simpler than selective dyeing of gelatin layers containing areas which are tanned and areas which are not tanned. The soft gelatin is in this case completely eliminated by stripping. There is no problem of differentiation.

There are two ways of obtaining coloured reliefs.

(*a*) The gelatin is already coloured with a substantive dye or a pigment; the formation of the image and stripping being carried out later.

(*b*) The hardened gelatin relief is obtained first then it is dyed with a solution of the dye.

Coloured images by forming reliefs in coloured gelatin layers. We have already seen that in the *carbon process* (para. 608) a layer of pigmented gelatin is sensitized with dichromate, exposed, 'developed' in hot water and transferred to a final support. Three images, coloured respectively yellow, cyan and magenta, obtained in this way can be superimposed to give an image in full colour. The gelatin is coloured either with an insoluble pigment precipitated in the gelatin (azo or vat dye) or with substantive dyes which have been listed above.

The old German *Duxochrome* process, known today as *Duxocolor*, used three emulsions dyed respectively cyan, magenta and yellow, coated on temporary film supports. Each film was exposed through the base, developed in a tanning developer, stripped in hot water and the silver image removed in a reducer before transferring to a single final support.

The formulas given for these three dyed emulsion films(3) included respectively the following dyes: chlorantine clear yellow, diphenyl yellow, and chlorantine green—brilliant violet 5R—direct clear blue and diphenyl blue-green. New coccine and pure yellow F4G, which are easily removed, were added to limit the penetration of light. *Duxocolor* films are, now, colour sensitized, so that prints can be made with negatives in complementary colours.

If the pigments are insoluble in acetone the cellulose support can simply be dissolved in a solvent after the transfer paper is applied, using a little gelatin. An ordinary positive film is used by first dyeing it with three solutions of substantive dyes.

The preparation of reliefs in pigmented layers has been experimented by the writer for three-colour cinematography: the raw positive stock had on one side a special emulsion made with a hard colloid and on the other side two superimposed emulsion layers. The lower emulsion was also made with a mixture of very hard special colloid whilst the outer emulsion was made with a soft gelatin. An insoluble yellow organic pigment was used in the latter.

The red separation negative was printed on the rear emulsion and the green was printed with red light on the lower emulsion on the other side. The blue separation positive was then printed on the upper yellow dyed emulsion.

The three images were simultaneously developed in a magenta colour forming developer. The double layer was exposed to light and treated with a tanning developer whilst the rear face was toned cyan with iron. The film was then treated in an acid stop bath, washed, bleached to remove the silver from the double layer, fixed and again washed. At this stage, it contained a cyan image on the rear face, mixed with an unwanted magenta image, and on the other side a magenta image covered with a layer of magenta and yellow gelatin. By treating in warm water the gelatin layer was superficially stripped leaving a yellow relief: the reversal in the tanning developer hardened the internal part of the layer which, in this way, remained on the film. Processing was completed by applying a bleaching agent to the blue-toned side which destroyed the unwanted magenta image, the bleaching compound then being neutralized by a stop bath before the final wash.

Colour images by dyeing reliefs. Three gelatin relief images on temporary supports which can be dyed cyan, magenta and yellow, respectively, using acid dyes, preferably substantive ones (see para. 621), are then transferred on to paper. The single images must be printed through the base if ordinary films, which have not been specially prepared for transfer, are used. In this case, after applying to the paper (which is gelatin coated), the support is dissolved in acetone. Special films sold commercially for the preparation of silk screen or Flexichrome prints can be used for normal transfer processes. When using Flexichrome film, the image can be stripped as described below.

624. The Flexichrome process

The Kodak Flexichrome process is not a process for reproducing colours but a process of *colouring* prints according to the tastes of the operator. When used in skilled hands it can give pleasant and commercial results.

The image to be reproduced is printed on film with a stripping layer, the exposure being made through the base. Development is in a tanning developer. It is then hot-water 'developed' (40°C) (140°F) and the silver is removed by bleaching and fixing in hypo, to remove the remaining silver bromide also. The gelatin relief obtained in this way is colourless. To make the image visible, it is treated after washing in a solution of black dye called 'modeller' and the excess drained off. The image-bearing layer is then stripped off with acidified warm water and the image is transferred on to a Dye Transfer type gelatin-coated paper. All that remains is to colour the relief.

The dyes in acid solution are successively applied uniformly with a brush. The excess is removed with blotting paper, then by rinsing in an acid solution. The contours are controlled by the relief itself which prevents the appearance of smudges. The large areas are coloured first and the small details are left until the end. One dye can easily replace another, which indicates that they are not substantive but, on the contrary, diffusible.

Flexichrome images can be transferred by imbibition (para. 627).

625. Principles of imbibition transfer

The gelatin relief, dyed with a soluble dye and still wet, placed in contact with another gelatin layer transfers part of its dye quickly forming an image. This method of printing was disclosed by E. Sanger-Shepperd and O. Bartlett in 1902.(4)

Imbibition transfer can be divided into two phases: preparation of the dyed relief matrix and transfer of the dye.

Relief matrices. An imbibition matrix is a gelatin relief obtained either by dichromate sensitization, tanning development, tanning bleaching, or finally by softening with hydrogen peroxide.

The gelatin forming the relief is generally *hardened*. This hardening increases the firmness of the latter which enables the two films to be readily separated after transfer and gives sharper images. It reduces the swelling of the gelatin. If it is not hardened, as with etching in hydrogen peroxide, the layer is hardened by a few minutes' treatment in 4% alum. It is important to bear in mind that the *degree of hardening changes with the length of time the matrix has been stored*, which can give differences of behaviour in the dye bath.

The *dyeing* time depends on the maximum *thickness* of the relief. This can be kept at 12 μ.

The amount of dye absorbed is greater at the surface than deeper down, but the maximum concentration is reached slightly below the surface.(5) The concentration of dye in the dyed gelatin is, for example, 35 times as great as that in the bath; on drying it exceeds 200 times.

The amount of dye absorbed by the gelatin increases with the *concentration of the bath*. Normally the curve as a function of this concentration reaches a maximum and above a critical point it is useless to increase the concentration, as the basic groups of the gelatin become saturated. However, if *aggregates* of dye are formed inside the colloid (for example with Direct Pink) the curve of absorption of dye as a function of the solution concentration continues to rise.(6) Dyes which polymerize to give these aggregates must be avoided.

The pH of the bath, as we shall see, has an influence on the degree of dyeing. The amount of dye absorbed decreases with the pH if the dye is an acid one, and increases if it is basic. For dye transfer to take place, its absorption must be readily reversible depending on the pH at which it is incorporated. Thus Bromberg and Maltzeva have shown that a film dyed in a bath of basic dye at a concentration A at pH 11, then immersed in a bath of lower concentration B at a pH of 8, has its colour intensity reduced to half.

When a gelatin layer is placed in water, it swells. The *degree of swelling* depends on the temperature, the acidity and the time of immersion. The swelling enables the dye to penetrate more rapidly, but on the contrary, the adsorbed dye reduces it. Sheppard, Houck and Dittmar(7) have stated that the swelling and dyeing are two antagonistic phenomena. The degree of swelling i is represented by the weight of liquid absorbed by a gram of dry gelatin at time t. The limit of swelling is $i\infty$. If k is a constant which increases as the thickness increases, we have the following empirical relation(6) for a given temperature t:

$$k = \frac{i}{\sqrt{t}} \log \frac{i\infty}{i\infty - i}$$

We know that the limit of swelling $i\infty$ of a gelatin is at a minimum between the isoelectric point and pH 7. It is three times greater in very acid or very alkaline media.

After stripping, the gelatin of a matrix is very swollen. If it is left to dry, it will exude, by contracting, a little liquid degraded gelatin which may form detrimental streaks. Ives and Kunz(8) recommend that the swelling should be reduced by immersing in a saturated solution of *sodium sulphate*. It is, however, better to wash the stripped matrix in cold water, drain and dye immediately.

The shape of the absorption curves as a function of the various factors already given depends on the *molecular structure of the dye* and its tendency to form aggregates.

Dyes suitable for imbibition transfer. There are in the first place the substantive acid dyes which have already been listed (para. 621). Some of them are specially suitable:(9)

Diamine blue BB (C), Alizarine blue (By), Chicago blue.

Thiocarmine R, Benzo fast pink 2BL (By), Rubinol 3G (By), Rubinol alizarine R (By), 3-azabenzanthrones.

Sulpho yellow (By), Thioflavine S (C), Thiazola yellow (By) and pyrazolone dyes bearing, on the CH_2 of the nucleus, a sulphonated azo group (Kodak: F.P. 1,099,740, U.S. prior. 1953).

Among the basic dyes, methylene blue, fuchsine and thioflavine can be used, or Rhoduline blue (By), Rhoduline red B (By), Capri blue GON (L) and Pyranine G (L).

Dyestuff concentration. 1%+0·1% acetic acid for the acid dyes. With the basic dyes, concentration can be as low as 0·015% but the concentration is not necessarily the same for each of the three images. Rinse after dyeing.

To study the penetration of the dye in the gelatin, the technique of Jelley and Pontius(5) can be used. This is to stop the diffusion by immediate freezing in solid carbon dioxide dissolved in alcohol. The layer is then dehydrated at −5°C in a current of dry nitrogen and is then cut in a microtome. Slices 5 μ thick are measured with a microdensitometer. To avoid local exhaustion of the dye at the gelatin surface, the solution is continuously agitated by using a rotating brush.

626. The transfer operation

The transfer layer can be made of *soft gelatin* or of gelatin containing a *mordant* which can increase the rate of dye diffusion: alumina, cuprous thiocyanate, lead or copper ferrocyanide, etc.

If the *thickness of the transfer layer* is equal to that of the matrix, and if the gelatins are of the same type, transfer of dye stops when the dye concentration in the matrix has dropped to 50%. During transfer, the amount of dye transferred is proportional to $\sqrt{t}$ where t is the time.

The transfer is carried out, after *wetting* the relief (if it has been dried), on to a transfer layer which has also been wetted. The wetting time must be sufficient to give a convenient transfer time, without unduly extending the course of the diffusion.

The *contact time* necessary for transfer is a function of the *dye density* of the matrix and of the *temperature*:(10) an increase of 20°C increases the rate by 2·2. An increase of pH from 3 to 8 only slightly increases the rate.

The *diffusion of the dye* from the matrix towards the gelatin layer, does not only take place in a *perpendicular* direction. In practice there is always, at the same time, a *lateral diffusion* (bleeding) which results in a loss of definition. Chmutov and Bromberg(11) have shown that the lateral diffusion is due to the following factors:

(*a*) Transfer time too long.

(*b*) Tendency of the dye to polymerize.

(*c*) *Contact pressure* insufficient to remove the water film present between the matrix and the transfer layer.

(*d*) Excessive drying of the print at too high a temperature.

To this must be added the unequal *expansion* of the two bases.

627. Colour prints on paper by imbibition

The first stage for obtaining colour prints on paper by imbibition is to prepare three gelatin reliefs on film. Three separation positives on three films having positive emulsions are printed. Exposure must be made through the base (which must not have an anti-halo coating). Development is carried out in a tanning developer or in a normal developer followed by a tanning bleach (see Chapter XXXII). In each case a stop bath is used. The three reliefs are obtained by stripping in warm water. They are dyed cyan, magenta and yellow respectively by immersing in dye solutions containing acetic acid and a little formalin. The dye concentration must be such that the dyeing time does not exceed 30 minutes. The three films are rinsed in running water or in a 0·5% solution of acetic acid. They can be checked by superimposing them.

The transfer paper, a fixed photographic paper, has a plain gelatin layer which is impregnated with a mordant using the following solution:

A	Aluminium sulphate	200 g
	Water	1000 cc
B	Sodium carbonate	40 g
	Water	500 cc

(Pour B into A; the resulting precipitate redissolves with agitation.)

After 5 minutes' wash, the paper is treated for 5 minutes in 5% sodium acetate and again washed in running water. The paper can be dried and kept.

To transfer the dyes on to the paper, the latter is wetted by bathing in water and the three matrices, kept in a solution of 0·5% acetic acid, are successively applied under pressure for 10–30 minutes. The order used is magenta, cyan and yellow. In order to facilitate registration of the two latter images on to the first, a very thin sheet of damp cellulose acetate is placed between the matrix and the paper with the exception of a margin by which the matrix and paper can be held together. Once the correct register has been achieved by sliding on the cellulose sheet, the latter is carefully withdrawn. The matrix, which is held firmly, drops on to the paper. In each transfer operation, the dye is literally sucked up by the paper gelatin.

Dye Transfer Process. The Kodak Dye Transfer Process, which is based on the Wash-off Relief process, is similar to that given above, using thin base Matrix film which is developed in a tanning developer. The reliefs are dyed without removing the silver image. Transfer is carried out on to a mordanted paper. Each sheet of Matrix film is perforated to facilitate registration on the pneumatic register board. The most critical part of the process is to determine the exposure time for the three films.

The Dye Transfer process enables a colour print on paper to be made in 1½ hours, excluding drying.

Pan Chroma Relief Film (Defender) has a thin panchromatic emulsion which is dyed grey to restrict penetration of light. It is used either to separate negatives (from colour transparencies) which are reversed in a *hydrogen peroxide* bath, or positives (from colour negatives) by printing through the base, tanning proportionally to the developed image and stripping in warm water.

The reliefs obtained in this way are treated in dye solutions (containing citric acid to increase the contrast), cleared in water, acidified in acetic acid, then transferred on to paper (mordanted with a mixture of aluminium sulphate and sodium carbonate) which is temporarily stuck to glass. The magenta, cyan and yellow images are transferred successively (time 5 minutes for each transfer).

Taylor⁽¹²⁾ had already, in 1923, disclosed softening with hydrogen peroxide (para. 596) for the preparation of imbibition transfer matrices.

Combination of carbro and imbibition. Legge⁽¹³⁾ perfected in 1947 a combination of carbro and imbibition using the Autotype papers. *The magenta and yellow matrices were made on 'Dyebro grey' paper* by the carbro process (see para. 609) and were stripped after transfer on to celluloid. They were impregnated with dyes which were transferred on to 'Autotype 214' which had been already mordanted. A cyan pigment image obtained by the carbro process on 'Autotype Monastral Carbro' paper was finally superimposed on the imbibition images to complete the three-colour system.

Transfer of Flexichrome images. Landau⁽¹⁴⁾ perfected the imbibition transfer of coloured images obtained by the Flexichrome process (para. 624) which enables a single matrix to be used for the preparation of several prints. The original image must be laterally reversed, for the transfer operation itself reverses laterally. After colouring, transfer is carried out on to alum-treated gel-coated paper previously bathed for 10 minutes in a solution containing 1% ammonium acetate and 8% anhydrous sodium sulphate. Transfer time 10 minutes followed by a wash in 5% acetic acid and drying.

A matrix whose gelatin surface is freed from residual salts by wetting with 2% acetic acid is again dyed black and coloured for use in a second transfer.

628. Colour films by imbibition

Three gelatin relief matrices corresponding to the three primary positives, impregnated with cyan, magenta and yellow dyes, by successive transfer on to wet gelatin-coated film give three-colour prints. The loss of contrast in prints used for projection generally requires a *compensating grey image* which is printed and developed at the same time as the sound track on the emulsion layer of the transfer film. This grey image can be printed from a green separation negative but it is better to use a duplicate negative corresponding to the combined separations (by successive printing on the same film).

The grey printer and the sound track can also be printed on to gelatin sensitized with a photosensitive mixture. For example, ammonium ferrioxalate developed after exposure with ferricyanide gives cyan images⁽¹⁵⁾ which can be blackened (para. 399).

Miller has shown that the grey gamma for imbibition processes only increases very slowly up to D = 1 which results in a loss of detail in the shadows. In addition the absence of a straight line in the low densities causes a loss of highlight detail.

Where there is undesirable transmission of the extreme red by the cyan dye, this can be corrected by adding a brownish green dye to the yellow dye, the yellow and the brownish green diffusing from the matrix to the gelatin at different rates in the shadows and the highlights.(16)

Printing the film. The precise register of the three images on wet film has presented difficult problems, for transfer is not instantaneous, taking about 3 minutes during which time the two films must be kept in perfect register. Printing can be carried out on a large drum, or a chain of small moving metallic blocks or, better, on a long steel band carrying a series of register pins on which the two films are kept during the course of transfer. The latter system is used by the *Technicolor* Company. The matrix film and the transfer film are married under water, the excess being squeezed out.(17) The pressure can be regulated using an auxiliary endless belt applied against the main belt on half the circumference of one of the marrying drums.(18) Three machines in series can have an output of 100 feet per minute.

We have already given (para. 626) the factors which can result in image diffusion and loss of resolving power.

Imbibition printing has certain advantages in spite of its complexity: very transparent images, use of simple types of film and daylight operation.

Production of matrices. Two methods have been used by *Technicolor* for the manufacture of matrix films.

(*a*) Each separation negative is optically printed through the base on to an ortho film whose emulsion is dyed orange to restrict light penetration. Contrast is controlled by inserting blue filters of varying density. The reliefs are obtained by tanning development and stripping in warm water without dissolving the residual silver bromide.(19)

(*b*) An original colour negative of the Eastman Color type is directly and successively printed on to three 'Tricolor Matrix' films which are respectively sensitive to blue, green and red. The contrast of the matrices is controlled by preliminary uniform fogging through the base using colour filters.(20)

The Tricolour Matrix film can only print 30 copies whilst a normal matrix can give double this number.

Negative making. The negatives are made with a special camera using three separate films (para. 502) or on tripack film developed in complementary colours by colour development (para. 514) such as Eastman Color and Ansco Color films. The first method is definitely superior to the second.

Starting from a colour negative, three separation positives are made which in turn provide three duplicate negatives. Alternatively the original negative is directly printed on to Tricolor Matrix film.

Registration defects are corrected in the optical printer by rotating a glass plate on its horizontal and vertical axes.

629. Pinatype

Pinatype is a process of imbibition transfer of dyes by means of a gelatin layer having a tanned image but *not stripped*. It is based on the differences of permeability and affinity for dyes of the two types of gelatin. Pinatype preceded Uvatype (transfer using reliefs): suggested in 1875 by E. Edwards, it was used in practice by L. Didier at the beginning of this century and then, abandoned in favour of the relief method, as the Pinatype matrices lose their permeability after a certain number of transfers and give less sharp images than those using reliefs.

A gelatin film sensitized with dichromate, exposed through the base from a positive, is washed then dyed for 15–30 minutes in a solution of 2–5% acid dye to which a few cc of ammonia is finally added. After rinsing, the matrix is applied in water to a gelatin-coated paper. The combination is removed and left for 15 minutes (more or less depending on the nature of the dye). The rate of diffusion depends on the temperature. After transfer of the cyan, magenta and yellow images, the dyes are precipitated with a solution of 2% copper sulphate containing 2% chrome alum. The print is finally washed for 5 minutes and dried.

The time of the first dyeing is always longer than the subsequent ones.

The dyes used for Pinatype are similar to those used for ordinary transfer: Diamine pure blue, Induline blue, Benzo pure blue GG, Lanafuchsine 6B, natural carmine, natural cochineal, Mikado yellow, thiazole yellow, thioflavine T, quinoline yellow and the benzidine disazo dyes containing 1:8-amino-naphthol-3:6-disulphonic acid.

630. Transfer of mordants or colour couplers

In principle, it is possible to transfer to a gelatin layer from a relief matrix any compound capable of becoming attached to the gelatin or becoming insoluble. The rate of transfer is greater as the molecular weight of the compound is lower. The process is always limited by image diffusion.

A transfer of *copper salts* into gelatin impregnated with ferrocyanide, of *dichromate* into gelatin containing sulphite, of *oxidizing agents* on to a layer containing leuco bases or *couplers* on to diazonium compounds have been suggested.(21) It is preferable to transfer metallic salts on to a layer containing *lead ferrocyanide* with formation of the corresponding insoluble ferrocyanide: an iron salt gives a cyan image, a titanic salt a yellow image, etc.

Twenty years ago, the *Brewstercolor Process*(22) used the transfer of a copper salt which was then converted to *cuprous iodide*—an excellent mordant for dyes.

The most interesting proposal is the rapid *printing of dyes in alcoholic solution* on to a collodian layer, using an alcohol permeable matrix (Menzel and Forstmann).(23)

---

1. Weidenbach V. A. and Karpovich E. A.: *Zh. prikl. Khimii*, 1948, 414–420; *Sci. et Ind. Phot.*, 1949, 380.

1b. By = Bayer; St.D = St. Denis; L = Leonhardt.

2. U.S.P. 2,008,457; M.L.B. = Meister Lucius and Bruning.

3. *FIAT Final Report No.* 897, *Aug.* 1946, 50 pages, H.M. Stationary Office London, and G.P. 626,682 (1929) and *Sci. Ind. Phot.*, 1949, 470.

4. F.P. 728,310. See also C. Sciamengo: U.S.P. 1,036,730 (1912); Wykoff and Handschlegl: U.S.P. 1,303,836 and 1,303,837 (1919); Handschegl: U.S.P. 1,316,791 and 1,295,028 (1919); Robert John: U.S.P. 1,374,853 and 1,453,258 (1921 and 1923); Donisthrope: U.S.P. 1,517,200 (1924); Kelley: U.S.P. 1,505,787 (1924); Taylor: U.S.P. 1,518,945 and 946 (1924).
5. Jelley E. E. and Pontius R. B.: *R.P.S. Cent. Conf. London*, 1953; *Sci. et Ind. Phot.*, 1953, 361.
6. Bromberg A. V. and Maltzeva O. S.: *Zh. Prikl Khimii*, 1947, 422–430, 539–547, 549–557; *Sci. et Ind. Phot.*, 1949, 232.
7. *Sci. et Ind. Phot.*, **17**, 104.
8. Ives C. E. and Kunz C. J.: *Amer. Phot.*, 1950, 60, 71.
9. (By) = Bayer; (L) = Leonhardt.
10. Bromberg A. V. and Maltzeva O. S.: *Zh. Prikl Khimii*, 1947, 422–430, 539–547, 549–557; *Sci. et Ind. Phot.*, 1949, 232.
11. Chmutov K. V. and Bromberg A. V.: *Zh. Prikl Khimii*, 1949, 261–271; *Sci. et Ind. Phot.*, 1950, 147.
12. U.S.P. 1,560,437, 1,560,438 (1923).
13. Legge C. N.: *Brit. Jour. Phot.*, 1947, 251.
14. Landau R.: *Sci. et Ind. Phot.*, 1951, 238.
15. Coote J. H.: *Brit. Kin.*, 1950, 83.
16. Technicolor: B.P. 550,688 (1941).
17. Technicolor: U.S.P. 1,661,157 (1923); 1,675,743 (1927); F.P. 647,328 (1927); 836,040 and C.A. 52,358 (1941).
18. Technicolor: F.P. C.A. 52,442 (1942).
19. Technicolor: F.P. 823,868 (1937).
20. Technicolor: B.P. 547,216; Ashton G.: *Brit. Jour. Phot.*, 1953 (Sept.).
21. Leyde E.: G.P. 745,850 (1942).
22. U.S.P. 2,070,222 and B.P. 449,678, 449,679, 449,749, 449,750. The separation negatives were obtained using a three strip camera and a system of rotating mirrors behind the lens.
23. G.P. 433,124 (1925).

Chapter XXXIV

PHOTOCHEMICAL DESTRUCTION AND FORMATION OF DYES

PHOTOCHEMICAL DESTRUCTION OF DYES

631. General considerations

It has been known from time immemorial that colours obtained with dyes fade in light. Although Herschel observed in 1842 that it was the absorbed radiations which brought about this destruction, it is to Cros that the credit must go for clearly showing, in 1881, the process for obtaining colour images by *decolorizing* a mixture of three dyes, cyan, magenta and yellow.

This bleaching is due to direct light action without an intermediate silver image. The red light, absorbed solely by the blue dye destroys it; green light, absorbed by the magenta dye destroys only this dye, and the blue light, absorbed by the yellow destroys the yellow dye.

The first attempts to produce a commercial paper decolorized by light were by H. J. Smith and W. Merkens in 1906 then 1910, under the names *Uto* and *Utocolor*. The low sensitivity to light, the instability after fixing, and the lack of neutrality in the greys due to different bleaching rates of each component, led to the process being abandoned. The study was taken up by G. Koegel,⁽¹⁾ M. Mudrovcic,⁽²⁾ E. Waltman,⁽³⁾ J. Eggert, B. Wendt, H. Binger, and A. Frölich of Agfa, and particularly by A. Polgar and C. Halmos.

It should however be emphasized that the photochemical destruction of dyes has at present only a theoretical and experimental interest. The results of all the attempts at practical realization have been deceptive. We consider, however, that the field of study which is in this way opened is so fascinating that the wide treatment which it will have in this chapter is merited.

632. The support colloid

The first attempts to make colour images by photochemical destruction of dyes, used *collodion* for the support or binder, almost exclusively, to avoid diffusion of the dyes during fixing and also because of the low water solubility of the sensitizers. Other cellulose esters could be used: *cellulose acetate* (40% acetyl), ethylcellulose, benzylcellulose, etc.

It is, however, better to use for the binder a hydrophilic colloid like *gelatin* or *polyvinyl alcohol.*(4) The latter is recommended when the pH is very low, $\leqslant 2$

Average gelatin concentration: 2–10%
Average polyvinylalcohol concentration: 10%
Average cellulose ester concentration: 5–10%.

633. The decolorizable dyes

Photochemical destruction of dyes is generally a *reduction or oxidation phenomenon*. The dyes must not be too sensitive or the fixed image will be unstable. This is why relatively stable substances are used, which are activated immediately prior to exposure, by a *sensitizer*.

The dyes which can be used in practice belong to the following groups:(4b) Diphenylmethane, triphenylmethane, phthaleins, azines, oxazines, thiazines, indulines, indoanilines, indigoids, cyanines, pyronines, azo-dyes. The latter form a separate group which will be considered later.

Blue Dyes

Capri blue
Nile blue
Victoria blue
Dianil blue, B, R, 4R
Methylene blue
Columbia blue
Cresyl blue 2BS
Meldola blue
Rosinduline blue
Direct blue 2B and 3B
Naphthylamine blue
Trypan blue
Chicago blue
Chicago blue 2R
Carbocyanines
Dicarbocyanines
Setoglaucine
Erioglaucine
Indigos

Magenta Dyes

Rosinduline 2B
Bluish safranines
Rhodamine B and 6G
Rhodamine S
Rosanilines
Fuchsine
Benzopurpurin 4B
Bluish eosin
Erythrosin
Bengal pink
Selenopyranine
Thiopyranine 6G
Isocyanines
Thiacarbocyanines
Selenacarbocyanines
α-hydroxyglutaconic dialdehdye dianil (HCl)
Thioindigos

Yellow Dyes

Auramine O and G
Fluorescein
Thiofluorescein
Naphthol yellow
Flavinduline O
Thioflavine T
Thioflavine S
Thiazol yellow
Resorcinol benzoins such as the hydrochloride of the methoxy or fluoborate derivative of the dimethyl ether
Euchrysin
Oxonium derivatives such as 3:6-dihydroxy-9-phenyl xanthonium
Thiacyanines

The respective proportions of each dye are adjusted so that the mixture has an approximately grey colour. Example: Capri blue 6 g + sulphopyranine G, 4 g + methoxyresorcinebenzoin 8 g per litre of solution. Safranine GG 1·5 g + flavinduline 0·15 g + indodicarbocyanine ethobromide 2·4 g.

Among the fugitive dyes, Niagara blue G (colour Index No. 502) and Victoria blue B (No. 729) are used in actinometry (*Jl. of Research. Bureau of Standards*, Sept. 1948, pp. 169–177). Diphenyl-10-10′-mesobenzodianthrene (a deep violet derivative of phenanthrene) can also be used; in a

1:10,000 solution it is bleached by the sun in a fraction of a second, by photo-oxidation (J. Sauvage, *Compt Rend. Ac. Sc. Paris*, 1947 (July) 247–249).

634. The sensitizers

If the decomposition of the dye by light is a *photoreduction* process, it is accelerated by readily oxidized substances (reducing agents): in fact Victoria violet, eosin, erythrosin and chlorophyll are rapidly bleached in the presence of *linoleic acid*, *oleic acid* or *ergosterol*. The reduction of methyl red in the presence of *phenylhydrazine* is catalyzed by chlorophyll. Methylene blue and uranine for example are decolorized in glycerin to give the leuco derivatives.

The dye behaves as a hydrogen acceptor. It is active in the presence of light when the molecule contains at least one —CH= or $>$C= linked to a salt-forming group or an atom of nitrogen, oxygen, sulphur or selenium. This is the case with auramine, rosaniline, fluorescein, etc. The linking of two nitrogen atoms slows down bleaching.

The active sensitizers contain either a —CH=CHR group as in *anethole* or a $>$C=S group as in *thiosinamine*. Phenyl isocyanate containing the group $>$C=O is, on the contrary, inactive.

$CH_3O—C_6H_4—CH=CH—CH_3$ anethole

$NH_2—CS—NH—CH_2—CH=CH_2$ thiosinamine

$C_6H_5—N=C=O$ phenyl isocyanate

Anethole and *thiosinamine* are the most active sensitizers known. Thiosinamine is a derivative of *thiourea* $NH_2—CS—NH_2$ in which one H is replaced by an allyl, $CH_2=CH—CH_2—$ radical. It is therefore *allylthiourea*.

The most active allylthiourea is *diethylallylthiourea* $(C_2H_5)_2N—CS—$ $—NH—CH_2—CH=CH_2$. It can be said in fact that the reducing action develops when the two hydrogens attached to nitrogen opposing an allyl group are blocked by alkyl groups. Only the last free hydrogen is used to reduce the dye in the photochemical reaction.

Unfortunately the solubility of the substituted thioureas is greatly reduced, which prohibits their use in gelatin. Polgar and Halmos⁽⁵⁾ restored their solubility in water by introducing *hydroxyl groups* OH into the alkyl groups. The general formula of these new compounds is

$$R_1R_2 : N—CS—NH—CH=CHR$$

in which at least one of the groups R_1 and R_2 contains OH. Examples:

N-β-hydroxyethyl-N′-allylthiourea
$OH—C_2H_4—NH—CS—NH—CH_2—CH=CH_2$

N-diβ-hydroxyethyl-N″-allylthiourea
$(OH)_2—C_2H_3—NH—CS—NH—CH_2—CH=CH_2$

N-bis(β-γ-dihydroxypropyl)-N′-allylthiourea

$[(OH)_2C_3H_5]_2—N—CS—NH—CH_2—CH{=}CH_2$

N-lactyl-N′-cinnamylthiourea

$OH . CO . CH_2—NH—CS—NH—CH_2—CH{=}CH—C_6H_5$

These compounds are prepared by reacting allyl isothiocyanate (for example) with an aminoalcohol or a hydroxyalkyl hydrazine. The reaction is spontaneous with the evolution of heat.

Among the other ureas which have been used experimentally are diphenylthiourea, α-naphthylthiourea, β-naphthylthiourea, β-dinaphthylallylthiourea, methylene thiourea, diallylurea, phenylurea, and phenylallylthiourea.

Other sensitizers are: the *thiosemicarbazides*(6) such as allylthiosemicarbazide $NH_2—NH—CS—NH—CH_2—CH{=}CH_2$, phenylallylthiosemicarbazide, β-naphthylallylthiosemicarbazide, *piperonal* derivatives, *oximes* such as benzaldoxime and campheroxime, etc. E. Waltman disclosed *p-methoxypropenylbenzene*. Also note *formaldehyde sulphoxylate* and *neosalvarsan*. The derivatives of guanidine, glyoxal, acrolein and formamidine have a weak action or none at all.

635. Ternary and binary systems

A strongly polarized substance like *zinc oxide* activates the photochemical transformation of many substances, particularly the dyes. The (+) and (−) charges of ZnO respectively promote a simultaneous oxidation and reduction. It is sufficient to mix zinc oxide with an oxidizable compound and a reducible compound, example the *ternary system*:

$$ZnO \begin{cases} +\textit{glucose} \rightarrow \text{oxidation produce} \\ \\ -\textit{methylene blue} \rightarrow \text{colourless leuco base} \end{cases}$$

Zinc oxide also reduces many dyes: malachite green, Nile blue, phenosafranine, indigo, thioindigo, coeruleine, pseudopurpurine, etc. Glucose can be replaced in various cases by citric acid, glycocoll, benzidine. Under the same conditions the azo dyes give colourless amines.

Certain dyes activate the decolorizing of other dyes, following a *binary system*: thus the triphenyl methanes behave in this way towards the safranines; eosin and naphthol yellow towards the acid dyes. The bleaching of pinachrome and pinacyanol is accelerated by methylene blue. Mudrovcic noticed that 4 drops of a 1:10,000 solution of methylene blue in 2 cc of a 1:10,000 solution of pinaverdol reduces the bleaching time from 2 hours to 2 minutes. Bleaching is retarded by pinakryptol green.

636. Concentration of sensitizer

When a mixture of dyes is exposed to light, it can be said that the rate of bleaching is not the same for each component. This results in an incorrect reproduction of the colours of the original. Rust and Polgar(7) studying the variation of bleaching time with concentration of sensitizer, stated that there is frequently a point of optimum concentration where the photochemical destruction of the three constituents has practically the same value (Fig. 113).

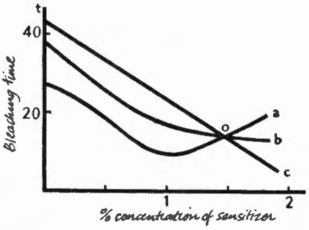


FIG. 113. Simultaneous decoloration with allylthiourea sensitizer.

637. Stabilization

A mixture of dyes, sensitized and spread on paper in the presence of a colloidal binder, will not keep indefinitely. After a time, fog is formed which is not destroyed by light. It also happens in some cases that the image produced by photochemical bleaching regains its colour.

These secondary reactions are inhibited by the presence of compounds having the general structure R^2R^3—N—CY—R^1 or R^3N—CY—R^1—R^2 where Y is O, S, Se or Te and R^1 and R^3 monovalent groups;(8) these compounds include the amides, the carbamides, the thiocarbamides, the amidines, the iminoethers, the hydrazides, etc. Simple compounds such as *acetamide* CH_3—CO . NH_2 give a life of six months. One can also use *chloracetamide*, *oxamide succinimide*, *ethylamidine hydrochloride*, *propionyl hydrazide*, *imidazole hydrochloride* or *diacetylimine*. About 10 g acetamide per gram of dye is used.

638. Fixing

The coloured layer, exposed to light under a colour positive gives, by bleaching, a positive copy which must be fixed. To fix, it is necessary on one hand to *remove the excess sensitizer and the reduction products*, and on the other *to make the dyes themselves less sensitive to light*. If perfect fixing is not possible, the colour picture must be kept in the dark and only taken out for examination.

Thiosinamine can be removed by washing in water. It is not so with diethylallylthiourea (diethylthiosinamine) which is insoluble in water. In this case it is necessary to treat the layer with mercuric chloride (poison) which forms a soluble complex with thiourea. For this, there must be an excess of thiourea in the fixing bath. The following procedure, for example, is suitable: first treat in 5% mercuric chloride acidified with 0·5% hydrochloric acid, then wash in a 5% solution of thiourea. The mercury salt can be incorporated in the layer.

For nitrocellulose layers sensitized with diethylallylthiourea, fixing is also carried out by exposure to *sulphur dioxide* vapour from a solution of sodium bisulphite.(9) On the surface of the layer oily droplets form due to the decomposition of the sensitizer, and these are removed with a wad of cotton soaked in light petrol.

Another method is to use *benzylcellulose* as the binder(10) and remove the sensitizer with a mixture of *benzene* and *anisole.*

With the water-soluble hydroxyalkylthioureas incorporated in gelatin, fixing by washing is easily performed.

After removal of the sensitizer, it is advisable to make the dyes more stable to light. For this, a bath of 20% tannin is used, in which the print is left for half an hour. It is better to precipitate the dyes with *complex metallic salts* such as the chlorostannates, the silicotungstates, the phosphotungstates(11) or the borofluorides.(12) At the same time as the dye, the residual thiourea is precipitated and made inactive. The following fixing solution is recommended:

Water	1000 cc
Silicotungstic acid	90 g
Ammonium chlorostannate	150 g

or failing that

Sodium borofluoride	120 g
Water	1000 cc

639. Examples of formulas of decolorizable coatings(13)

A	Water	700 cc
	Gelatin	10 g
	Capri blue	6 g
	Thiopyranine G (sulphate)	4 g
	Methoxyresorcinolbenzoin (chloride)	8 g
	N-diβ-hydroxyethyl-N′—allylthiourea	100 g
	N—β—hydroxyethyl—N′—allylthiourea	50 g
	Oxamide	75 g
B	Water	1000 cc
	Polyvinyl alcohol	75 g
	Basic dyes (mixture)	3·5 g
	Di-hydroxymethylallylthiourea	50 g
	Acetamide	50 g
	Sulphuric acid 50%	30 g
C	Cellulose acetate	30 g
	Acetone	200 g
	Methanol	50 g
	Cresyl brilliant blue	0·08 g
	Rhodamine S	0·05 g
	Thiofluorescein	0·10 g
	Oxalic acid	10 g
	Diethylallylthiourea	12 g
	Succinimide	10 g

Coat on paper and dry.

640. Bleaching by oxidation

Bleaching of dyes is frequently due only to atmospheric oxygen. The finer the state of division of the dye attached to the fibre, the easier it is to destroy it. Giles and Macaulay have recently made a study of this phenomenon(13b) and noted the influence of certain substituents in the dye molecule by their tendency to form sub-microscopic crystalline aggregates or mono-molecular layers.

The azo dyes are particularly prone to light fading in the presence of oxidizing agents. The destruction is irreversible. The best sensitizers are *hydrogen peroxide* and the *per-salts* in general. Sulphonated anthraquinones have also been disclosed (in acid solution): they are later eliminated by a solvent.(13c)

Reducing agents stabilize them to light: these include the ferrous salts and the ferrocyanides, the thiosulphates and arsenites. Stabilization can also be effected with copper salts which mordant the dye on the fibre. The dyestuff decomposition products also behave as stabilizers.

Many azo dyes are suitable. Seyewetz disclosed diamine pure blue 2B, rocelline (red) and chrysoidine (yellow). We would also mention the following compounds:

1-p-sulphobenzene-azo-N-phenyl-β-naphthylamine; diphenyl-4:4′-bis(1-azo-N-phenyl-β-naphthylamine); 2:2′-(4:4′-diphenyl)-bis-(3-phenyl-α-β-naphtho-1:2:3-triazolium nitrate); and neutral wool blue R, chrome blue R, acid amaranth, azorubine, chrysoine, direct brilliant yellow, metanil yellow and acid yellow SS.

The derivatives of N-alkyl-β-naphthylamine are more stable to light.

641. Decolorizable layers based on silver salts of organic dyes

G. Ungar(14) claimed to have obtained light decolorizable layers using silver salts of dyes. Here is the operating method which we reproduce without prejudice.

(*a*) A coloured gelatin-coated plate is immersed in a solution of 5% silver nitrate. The silver salt of the dye is precipitated in the colloid. The plate can then be washed in distilled water, then in running water for 10 mins. Sensitized for 20 mins. in 1·5% *hydrogen peroxide*, it gives images by exposure to sunlight. With *dianil blue* at a concentration of 0·1 g per sq. ft. or *anthracene yellow*, 0·4 g per sq. ft., bleaching is complete in 30 mins.

The silver produced by the photochemical decomposition must be removed in a reducer. The dye is then converted into another insoluble salt, with cupric chloride for example, which is more stable than the silver salt, and the silver chloride produced is removed with hypo.

(*b*) *A developable latent image* is produced using a coating prepared as follows: A solution of dyed gelatin is precipitated with an excess of silver nitrate. The emulsion is set and washed with distilled water and finally digested at 60–80°C for at least 30 mins. It is coated to give 0·1 to 0·2 g of dye per sq. ft.

With the *silver salt of eosin*, 3 seconds in sunlight is enough. With the silver salt of *anthracene blue* about 15 seconds is required.

The decomposition product of the silver salt, by the developer, is removed by washing. The silver-dye remaining is converted to the cupric compound with cupric chloride and the resulting silver chloride is fixed in hypo.

We would note that the following dyes are also precipitated as silver salts: fluoresceine, quinoline yellow, naphthol yellow, thiazol yellow, fast phosphine, erythrosin, congo red, rocelline, sulphonated thioindigo, sulphonated indigo, acid brilliant blue, Chicago blue, etc.

COLOUR IMAGES BY FORMATION OF AZO DYES FROM DIAZOSULPHONATES

642. The photochemical destruction of dyes is a selective phenomenon which enables direct multicolour images to be obtained. Each primary colour, blue, green, or red, acts on a separate substance which absorbs it.

This is not the case with the *photochemical formation of dyes*, for the starting point, here, is a colourless substance with no selective properties as required in three-colour work. *Independent monochromatic prints* must always be made by printing from the appropriate separation negatives, the monochromes then being assembled. Another method is to expose under the red negative a paper coated with a layer of photosensitive blue dye former; fix the blue image obtained in this way. Recoat with a magenta forming layer, expose under the green negative and fix the resulting magenta image, and then again coat with a photosensitive former, this time yellow, which is exposed under the blue negative. The final image is a three-colour one.

Amongst the oldest known substances which will produce colour images under the action of light, we would mention guaiacum which turns blue in sunlight.(146)

643. The azo dyes

An *aromatic amine* such as aniline $C_6H_5\text{—}NH_2$ treated with *nitrous acid* HNO_2 in the presence of hydrochloric acid forms a *diazonium compound*

$$\underset{\text{Aniline}}{C_6H_5\text{—}NH_2} + \underset{\text{Nitrous acid}}{HNO_2} + HCl \rightarrow \underset{\text{Benzene diazonium chloride}}{C_6H_5\text{—}N{=}N\text{—}Cl} + 2H_2O$$

characterized by the group —N=N—.

The *diazonium compounds* are generally unstable and must be prepared below 4°C.

The *diazonium compounds* have the remarkable property of combining with *phenols* ArOH or *amines* $ArNH_2$ to produce *azo dyestuffs*. The reaction, called coupling, is instantaneous. For example, the diazonium compound of toluidine $CH_3 . C_6H_4\text{—}NH_2$ is $CH_3 . C_6H_4\text{—}N{=}N\text{—}Cl$. Treated with phenol dissolved in caustic soda it gives hydroxybenzene-azo-toluene (sodium salt)

$$\underset{\text{Diazonium compound}}{CH_3 \,.\, C_6H_5—N{=}N—Cl} + \underset{\text{Sodium phenate}}{C_6H_5—ONa} \rightarrow \underset{\text{Azo dye}}{CH_3 \,.\, C_6H_4—N{=}N—C_6H_4—ONa} + HCl$$

which can be precipitated from solution with hydrochloric acid and recrystallized from alcohol as yellow-orange needles.

By double diazotization, the *tetrazonium* derivatives are obtained which give the *disazo dyes.*

The *mazo dyes from phenols and naphthols* are generally insoluble in water. Examples:

m-nitro-p-toluene-diazonium chloride+β-naphthol=magenta azo dye.

p-nitro-o-toluidine-diazonium chloride+β-naphthol=orange azo dye.

Diazotized dianisidine+2 $OH \,.\, C_{10}H_6—(NH \,.\, CO \,.\, C_6H_5)_3$=blue azo dye.

They are made soluble by sulphonation or by introducing a carboxyl group into the molecule. Thus *tropeolin O* is prepared from diazotized sulphanilic acid $SO_3H—C_6H_4—NH_2$ and resorcinal $C_6H_4{:}(OH)_2$; *alizarin yellow* results from coupling diazotized m-nitroaniline $NO_2—C_6H_4—N{=}N—Cl$ with salicylic acid $OH—C_6H_4—COOH$. *Anthracene yellow* is a combination of diazotized thioaniline and salicylic acid; similarly diazo compounds like those from xylidine couple with naphthol sulphonic acids to give the *ponceau reds.*

The *amino azo dyes* are more soluble than the phenolic ones. They are also less important. The best known in this group is *chrysoidine*, an orange-yellow basic dye from diazobenzene and m-phenylene diamine.

644. Diazosulphonates (or diazosulphites)

Diazonium compounds treated with *sodium sulphite* Na_2SO_3 form stable compounds (antidiazosulphonates) which have lost their property of coupling with phenols or amines.

$$R—C_6H_4—N{=}N—SO_3Na$$

According to Bamberger's nomenclature, confirmed by Hodgson, a diazosulphite is the isomeric, coloured and instable form (or *syn*diazosulphonate) of a stable *anti*diazosulphonate.

$$\underset{\textit{Syn}\text{diazosulphonate}}{C_6H_5—N{=}N—O—SO—OK} \xrightarrow[\text{water}]{} \underset{\textit{Anti}\text{diazosulphonate}}{C_6H_5—N{=}N—SO^2—OK}$$

Now the *diazosulphonates decompose in light to regenerate the diazonium compound* which is again able to combine with azo couplers. Feer had the idea in 1889(15) to use this property to obtain colour images photochemically. The process was taken up by A. and L. Lumière and A. Seyewetz(16) in 1896, then more recently by Schmidt and Neurod(17) and by R. Lantz and the 'Sté. des Mat. Col. de Saint Denis'.(18)

A *paper impregnated with a diazosulphonate* and exposed to light under a separation negative gives a *positive latent image.* This latent image is composed of the diazonium compound resulting from the photodecomposition of the diazosulphonate. Treated in an alkaline solution of a phenol, the exposed layer combines with the latter where the diazonium compound has been re-formed, to give an *azo dye.* The excess diazosulphonate is eliminated to give a monochrome image.

The coupler can be added directly to the diazosulphonate before coating on to paper. Under these conditions, the azo dye is formed as and when the diazonium compound is liberated by light. The appearance of the coloured image can therefore be watched during exposure, which is stopped at the right time.

The diazosulphonates are as sensitive to light as the normal diazonium compounds, but whilst the latter give a positive from a positive, the diazosulphonates give a positive starting from a negative. Their great disadvantage is that they do not keep in the coated state, which makes it necessary to print immediately after sensitizing, and above all, the difficulty, or even impossibility, of completely eliminating all excess, which prevents any practical application.

645. Preparation of the diazosulphonates

Fischer(19) and Haller(20) prepared the diazosulphonates by adding a *solution of sodium sulphite* to a diazonium salt and then precipitating the sulphonate with excess caustic soda. A purer product is obtained by *precipitating with salt.* Examples:(21)

17·8 g of chloro-4-amino-2-toluene is dissolved in 15 cc hydrochloric acid (S.G. 1·195) added to 150 cc water. It is cooled by adding 300 g crushed ice. When the temperature reaches 0°C, 7 g sodium nitrite in 50 cc water is added with stirring. The diazotized solution is then poured into 150 cc water containing 13 g anhydrous sodium sulphite and 6 g of sodium carbonate. After leaving for 1 hour, 12% salt is added. The diazosulphonate precipitates. It is filtered off, washed with a little cold water and dried. It can be purified by dissolving in a little water, filtering and again precipitating with salt.

Work the same way with 32·3 g of diethoxy-2:5-benzoylamino-4-aminoazobenzene, 25 cc HCl S.G. 1·16 (diluted to 300 cc) 100 g ice, 7 g nitrite, 13 g sulphite and 11 g carbonate (with 25 cc water and 50 g ice). In this operation the solution is heated to 65–70°C and precipitated with 50 g salt.

Not more than 2 mols. sulphite per molecule of amine should be used or there is risk of forming the hydrazine.

646. Colours obtained with diazosulphonates

Blue and blue-green images

Diazosulphonate	*Coupler*
Dianisidine (tetrazotized)	1:8-aminonaphthol
Dianisidine	3-benzamido-β-naphthol
4′-methoxy-4-aminodiphenylamine	2′-hydroxy-3′-naphthoylamino-benzene
do	2′-hydroxy-3′-naphthoylamino-1-naphthalene
do	2′-hydroxy-3′-naphthoylamino-2-naphthalene
do	2′-hydroxy-3′-naphthoylchloro-4-amino-2-toluene
do	2′-hydroxy-3′-naphthoylamino-2-toluene
1-alkoxy-8-naphthylamine	Phenylnaphthylamine
Diethoxy-2:5-benzoylamino-4-amino benzene	2′-hydroxy-3′-naphthoylamino-benzene

Magenta images

m-nitro-p-toluidine	β-naphthol
o-anisidine	β-hydroxynaphthoic esters
o-chloranisidine	β-naphthol
amino-2-methoxybenzene	2′-hydroxy-3′-naphthoyl derivatives
chloro-5-amino-2-methoxybenzene	2′-hydroxy-3′-naphthoyl derivatives
m-xylidine	2′-hydroxy-3′-napthoylamino-1-naphthalene
o-anisidine	2′-hydroxy-3-naphthoylamino-benzene

Yellow images

o-toluidine	m-aminophenol
tolidine (tetrazotized)	acetoacetanilide
di(acetoacetamido)4:4′dimethyl-3:3′ diphenyl	2-hydroxy-3′-naphtholyamino-benzine
aniline	diacetoacet-toluidide
o-toluidine or p-toluidine	do.
chloro-4-amino-2-toluene	do.

As a general rule, neither the diazonium compound nor the phenol need have *solubilizing groups* SO_3H and COOH. Thus the dye produced resists fixation by washing.

According to von Poser, Schmidt and Werner(22) the diazonium compound should not contain an amino group, but rather, two esterified hydroxyl groups. R. Lantz, however, used the same nuclei containing alkoxy (or halogen) groups and simultaneously, in the para position, an amino group blocked by an acid radical such as benzoylamino —NH—CO—C_6H_5.

The coupler is usually a β-naphthol, a β-hydroxy naphthoic acid or acetoacetic acid. In the last two cases the solubilizing power of the acid radical must be suppressed by combining it, as an anilide, with an aromatic amine.

The diazosulphonates are available, ready prepared, under the name 'Photorapid dyes'. In France they are sold by the Cie Française des Matières Colorantes, for printing fabrics.

PHOTOCHEMICAL COLOURING OF ORGANIC COMPOUNDS

647. Leuco bases

Reduction of organic dyestuffs gives the compounds called *leuco bases*. These leuco bases again give the dyes by oxidation. O. Gros, having stated in 1901 that the oxidation of leuco bases is assisted by light, had the idea of using this phenomenon in the production of colour images.

The best oxidation sensitizers are the *nitro compounds*. Nitrocellulose, which can be used as a binder, itself works in this way. As a nitroderivative, *nitromannitol* can be chosen. Oxidizing agents other than nitrocompounds have the disadvantage that they oxidize the leuco bases in darkness.

The photochemical oxidation is accelerated by basic organic substances. The stability of the sensitive layer is increased if the base has a high molecular weight: thus *quinoline* gives good results. The aromatic amines are less effective than the aliphatic amines or the heterocyclic bases.

A sensitive layer can be prepared by coating on paper a leuco base dissolved in an organic solvent, with twice its weight of nitrocellulose (collodion) and containing a base and a nitrosensitizer.

The triphenylmethane and diphenylmethane dyes and the rhodamines are most frequently used: chloroethyl green, setocyanine, setoglaucine, rosaniline, auramine, fluorescein, rhodamine B, etc.

The leuco base layers have the disadvantage of losing their sensitivity and stability. They are difficult to fix; this is usually done by dissolving the leuco base in 10% monochloracetic acid, or by several successive washes in benzene. B.P. 546,637 (Kodak) claims that the oxidation of leuco bases of the triphenylmethane dyes, having an amino group in the para position of at least two phenyl groups, can be accelerated by ferric, mercuric or cupric salts. They are fixed by exposure to ammonia vapour.

Indigosols. The leuco bases of the indigoid dyes react with sulphuryl chloride to form the *leuco-sulpho-esters* known as *indigosols*: slightly coloured substances, soluble in water and relatively stable to oxidizing agents in alkaline medium, but readily oxidized in acid medium. Exposed to light, they are supposed to undergo *photo oxidation* which regenerates the original colour.

In fact, the author's experiments to establish their light sensitivity have been fruitless.

648. Naphthoquinones

We know that the naphthols, and generally the phenols, combine with p-diamines in the presence of an oxidizing agent to give the coloured indophenols. This type of reaction is used in colour development. The *naphthoquinones*, the oxidation products of the dinaphthols, also have the property of condensing with *amines* and other compounds containing a *reactive methylene group* —CH_2—, but directly, without the intervention of an oxidizing agent, as they are themselves oxidizing substances: the products formed are the quinoanilines or the quinomethines.(23)

Now the naphthoquinones are decomposed by light, the decomposition products losing their property of reacting with amines or methylene compounds. This can be used as a method of obtaining monochrome images.(24) A foil or paper is sensitized with a 2% solution of the *sodium salt of* 1:2-*naphthoquinone*-4-*sulphonic acid* (sulphonation makes the naphthoquinone soluble and blocks the 4-position); by exposure under a positive, a visible image of quinone decomposition products is formed. The remaining unaltered sulphonated naphthoquinone is then combined with an amine or a methylene compound giving a positive coloured image.

By treating the exposed layer with 1% aniline hydrochloride, the image develops red. The reactive methylene compounds which have been described in connection with colour development, give images of very diverse colours. By incorporating non-basic couplers with the naphthoquinone, development can be carried out with ammonia fumes after exposure.(25)

Another process is to impregnate a paper with a 2% solution of the sodium salt of anthraquinone-2:6-disulphonic acid, 10/15% copper formate and 10% glycerin. The dried paper is exposed to light and developed by heating to 100–170°C; the anthraquinone compound is reduced by the light to a hydroanthraquinone which in turn reduces the copper salt at high temperatures giving a negative red-brown image.(25b)

649. Organic bases

The organic bases are oxydized by light, especially ultra-violet radiations. The reaction is accelerated by oxydizing agents such as 1% potassium nitrate. The sensitized layer can be exposed wet or dry. In either case a colouring material is formed which is mordanted on to the fibre.

With *o-toluidine* exposed wet, brownish-yellow colours are obtained, and exposed dry, purplish-brown. *Benzidine* gives a deep brown. *Naphthylamines* and *aminophenols* can also be used.

The heterocyclic bases and particularly pyridine derivatives are also photosensitive. Their photochemical oxidation products can condense with primary amines to produce dyes. However, a colour image can be produced directly using an alcoholic solution of 2-*benzylpyridine* which is coated on a support such as leather; by exposure under a negative, a brownish-orange positive is formed which can be fixed with acidified water.

The *mono-* and *poly-hydroxybenzenes* are unstable to light as are the organic bases, the reaction being catalyzed by oxydizing agents. The images obtained in each case can be intensified by coupling with diazonium compounds.

649b. Photosensitive plastics

Some synthetic resins, from phenol or vinyl compounds, are photosensitive. Chlorovinyl resins, exposed to light, are decomposed, with HCl formation. When the latter acts upon a colour former, an image is obtained. This image, generally brown, is dispersed in the plastic material. Several minutes' heating at 160°C is required. *Calimor* film is a typical example.

DIAZOTYPES

650. Principles of Diazotype process

Diazotypes are monochrome colour images prepared from *diazonium compounds* which are sensitive to light.

Although diazotypes are almost entirely used in the reproduction of drawings to replace blueprints they can be used for the preparation of monochrome images for three-colour work.(26)

We have already examined the photochemical decomposition of the diazosulphonates. In this case it is the diazonium compound itself which is the photosensitive material.(27) Through the action of light it is decomposed to a phenol, nitrogen, and hydrochloric acid:

$$\underset{\text{Diazonium compound}}{C_6H_5{-}N{=}N{-}Cl + H_2O} \rightarrow \underset{\text{Phenol}}{C_6H_5OH} + N_2 + HCl$$

The remaining unaffected *diazonium compound* is treated by a phenol *in the presence of alkali*, to give an insoluble *azo* dyestuff which is mordanted on to the paper or cloth fibres. The exposed areas of the layer remain white. The image obtained is therefore a *positive* and printing must consequently be done from a positive.

In practice the sensitive diazonium salt together with a phenol and an organic acid are coated together on paper.(28) Due to the presence of the acid, the diazonium compound cannot combine with the phenol. To bring about coupling it is sufficient, after exposure through a drawing, to immerse the paper in an alkaline solution, or better, to expose it *dry* to ammonia vapour: the unexposed diazonium compound combines immediately with the phenol, producing an image of coloured lines on a white background.

Dry development, disclosed by Kögel in 1921 (Ozalid paper) was an important advance, for operations were simplified and the paper was not distorted.

651. Usable diazonium compounds

The diazonium compound must be stable at ordinary temperature and very sensitive to light. Furthermore it must be sufficiently soluble to be applied to the paper and be sufficiently dark coloured to enable the appearance of the image to be observed. The phenol produced during photochemical decomposition must not be readily oxidized or the image will become yellow in time.

The diazonium salts which are suitable for this purpose contain an amino group in the para position. Frequently this amino group is substituted by 2 alkyl or acyl groups. The parent amines are:

ass. dimethyl-p-phenylenediamine $(CH_3)_2:N—C_6H_4—NH_2$
ass. diethyl-p-phenylenediamine and its 3-carboxy derivative
ass. dibenzyl-p-phenylenediamine
ass. di-isoamyl-p-phenylenediamine
ass. di-isoamyl-2:6-dimethyl-p-phenylenediamine
3:6-diethoxy-benzoyl-p-phenylenediamine
3:6-dimethoxy-benzoyl-p-phenylenediamine
p-amino diphenylamine
dianisidine(29)
3:3′-dichloroanisidine
dinaphthysidine
2-amino-dimethylhydroquinone.

Examples: diazotized *diethyl-p-phenylenediamine* is dissolved in water as a 2% solution. Citric acid or potassium acid citrate is added to the solution with an emulsion of β-naphthol; brownish-black image. The diazonium compound of *amino-dimethylhydroquinone* mixed with amino-sulphonic acid H gives a violet image. Diazotized *chlorobenzene-sulphonate of cyclohexyl-p-phenylenediamine* gives a blue-black image with phloroglucinol.(30)

The diazonium compounds of diphenylamine derivatives

$$R—C_6H_4—NH—C_6H_4—N{=}N—Cl$$

are particularly suitable for diazotypes: they are very stable and sensitive to light, much more than the diethyl-p-phenylenediamine derivative. The colours obtained with the various couplers are:

phenol	yellow image
1-naphthol-4-sulphonic acid	red-violet image
2-naphthol-6-sulphonic acid	red-violet image
1-naphthol-3:8-disulphonic acid	blue image
2-naphthol-3:6-disulphonic acid	blue-violet image
aceto H acid	blue image
aceto γ acid	violet image
phenylmethylpyrazolone-p-sulphonic acid	orange-red image.

The *tetrazo* compounds, such as those of dianisidine, can be developed in neutral or even acid medium.

The introduction of the substituents CH_3O—, C_2H_5O—, $(CH_3)_2N$—, CH_3CONH—, in the 4′— position gives bluer colours. The groups NO_2 and Cl in the 4′— position give, on the contrary, redder tones.

I. Lewkojew, W. Petrow and W. Durmaschkina have disclosed that the *4′-acetamino* and *4′-methoxy-4-diazodiphenylamine* give the most soluble and sensitive salts, intense colours and pure whites.

With *1-amino-2-naphthol-4-sulphonic acid* a very stable *anhydride* of the diazonium compound is formed in which the groups SO_3H and $>N{=}NOH$ are linked together following the scheme $>SO_2{-}O{-}N{=}N<$. Together with an organic acid and a coupler, this anhydride can be coated on paper: resorcinol for example gives a violet-black image.

The sulphonated amines, *Diazo light yellow G* and *Diazo light yellow 2G* by Bayer, give after diazotization, stable colours. The two amines have the respective formulas:

$$NH_2{-}C_6H_4{-}CO{-}NH{-}C_6H_3(SO_3H){-}CH{=}CH{-}$$
$$\qquad{-}(SO_3H)C_6H_3{-}NH{-}CO{-}C_6H_4{-}NH_2$$

$$NH_2{-}C_6H_4{-}CO{-}NH{-}C_6H_3(SO_3H){-}NH{-}CO{-}$$
$$\qquad{-}NH(SO_3H)C_6H_3{-}NH{-}CO{-}C_6H_4{-}NH_2$$

Paper which is already dyed can be diazotized. With the yellow 2G and resorcinol, a yellow image is produced; deep violet with α-naphthylamine and violet with H acid.

Instead of using the diazonium chlorides it is sometimes advantageous to prepare the *organic salts* (oxalates, citrates, etc.) which are more sensitive to light.(31) Complex inorganic salts also give good results: *chlorostanates* obtained by the action of tin on the diazonium chloride, *fluoborates*,(32) *fluorosulphonates*(33) and *hydroborofluorides*.(34)

Example: 20 parts of the chorostannate of the diazonium compound of di-isoamyl-2:6-dimethyl-p-phenylenediamine, 10 parts of citric acid and 5 parts of 2:7-dihydroxynaphthalene in 1000 parts water are coated on to paper. After drying, exposure and development in ammonia vapour, a deep violet image is obtained.

p-aminophenol OH . $C_6H_4{-}NH_2$ treated with hydrofluorboric acid gives a salt which, treated with amyl nitrite, can be converted to a diazonium compound in alcoholic solution.(35) It is also possible to condense the diazonium compounds with secondary organic bases.(36) The addition of *boric acid* to the organic acid, used to prevent premature coupling, was disclosed by Kalle.(37) The latter also added an *antioxidant* derived from sulphur (0·1–10% thiourea, allylthiourea, thioglycollic acid, etc.) and aldehydes to prevent the image from yellowing.(38)

The antioxidant can also be hypo (1–5%), Seignette's salt (5–10%), glucose, citric acid, hydroxylamine (0·2%), pyrogallol (0·2%) or even a dye such as methylene blue chlorozincate (0·05%) (see Mester L.: *Sci. Ind. Phot.*, 1952, 337).

Among the improvements made to diazo prints are:

Use of stabilizing *guanidine* compounds as additives or couplers:(39) as a stabilizing additive phenylbiguanidine C_6H_5—NH—(C : NH)—NH—(C : NH)—NH_2 can be noted, and 7-hydroxynaphthalene-1-guanidine (hydrochloride) OH—$C_{10}H_6$—NH—(C : NH)—NH_2 . HCl can be used as a coupler.

Use of *aminodiphenylamine* diazonium compounds with sulphonated naphthols such as R salt (2-naphthol-3:6-disulphonic acid) gives blue images. To avoid the crystallization which occurs with these compounds, attributed by J. P. Sisley to the formation of a complex(40) (acid salt of 4-diazodiphenylamine-2-naphthol-3:6-disulphonic acid) a sulphonic acid such as naphthalene-1:3:6-trisulphonic acid must be added to dissolve it.

Another class of very stable diazonium compounds which are extremely sensitive to light are those derived from amino bases containing *imidazol* groups; such as N-methyl-C-methyl-aminobenzimidazol investigated by Schuster and Pinnov,(41) which give, for example, a red image with Schaeffer's salt. These imidazols were used by Freyss and Frangialli.(42)

652. Suitable couplers

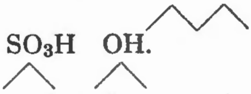
The couplers (or formers) which can combine with the diazonium compounds are the phenols, naphthols, aminonaphthols, sulphonated naphthols, pyrazolones, etc. For example, phenol, cresols, resorcinol, orcinol, phloroglucinol, α-naphthol, β-naphthol, o-hydroxybiphenyl, o:o′-dihydroxybiphenyl, 1:6-dihydroxy naphthalene, 2:7-dihydroxynaphthalene, 2:8-dihydroxynaphthalene, 1:5-dihydroxynaphthalene, 1-amino-7-naphthol, 4-sulpho-8-sulphamido-1-naphthol, 8-chloro-1-naphthol-3:6-disulphonic acid, 5-dimethylamino-1-naphthol, phenylmethylpyrazolone, Schaeffer's salt, Newile's salt, R salt, RG salt, H acid, J acid and its derivatives, γ-acid and derivatives, etc.

Coupling is easier when the coupler has many positive substituants; so *phloroglucinol* with 3(OH), is better than resorcinol which only has 2(OH) groups.

Couplers are obtained by condensing phloroglucinol with primary or secondary amines(43) for semi-wet development. For the same purpose the *hydroxynaphthoimidazoles*(44) can be used, especially those from β-naphthol like 7-naphthol-1:2-imidazol in which the —N═CH—NH— chain linking the 1 and 2 positions of the naphthol nucleus should be noted.

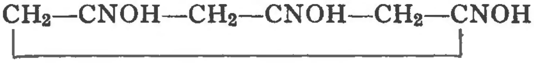
The diazonium compound can be prevented from coupling, by blocking the phenolic function, which will then react only in definitely alkaline media.

For this, Frangialli and Lantz used *naphthalene sulphones*(45) where α-naphthol is sulphonated in the 8—position. In the stable state the link SO_2—O is produced, which, in the presence of alkalis becomes SO_3H OH.



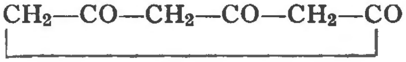
Gay(46) blocked the hydroxyl group by *acetylation*, using, for example, 2-acetylamino-8-acetoxy-naphthalene-6-sulphonic acid.

Van der Grinten⁽⁴⁷⁾ used *hydroxylamine*. Thus with phloroglucinol, tri-[illegible]hexamethylene-triamine



$$\underbrace{CH_2—CNOH—CH_2—CNOH—CH_2—CNOH}$$

was produced, which was decomposed at the time of coupling to a triketone, isomeric with phloroglucinol



$$\underbrace{CH_2—CO—CH_2—CO—CH_2—CO}$$

New series of couplers, disclosed by General Aniline Co., comprise quinoline derivatives such as hydroxyquinoline and quaternary salts of 2-methylquinaline (U.S.P. 2,542,850 and B.P. 616,557), hydroxypyridone (B.P. 644,186), pyrazolonecarboxylic acid (B.P. 655,007) cyclohexanedione (U.S.P. 2,500,099), cyanacetamine (B.P. 544,186). Kalle claimed hydroxybenzotriazole (G.P. 838,692) and 2:3-dihydroxynaphthalene-6-sulphonic acid (F.P. 1,030,889).

653. Practical formulas for dry diazo papers

The coating solution for a photosensitive diazo material contains the following constituents:

a binder;
a diazonium salt;
a coupler (or former);
an acid;
an antioxidant (thiourea).

Finally a hygroscopic *mineral salt* is added such as aluminium or zinc sulphate, and a *solubilizing agent* when the diazonium salt tends to precipitate from the solution. The solubilizing agent is generally 1:3:6-*naphthalene-trisulphonic acid* (known in France as Diazophile S Francolor).

The binder is a natural or synthetic colloid. It simplifies coating and prevents the solution from penetrating too far into the paper. Gelatin, carboxy-methylcellulose, polyvinyl alcohol and silica gel, etc., can be used.

The diazonium salts most frequently used in commerce are

the zinc chloride salt of diazotized diethyl-p-phenylenediamine;
the diazonium chloride of p-aminodiphenylamine;
the diazo anhydride of 1:2:4-aminonaphthol sulphonic acid;
the diazo anhydride of 2:1:5-aminonaphthol sulphonic acid.

The following formula gives a black line:⁽⁴⁷ᵇ⁾

Zinc chloride salt of diazotized diethyl-p-phenylenediamine	30 g
Aluminium sulphate	30 g
Tartaric acid	30 g
Citric acid	30 g
Phosphoric acid	0·2 g
Thiourea	50 g
Phloroglucinol	2·8 g
Dichlororesorcinol	0·3 g
1:3:6-naphthalene-trisulphonic acid (Diazophile S)	5 g
Water to	1000 cc

A black image is also obtained using Sisley's formula which is applied to a paper already treated with alum and 3% sodium chlorostannate:

Diazotized N.N. dibenzyl-p-phenylene-diamine	10 g
Oxalic acid	20 g
Ammonium chloride	50 g
Hydroxylamine sulphate	12 g
Glucose	50 g
Gelatin	10 g
Thiourea	20 g
Phloroglucinol	2 g
Resorcinol	2 g

The paper is dried until it contains less than 2% water.

The *zinc chloride salt of diazotized diethyl-p-phenylenediamine* is often used in the following formula recommended by la Compagnie Française des Matières Colorantes:

Water to	1000 cc
Diazonium salt	30 g
Aluminium sulphate	30 g
Tartaric acid	20 g
Thiourea	10 g
Coupler (except phloroglucinol—2·5 g)	10 g

The colour obtained varies with the coupler:

Phloroglucinol	black
R-salt	blue-violet
G-salt	purplish-brown
F-salt	red-brown
Resorcinol	sepia
Sulphophenylmethylpyrazolone	red (unstable soln.)

The *p-diazonium chloride of diphenylamine* gives different colours. The basic formula is:

Water to	1000 cc
Diazonium salt	10 g
Tartaric acid	30 g
Thioureau	5 g
Diazophile S	10 g
Coupler (except phloroglucinol—1·5 g)	10 g

Phloroglucinol	violet
R-salt	blue
G-salt	violet
F-salt	violet
Resorcinol	yellow-brown
Sulphophenylmethylpyrazolone	red (unstable soln.)

With the *diazo anhydride of* 1:2:4-*aminonaphthol sulphonic* acid, and the formula

Water to	1000 cc
Diazonium compound	10 g
Thiourea	5 g
Coupler (phloroglucinol—5 g)	10 g

the colours are

Phloroglucinol	blood red
Resorcinol	red

Reminder: *R salt* is the sodium salt of 2-naphthol-3:6-disulphonic acid.
G salt is the sodium salt of 2-naphthol-6:8-disulphonic acid.

654. Semi-wet development

The paper contains only the sensitive diazonium salt. After exposure it is developed by dampening with an alkaline solution of the coupler.

A developer for semi-wet development, essentially contains the coupler and an alkali. In addition it may contain inorganic salts to stabilize the image, an antioxidant such as thiourea or hypo and finally a wetting agent such as iso-octanol. The pH depends upon the diazonium compound. It can vary between 5·5 and 10 and is maintained by buffering substances such as formates, acetates, phosphates, borates and carbonates. R. Delattre gives the following formulas for sepia lines with β-naphthol:

Paper	p-diazonium chloride of diphenylamine	10 g
	Tartaric acid	30 g
	1:3:6-naphthalene-trisulphonic acid (Diazophile S)	8 g
	Water to	1000 cc

Developer	β-naphthol	10–11·5 g
	Trisodium phosphate	80 g
	Water to	1000 cc

Hypo must not be added to this developer as a powder, as it prevents the β-naphthol from dissolving.

Another current developer is:

Phloroglucinol	2·5 g
Resorcinol	7·5 g
Sodium carbonate anh.	40 g
Sodium sulphite anh.	40 g
Sodium chloride	150 g
Water to	1000 cc

In all cases the reaction must be rapid, and therefore the diazonium compound very active, in order to avoid smears due to the diffusion of the diazonium compound through the paper. Various solutions have been proposed to remedy this defect: use of diazonium compounds which react in a *slightly acid medium* with a final addition of organic alkaline salts; development in the presence of *sodium chloride* which suppresses the dissolving of the diazonium compound; addition of *chlorostannates* which form compounds of reduced solubility with the diazonium compounds;(48) improved wetting by the use of *wetting agents*; use of formalin in the developer to obtain a more stable colour (Sisley).

Derivatives of 3:3′-dichloroanisidine have been disclosed as diazonium compounds which will react in a slightly acid medium and 2:5-dialkoxy anilines which give black images with phloroglucinol at pH 6–7. Among the other diazotizable bases which can be used in the wet process are derivatives of indoles and carbazoles together with diazosulphanilic acid.(49)

The mildly alkaline medium on the other hand can be produced by the reaction of basic aluminium acetate and alkali fluoride.(50) The alkali is produced as the reaction proceeds.

The preparation of *stable diazonium compounds* without adding organic acids is carried out by precipitation with *sodium chloride* or *sulphuric acid* in the presence of formalin.(51) Sodium chloride can be advantageously replaced by salts of cadmium,(52) zinc,(53) magnesium, tin, aluminium,(54) manganese,(55) or cobalt.(56)

655. Protein diazonium compounds

The *peptides* and the *polypeptides* derived from cyclic nuclei will form diazonium compounds with nitrous acid: these include *phenylalanine*, *tryptophane*, and *tyrosine*. The diazonium compound of tyrosine, for example, prepared by Sisley is very sensitive to light. During the reaction a nitroso group is first introduced into the benzene ring, and it is this nitroso group which is converted to a diazo group, finally giving the diazonium nitrate. Morel and

Sisley(57) have also prepared the diazonium compound of the *fibroin of silk*; this compound gives various colours with the couplers.

Casein, containing about 4% of tyrosine, gives a yellow photosensitive diazonium compound. The azo dyes produced are dark coloured, and very fast. Borgesius and Waterman have used diazocasein for the preparation of diazotype papers.(58) As this product is insoluble in non-alkaline water, it must be applied as a suspension.

The diazotization of *keratine of wool* has also been studied.

Wool and *silk* have been diazotized by L. Mester(59) with a solution formed by one part N/16 nitrite and 20 parts N/16 HCl. Treatment: 40–50 mins. at 38°C. The tissue turns yellow. It is washed and dried at 50°C. Exposure: 5–10 mins. at 20 cm from a 500 W mercury lamp. Maximum sensitivity at 405 mμ.

656. Manufacture of diazo papers

The diazo sensitizing solution is easy to prepare. Only moderate temperatures should be used to avoid decomposing the diazonium salt. The zinc chloride salt of diazotized N.N.diethyl-p-phenylenediamine is more stable than most, as it can be taken up to 50°C.

The solution is applied with a roller. The excess liquid is then removed by blowing off and then the layer is made even by an 'air doctor', a high-pressure air jet across the paper, and directed on to it obliquely. The coating speed is higher than 100 feet per minute. The drying chamber is divided into several zones. One machine of this type is made by the John Waldron Corp. in U.S.A. and another by T. H. Dixon Ltd. in England.

657. Sensitometry of diazotype layers

The spectral sensitivity of diazo layers has been said to have a maximum at 375 mμ. Turner found that this maximum is nearer 400 mμ (*Brit. Jour. Phot.*, 1953, 420).

The quantum yield at 365 mμ varies between 0·2 and 0·74 depending on the product used. It was determined by measuring the volume of nitrogen produced (*Rec. Trav. Chim. Pays Bas*, 1952, 848).

The characteristic curve has no straight line. The more absorbant the layer, the higher the contrast. Sensitized cellophane has a straighter line than paper, but as a general rule the toe is short; it turns quickly and the curve becomes convex for a short period then flattens off at higher densities increasing very gently for a considerable distance.

658. Reflex printing

Reflex printing is a method of document reproduction by exposing *through* the sensitive paper. The light passes through the support and the sensitive layer, before being *reflected* by the surface of the document.

Reproduction would not be possible without placing a *screen* between the paper and the source, as the diazonium compound would be completely destroyed before any reflection from the document had taken place.

In the Van der Grinten *Retoce* process, a special diazo paper is placed with its sensitive surface facing the document to be reproduced, in a frame. A screen of 'Securit' glass having 120 lines per cm is placed on the diazo paper. This is prepared with a light coloured diazonium compound to restrict the penetration of the active ultraviolet rays as little as possible. Exposure is made with an arc lamp. The light penetrates the gaps in the screen, through the paper and the sensitive layer, which it decomposes, and is reflected by the document. The reflected light then affects the parts previously protected by the screen to form a clear image proportional to the light reflected.

659. Diazo films

A flexible film support, generally of *cellophane*, is impregnated with a diazonium compound through part of its thickness by immersing in an alcoholic or aqueous-alcoholic solution of the sensitive material.

Mercury-diazo. Metallic diazo compounds can also be used. A support, impregnated for example with a *diazonium compound* and a *mercury salt* gives copies (when exposed to ultra-violet) whose resolving power exceeds 1200 lines per mm. Physical development is used: the silver is deposited in the exposed areas giving a very high contrast.

Alink, Dippel and Keuning used a layer of sulphonated diazo-o-cresol + mercurous nitrate (*Sci. Ind. Phot.*, **13**, 116; **18**, 305; **19**, 225 and 255). The unexposed film does not keep and is 700,000 times slower than Microfile film (*Phot. Jour.*, 1950, 34).

Sensitized acetate. Cellulose acetate sensitized with various diazonium compounds enables monochrome positives to be obtained for controlling the retouching of screen positives for photomechanical reproduction or for the reproduction of plans.

A swelling agent is necessary for sensitizing: acetone or alcohol + acetone for example. The solution is applied with a roller or by dipping followed by removal of the excess liquid. In place of 1000 cc water in an ordinary formula, 250 cc distilled water, 250 cc acetone and 500 cc 95% alcohol is used.

The three primary subtractive colours can be obtained, for example, by the following diazo compounds:

Cyan: 4-diazo-3-methyl-monoethylaniline + R acid.
Magenta: 1-diazo-2-hydroxynaphthalene-4-sulphonic acid + resorcinol.
Yellow: 4-diazo-3-methyl-monoethylaniline + phenol.

Diazotized diphenylamines (see para. 651) give, with 1:3:8-naphthol-disulphonic acid or aceto H acid, blue images—with 1:4- and 2:6-naphthol-sulphonic acids magenta images—with phenol, yellow images. Many other combinations can be found.

1. *Phot. Korr.*, 1918, **55,** 224; 1920, **57,** 120; 1922, **59,** 62; 1926, **62,** 119; 1931, **67,** 197.
2. *Zeit. Wiss. Phot.*, 1926, **126,** 171; *Sci. Ind. Phot.*, 1929, **1,** 9.
3. G.P. 473,285.
4. Polgar A. and Ch. Halmos.: F.P. 847,596.

4b. The dyes dispersed in a monomolecular state like methylene blue are more easily decolorized by light than the colloidal ones like naphthol green, with exception (erythrosin). The semi-colloidal dyes (eosin) have an intermediate sensitivity.

5. F.P. 845,395.
6. Thiosemicarbazide is a combination of hydrazine NH_2-NH_2 and isothiocyanic acid HSCN:NH_2-NH-CS-NH_2. It is therefore an amino substituted thiourea.
7. F.P. 781,813 (1935).
8. Polgar and Halmos: F.P. 846,996 (1939).
9. I.G.F.: F.P. 695,364.
10. I.G.F.: F.P. 690,386 and 695,426.
11. Polgar and Halmos: F.P. 847,597.
12. I.G.F.: F.P. 690,386.
13. Polgar and Halmos.

13b. Giles and Macaulay: *R.P.S. Cent. Conf.*, London 1953.

13c. Kalle: F.P. 870,244 (1941).

14. *Zeit. Wiss. Phot.*, 1934, **33, No. 8,** 177.

14b. Studied by Hagemann and Senebier in the 18th Cent., then by Wollaston in 1804. See *Sci. et Ind. Phot.*, 1928, 27; 1929, 178.

15. G.P. 53,455. The first diazosulphonate was prepared by Schmitt and Glutz in 1869.
16. *Bull. Soc. Fr. de Photogr.*, Feb. 1896.
17. F.P. 729,841.
18. F.P. 760,784 and add. 45,829.
19. *Ann. d. chimie*, **190,** 73.
20. *Ber.*, **18,** 90.
21. Lantz R.: *Loc. cit.*
22. G.P. 694,078 (1940).
23. *Ber.*, **38,** 3685*; Zeit. Physiol. Chemie*, **41,** 379.
24. I.G.F.: F.P. 648,659.
25. I.G.F.: F.P. Add., 35,018.

25b. Schoen and General Aniline: G.P. 814,999 (1949).

26. Kalle: F.P. 662,092; Langguth and Hummel: B.P. 274,129.
27. Phenomenon stated by West in 1885 and used by Green, Cross and Bevan: G.P. 56,606.
28. The reaction can be accelerated by ferric ammonium oxalate working via the ferrous salt produced by photochemical reduction: U.S.P. 2,027,229.
29. F.P. 612,562.
30. Kalle: F.P. 665,132 and 709,669.
31. Starotin L.: F.P. 689,318.
32. *Ber.:* 1927, **60,** 115 and 1186; I.G.F.: F.P. 657,695 and 672,466.
33. I.G.F.: B.P. 303,427.
34. I.G.F.: B.P. 317,335.
35. Philips: F.P. 743,659.
36. *Ber.*, **148,** 893; *Ann.*, **235,** 263; I.G.F.: F.P. 670,216.
37. F.P. 657,851.
38. F.P. 687,956.
39. Kalle: F.P. 679,484; 683,504.
40. XVII^{e} Congrès de Chimie Industrielle.
41. *Ber.*, **29,** 1055.
42. F.P. 695,006.

43. Kalle: G.P. 639,125.
44. La Cellophane: F.P. 849,407.
45. F.P. 684,881.
46. F.P. 616,562.
47. F.P. 616,562.
47b. Delattre R.: *Chimie et Ind.*, 1948, 236.
48. 0·1 % of a tin salt can also be added to the developer.
49. La Cellophane: F.P. 813,263.
50. La Cellophane: F.P. 815,400.
51. Kalle: F.P. 765,908.
52. Kalle: F.P. 657,852.
53. F.P. 600,311; 734,899; 769,810.
54. I.G.F.: F.P. 777,126.
55. F.P. 818,683.
56. I.G.F.: F.P. 849,724.
57. *Bull. Soc. Chim.:* 1927, 994; 1928, 881.
58. *Jl. Soc. Dyers and Col.*, 1940, 23.
59. Mester L.: *Sci. et Ind. Phot.*, 1955, 354–362.

PART FOUR

Colour Sensitization

Chapter XXXV

THE SENSITIZING DYES

660. Historical

Photographic emulsions are naturally sensitive only to the ultra-violet, violet and blue spectral regions. To make them sensitive to the other colours, green, yellow, red and infra red—or to *ortho-* or *panchromatize* as we say—it is necessary to incorporate certain special dyes—'sensitizers'.

The phenomenon of *colour sensitization* was discovered by Vögel in 1873 using a collodion plate dyed with *coralline.* The fact at first passed unnoticed, but was confirmed by Becquerel using *chlorophyll,* and mainly by Waterhouse who, two years after Vögel, showed that collodion plates become sensitive to green when they are bathed in a very dilute solution of eosin. Taillefer and Clayton used this dye to sensitize silver gelatino-bromide emulsions; in 1883 they took out a patent and marketed the first commercial plates of this type under the name of 'isochromatic plates'.

In 1884 Vögel found that a blue dye, *cyanine*, and a red dye, *quinoline red*, were sensitizers for the red and the green, respectively. A mixture of them was named 'azaline'.

The same year, Eder discovered that *erythrosin,* a dye related to eosin, was greatly superior to the latter as a green sensitizer. Erythrosin remained for a long time the only industrial sensitizer.

In addition, Higgs advocated '*alizarin blue*' with bisulphite, and Lehman, *nigrosine,* for infra red photography. For the latter purpose, Eder and Valenta tried a great number of compounds, Columbia green and diazo black BHN amongst others, whose interest is purely historical.

The use of *cyanine* as a colour sensitizer was of great interest, not for its intrinsic qualities, which were rather mediocre, but because it is the first member of an important family of dyes which, for the most part, have remarkable sensitizing properties. The study of these dyes is therefore of outstanding importance in photographic chemistry.

Greville Williams obtained *cyanine* in 1856 by the action of caustic soda on the amyl iodide of an impure lepidine (organic base derived from quinoline). Miethe and Traube prepared a related compound *ethyl red* which is an isocyanine sensitizing in the green, and in 1904 W. König succeeded in synthesizing a complete series of these isocyanines: *pinachrome*, *pinaverdol,* and *orthochrome T* made by 'Meister Lucius of Brüning, of Hoechst'. These dyes are sensitizers for green.

Another important step was made by Homolka, pupil of Koenig, who succeeded in preparing, in 1905, another type of cyanine which sensitized in the red this time, *pinacyanol*, first member of the carbocyanine group. Pinacyanol was used for 20 years in the majority of panchromatic emulsions. Only the Hoechst *dicyanine*, an infra red sensitizer, was of equal importance to the latter.

The constitution of the cyanines was for a long time a controversial subject: Hoogewerf and Van Dorp, Kaufman and Vonderwahl, Koenig, etc., attempted to elucidate this question which was not solved until after the first world war, by Mills and Pope in England.

From then, a large and increasing number of various cyanines have been synthesized: *isocyanines*, *pseudocyanines*, *carbocyanines*, *polycarbocyanines*, *merocyanines*, containing in their molecules sulphur, selenium, oxygen, or indoline radicals, giving them remarkable sensitizing properties with neither reduction of the general sensitivity nor formation of fog.

These new dyes were derived from the work carried out by Mills in 1921, on the cyanines prepared from thiazole bases (containing a sulphur atom in the nucleus), bases already used by Hoffmann in 1880. The industrial use of the thiazole, selenazole or oxazole dyes did not become general until 1928 when true orthochromatic and panchromatic emulsions of high sensitivity were marketed.

Until this time, various other dyes were in favour: Adams and Haller's *kryptocyanine* (1918), for the infra red which supplanted dicyanine, Koenig's *pinaflavol* (1919) for the green, Lumière and Barbier's *pantochrome* (1920) for green and red, Mees and Gatekunst's *naphthacyanol* (1922) for the extreme red, and above all T. Clarke's *neocyanine* (1925) for the infra red.

The synthesis of the *polycarbocyanines* having two nuclei joined by a very long chain has, since 1930, enabled the infra red sensitivity to be extended still further. The best known of these dyes is Brooker's xenocyanine. This will be discussed more fully later.

Lastly, in 1933–34, Kendall in England, and Brooker in the U.S.A., discovered the sensitizing properties of *merocyanines*. These most interesting compounds are now precious for sensitizing colour emulsions.

Before beginning the study of the sensitizing dyes in the following chapters, the dyestuffs in general will be discussed; the relation which exists between constitution and colour, and upon the heterocyclic bases, the knowledge of which is necessary, to understand the chemistry of the cyanines.

Finally it should be noted that the cyanines are rapidly decolorized by light, and because of this cannot be used normally for dyeing, with the exception of the indo-cyanides, although their tinctoral power is great. Frequently, however, they have bactericidal properties.

THE DYESTUFFS: CONSTITUTION AND COLOUR

661. Chromophores

When some of the hydrogen atoms of a large number of colourless cyclic compounds are substituted by certain chemical groups, they become coloured.

The groups which produce this colour, in colourless molecules, are termed *chromophores*. The principle ones are:

nitro	*nitroso*	*keto*	*thioketo*	*azo*	*vinyl*
$\mathrm{{-}NO_2}$	$\mathrm{{-}N{=}O}$	$\mathrm{{-}(C{=}O){-}}$	$\mathrm{{-}(C{=}S){-}}$	$\mathrm{{-}N{=}N{-}}$	$\mathrm{{-}CH{=}CH{-}}$

From the physical point of view, the chromophores displace the absorption bands from the ultra-violet towards the violet then to the longer wavelengths. When the chromophore produces too small an action to be immediately noticed, it must be repeated several times before the colour appears. The first colour produced is yellow (absorption in the violet), then orange (absorption in the blue), then red (absorption in the blue-green), followed by magenta (absorption in the green), violet (absorption in the yellow-green), blue (absorption in the orange), and green (absorption red and violet). Generally the absorption is complex, divided into several irregular bands.

Thus *ethyl benzene* $\mathrm{C_6H_5{-}CH_2{-}CH_3}$ is colourless. Acetophenone $\mathrm{C_6H_5{-}CO{-}CH_3}$ containing the chromophore $\mathrm{{-}CO{-}}$ is hardly yellow. But if a second $\mathrm{{-}CO{-}}$ group is introduced, *methylphenyldiketone* $\mathrm{C_6H_5{-}CO{-}CO{-}CH_3}$ is obtained and this is yellow. By introducing a third $\mathrm{{-}CO{-}}$ orange *methylphenyltriketone* $\mathrm{C_6H_5{-}CO{-}CO{-}CO{-}CH_3}$ is obtained.

Styrene $\mathrm{C_6H_5{-}CH{=}CH_2}$ is colourless. Diphenylhexatriene $\mathrm{C_6H_5{-}CH{=}CH{-}CH{=}CH{-}CH{=}CH{-}C_6H_5}$ is light yellow; it contains three vinyl groups $\mathrm{{-}CH{=}CH{-}}$. This phenomenon will be dealt with later when the *cyanines* are considered.

By replacing atoms of *oxygen* by heavier atoms, such as sulphur or selenium, a stronger colour is produced; benzoic acid $\mathrm{C_6H_5{-}COOH}$ which is colourless corresponds to the purple dithiobenzoic acid $\mathrm{C_6H_5{-}CSSH}$.

The most powerful of the chromophores is the azo group$\mathrm{{-}N{=}N{-}}$. By weighting the molecule the coloration can be considerably increased. For example, the compound $\mathrm{CH_3{-}N{=}N{-}CH_3}$ is light yellow; by replacing a methyl group by phenyl, which is heavier, displacement of absorption towards the longer wavelengths results; in fact methylazobenzene $\mathrm{CH_3{-}N{=}N{-}C_6H_5}$ is orange-yellow, whilst azobenzene $\mathrm{C_6H_5{-}N{=}N{-}C_6H_5}$ is orange-red.

The *nitro group* $\mathrm{{-}NO_2}$ is an effective chromophore, but it must be repeated several times to produce an appreciable action; benzene $\mathrm{C_6H_6}$ is colourless; nitrobenzene $\mathrm{C_6H_5{-}NO_2}$ is light yellow; 1:2:3:5-tetranitrobenzene $\mathrm{C_6H_2(NO_2)_4}$ is deep yellow. The position of the chromophore is also important for p-dinitrobenzene is colourless.

Changing a phenol to the corresponding *quinone* produces a very definite coloration; pyrocatechin $\mathrm{C_6H_4(OH)_2}$ is colourless, whilst the orthoquinone $\mathrm{C_6H_4({=}O)_2}$ is red; hydroquinone is colourless, the paraquinone is golden yellow.

The colour-producing action of the chromophoric groups is attributed to the presence in these groups, of *an atom whose maximum valency is not saturated*. This maximum valency is 4 for carbon, 4 for nitrogen, and perhaps 3 for oxygen. Thus the carbon atoms of the ethylene link —CH=CH— can be considered as having 3 valencies filled. The benzene nucleus itself with its 6 *trivalent-like carbon* atoms (see para. 849) is only a closed chain chromophoric system; this explains why the aromatic compounds form coloured compounds whilst the aliphatic compounds do not.

A chromophoric atom, co-ordinately unsaturated, can *carry a charge* which has the effect of increasing its light absorption, which in the end is attributed to an electromagnetic effect.

When two chromophores are found together in the same molecule, they strengthen their actions mutually; the absorption is increased and displaced in two directions simultaneously.

662. Auxochromes

Coloured molecules containing *chromophoric* groups are termed *chromogenes.* They are not dyes, that is to say, they have no affinity for animal or vegetable fibres.

The union of a chromogene with a substantive group such as SO_3H, Cl, Br, COOH, OH, SH, NH_2, NH . R, NR_2, etc., produces the dye. These substantive groups are termed *auxochromes.* For example, in picric acid (yellow dyestuff) 2:4:6-trinitrophenol $OH . C_6H_2 . (NO_2)_3$, the chromophore is $—NO_2$, the chromogene $—C_6H_2(NO_2)_3$ and the auxochrome, —OH.

The auxochrome groups modify to a greater or lesser degree the colour of the chromogene; the most active in this respect are the groups NH_2, NH . R, NR_2 and OH. Thus hydroxyazobenzene $C_6H_5—N=N—C_6H_4OH$ is more strongly coloured than the chromogene azobenzene.

By replacing the hydrogen atom of a hydroxyl group by a metal, preferably an alkali metal, the auxochromic power is increased. Its replacement by an alkyl or acetyl group on the contrary reduces this power.

The acid groups —COOH and $—SO_3H$ have but a slight effect on the colour of the chromogene. The acetylation of the NH_2 group or replacement of one of its hydrogen atoms by metal, and also the etherification of the hydroxyl group, can destroy the properties of the auxochrome.

The deepening of the colour can be carried out equally well in the presence of the auxochromes OH, SH, NH_2, NHR or by *weighting the molecule*; for example the replacement of a phenyl radical by a naphthyl radical in a red dye results in a violet dye.

When the molecular weight is increased indefinitely, a *second order colour* is obtained; the principal absorption band passes from the ultra-violet through the visible spectral region to the red. The colour is then blue-green. A second band originating in the ultra-violet follows the principal band; if it is found in the violet whilst the latter is still in the red, the colour of the substance becomes green. By further weighting the molecule, the principal band passes into the infra red, and only the remaining absorption band shows the second order colour which then passes through green to yellow and orange. Thus p-nitrosodimethylaniline $NO—C_6H_4—N(CH_3)_2$ is green, whilst p-nitrosophenylaniline $NO—C_6H_4—NH . C_6H_5$ which is heavier is yellow, and p-nitrosodiphenylaniline $NO—C_6H_4—N(C_6H_5)_2$ is orange.

663. Dyes

Usual organic dyes are either *acid* or *basic*. Neutral ones are rare: they are represented by merocyanines which are 'internal ionoids'.

The *acid dyes* dye animal substances—gelatin, wool and silk—in acid solution: these include metanil yellow, quinoline yellow, the ponceaux reds, the bordeaux, eosine, erythrosin, and all the sulphonated dyes. They do not dye vegetable fibres. A special group—the *substantive dyes*—can dye unmordanted cotton (para. 621).

The basic dyes, with certain exceptions, do not dye gelatin. They dye wool and silk in neutral solution, in addition to cotton mordanted with tannin. Among these dyes are auramine, phosphine, chrysoidine, fuchsine, safranine, rhodamine B, acridine orange and red, methylene blue, Capri blue, aniline violet, brilliant green, malachite green, and the cyanines. The basic dyes are precipitated by a solution of tannin and 10% sodium acetate.

The principal groups of dyes in current use are classed in the following table, pages 734 and 735.

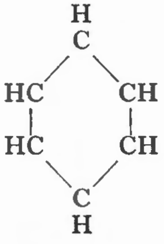
Most of the dyestuffs shown in the table are derived from the benzene molecules whose constitution is the most familiar. There are, however, a large number of dyes which are derived exclusively from the *heterocyclic bases;* among these are found the cyanines.

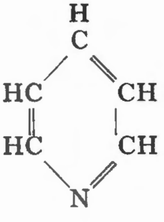
THE CYANINES

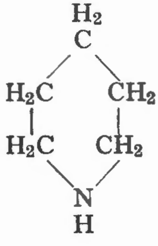
664. The Heterocyclic bases

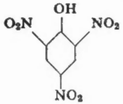
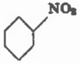
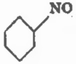
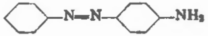
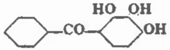
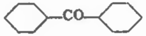
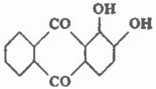
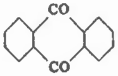
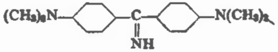
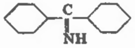
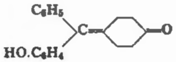
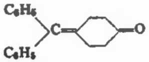
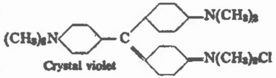
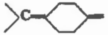
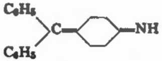
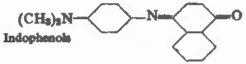
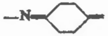
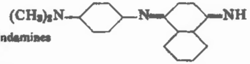
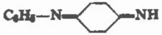
The bases from which the cyanines are prepared are cyclic compounds analogous to the aromatic compounds but in which one =CH— is replaced by an atom of oxygen, sulphur, selenium, etc.

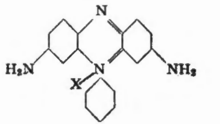
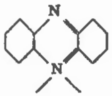
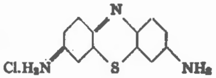
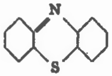
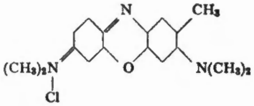
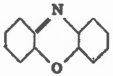
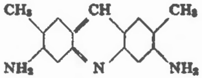
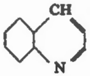
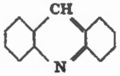
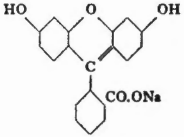
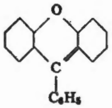
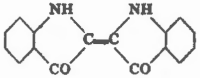
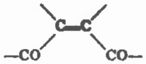
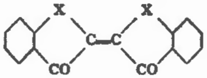
A. *Derivatives with a 6 atomic nucleus.* These are principally *pyridine* and *piperidine* (or hexahydropyridine). Pyridine is the organic base found in many vegetable alkaloids. The homologues of pyridine (*picolines*) are the result of substituting the nuclear hydrogens with alkyl radicals.

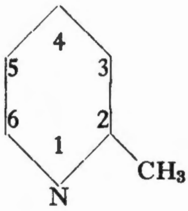

Benzene


Pyridene

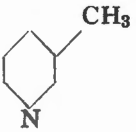

Piperidine

Group	Example	Chromophore	Chromogene	Auxochrome
Nitro dye	Trinitrophenol 	$-NO_2$		$-OH$
Nitroso dye	p-nitrosodimethylaniline 	$-NO$		$-N(CH_3)_2$
Azo dye	Aminoazobenzene 	$-N{=}N-$		$-NH_2$
Hydroxyketone	Alizarine yellow 	$-CO-$		3 OH
Anthroquinone dyes	1:2 dihydroxyanthraquinone 	$-CO-$ $-CO-$		2 OH
Iminodiphenyl-methane	Auramine 	 $-\underset{NH}{\overset{\mid}{C}}-$		$-N(CH_3)_2$
Triphenyl methane	Aurine 			$-OH$
	 Crystal violet			$2(N(CH_3)_2)$
Quinone imide	 Indophenols			$(CH_3)_2N-$
	 Indamines			

Group	Example	Chromophore	Chromogene	Auxochrome
Azines	Safranines 			2 NH$_2$
Thiazines	Lauth violet 	=N— —S—		2 NH$_2$
Oxazines	Capri blue 	=N— —O—		2 NR$_2$
Quinoline Acridine	Acridine yellow 	=CH— =N—	 	2 NH$_2$
Pthalein	Fluoresceine 	—O—  $-\underset{\mid}{C}=$		2 OH CO.ONa
Indigos	Indigo 			2 NH

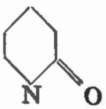


2-methypyridene
or α-picoline



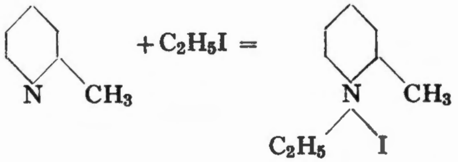
3-methylpyridene
or β-picoline

4-methylpyridene
or γ-picoline



Pyridone

The pyridine bases when oxydized yield the *pyridones*. By treating with alkyl iodides or bromides, crystalline addition compounds such as pyridine ethiodide are obtained:

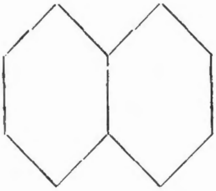


Ethyliodide

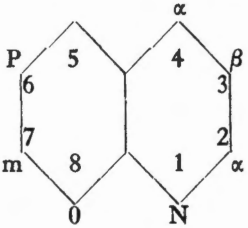
α-picoline

Piridine ethiodide

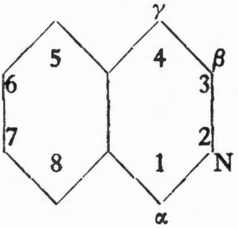
Quinoline bases. Quinoline is a nitrogenous base corresponding to naphthalene, and has an isomer, *isoquinoline*. The alkyl derivatives of quinoline are *quinaldine* (substituted in the α position) and *lepidine* (substituted in the γ position) and the alkoxy compounds such as p-ethoxyquinaldine.



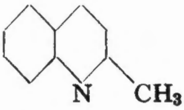
Naphthaline



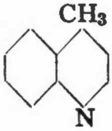
Quinoline



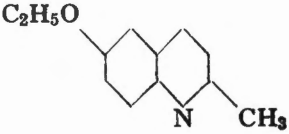
Isoquinoline



Quinaldine
or α-methylquinoline

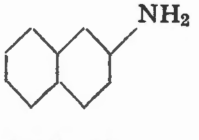


Lepidine
or γ-methylquinoline

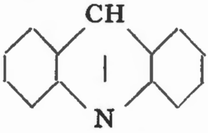


p-ethoxyquinaldine

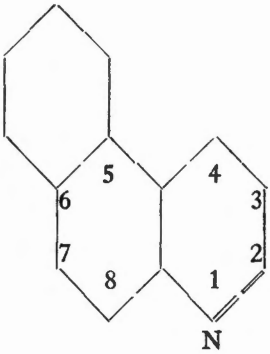
If the benzene nucleus in quinoline is replaced by a naphthaline nucleus, the *naphthoquinolines* are obtained, such as β-naphthoquinoline obtained from β-naphthylamine. Similarly, *β-naphthoquinaldine* can be obtained.



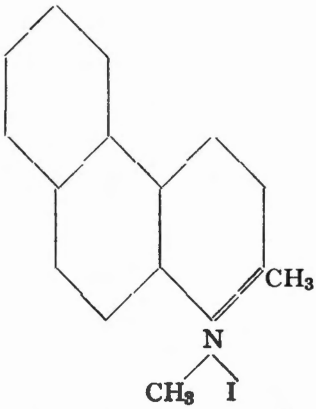
Naphthylamine



Acridine



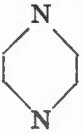
β-naphthoquinoline



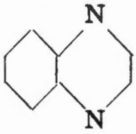
Methyliodide of β-naphthoquinaldine

Corresponding to anthracene is the heterocyclic base: *acridine*. The quinoline and acridine bases form, like the pyridines, the alkyl iodides in which the nitrogen is pentavalent; for example β-naphthoquinaldine methiodide.

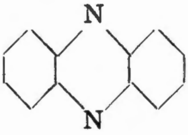
Diazines. By replacing, in a benzene hydrocarbon, two CH groups by *two* nitrogen atoms, three *diazines*, ortho, meta or para are obtained. p-diazines include the *pyrazines*, the *quinoxalines* and the *phenazines*. A m-diazine, *quinazoline*, corresponds to quinoline.



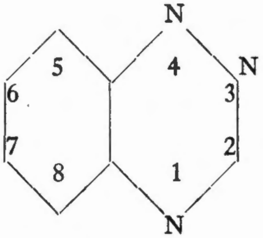
Aldine
or parazine



Quinoxaline



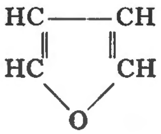
Phenazine



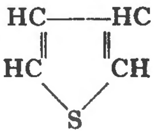
Quinazoline

Benzopyrilium. The pyrilium nucleus is similar to that of pyridine in which the nitrogen atom has been replaced by an oxygen atom. Benzopyrilium corresponds to quinoline.

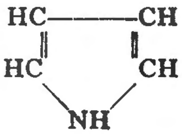
B. 5 *atomic nuclei.* A large number of compounds analogous to the aromatic compounds are related to *furfurane*, to *thiophene* and to *pyrrol* containing 4 carbon atoms which can be considered as benzene in which a —CH=CH— is replaced by O, S or NH.



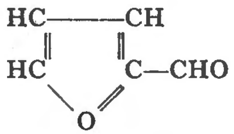
Furfurane



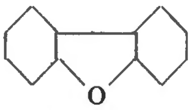
Thiophene



Pyrrol

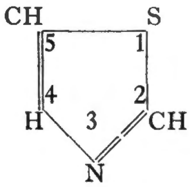


Aldehyde pyromucic

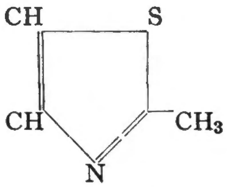


Dibenzoylfurfurane
or oxide of diphenylene

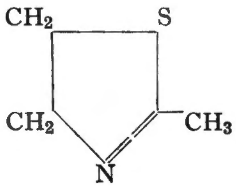
By replacing a —CH= group by nitrogen in the nucleus of thiophene, a *thiazole* is formed, a very important base having properties similar to those of pyridine. The methyl derivatives are principally 2-*methylthiazole* and 2-*methylthiazoline* (hydrogenated methylthiazole). *Benzthiazole* corresponds to quinoline, and its methyl derivative is 2-*methylbenzthiazole*, whilst the α and β-*naphthothiazoles* correspond to naphthoquinoline.



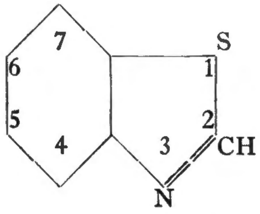
Thiazole



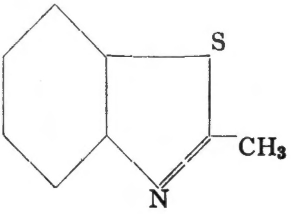
2-methylthiazole



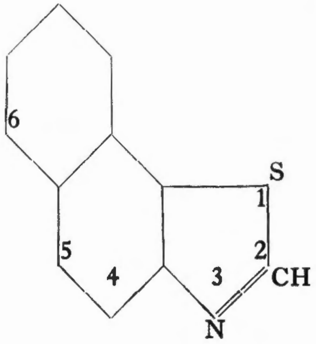
2-methylthiazoline



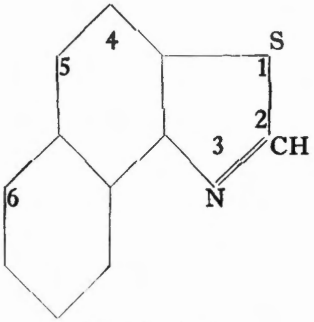
Benzthiazole



2-methylbenzthiazole

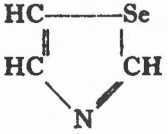


α-naphthothiazole

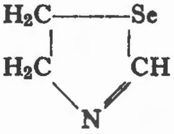


β-naphthothiazole

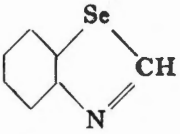
Starting with selenium or tellurium compounds the *selenazoles* and the *tellurazoles* can be prepared following the same scheme. By substituting oxygen for sulphur, the *oxazoles* are formed.



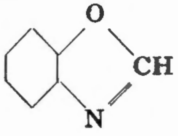
Selenazole



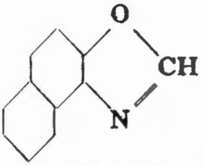
Selenazolene



Benzoselenazole

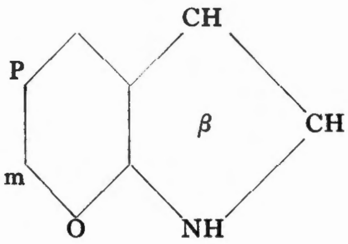


Benzoxazole

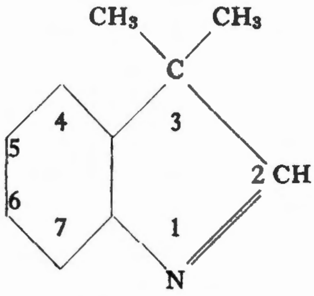


β-naphthoxazole

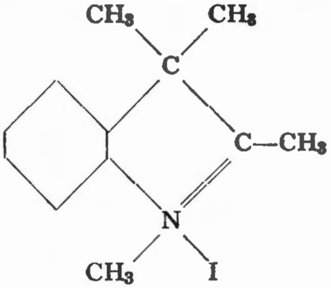
Indole. The pyrrol corresponding to naphthalene is *indole* which gives the indoline derivatives such as ββ-dimethylindoline, which forms addition compounds with the alkyl halides in the same way as the quinoline, thiazole, selenazole and oxazole bases; for example, αββ-trimethylindoline methiodide is obtained by reacting methyl iodide with αββ-trimethylindoline:



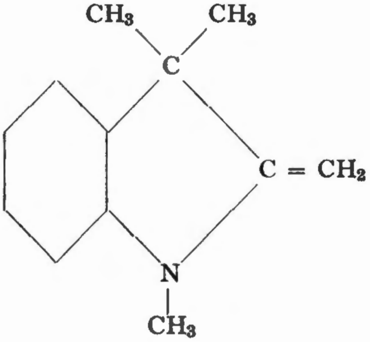
Indole



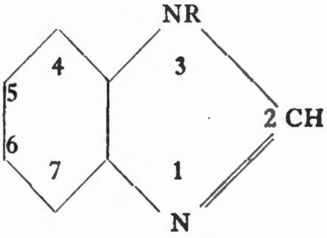
ββ-dimethylindolene



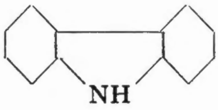
Methyliodide of αββ-trimethyl-indolene



Fischer's Base



Benziminazole



Carbazole

Benziminazole: this nucleus, containing two nitrogen atoms is similar to indoline in which the $=C(CH_3)_2$ is replaced by $=N—R$.

Carbazole is a pyrrol containing two benzene rings—one on each side of the NH group.

Important note.—The numbering of thiazoles (and other 5 atomic heterocyclic nuclei) can be done in two different manners:

(*a*) The *1* position corresponds to the sulphur atom, the nitrogen being in the *3* position.

(*b*) The *1* position corresponds to the central carbon atom, and the *2* position to the nitrogen atom.

The first method (*a*) *is now commonly used in English language literature*, and therefore approved by the translator. The second method (*b*) is used in the French edition, because it is found in all fundamental works on cyanines (even in English).

This dualism of numbering systems can bring some confusion when reading original texts.

Concerning α- and β-naphthothiazoles, some writers put α for β and β for α.

665. General constitution of the cyanines

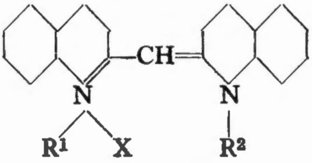
The action of alkali on the α-methyl alkiodides of the heterocyclic bases produces dyestuffs—the *cyanines*.

The sensitization of the silver halides by the cyanines is dependant on their molecular structure. The sensitization maximum is a function of their spectral absorption, that is to say their colour. Thus the yellow cyanines sensitize in the blue, the red cyanines in the green whilst the blue ones sensitize in the red.

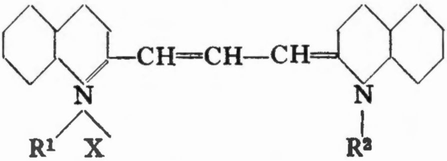
The essential constitution of the cyanines is *two heterocyclic nuclei* (which have just been described) joined by a *carbon chain*. This carbon chain is of the form —CH=(CH—CH=)$_n$. Schematically this is

$$\left[\begin{array}{c}\text{Heterocyclic nucleus}\\\text{containing pentavalent}\\\text{nitrogen}\end{array}\right]\text{—CH=(CH—CH=)}_n\left[\begin{array}{c}\text{Heterocyclic nucleus}\\\text{containing trivalent}\\\text{nitrogen}\end{array}\right]$$

where n is 0, 1, 2, 3, 4, 5. The nuclei are attached to the chain *via* their α or γ carbon atoms. Depending on the length of the chain there will be a *simple cyanine* with a single —CH= or a *carbocyanine* where n is different from 0.



Cyanine quinolic



Carbocyanine quinolic

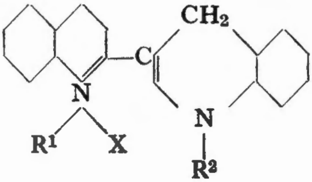
It will be noted in these formulas that there are two nitrogen auxochromes which are called the *positive centres* linked by a chain of chromophoric *vinyl groups*. In the simple cyanine the chain is

$$\equiv N{=}\overset{|}{C}{-}CH{=}\overset{|}{C}{-}N{=}$$

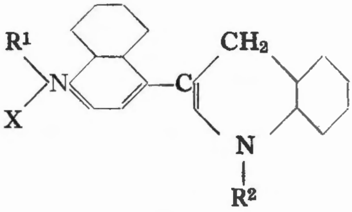
and in the carbocyanine,

$$\equiv N{=}\overset{|}{C}{-}CH{=}CH{-}CH{=}\overset{|}{C}{-}N{=}$$

In a particular case, the —CH= link is absent, and the two nuclei are attached directly to each other, giving the *apocyanines*⁽¹⁾—weak sensitizers and products of secondary reactions.



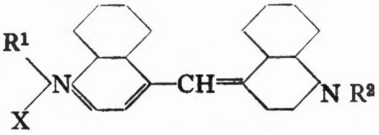
Xantho-apocyanine



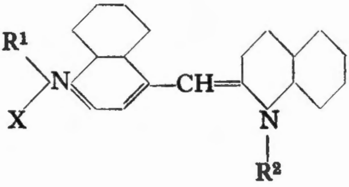
Erytho-apocyanine

The thiazole, selenazole, oxazole and indoline bases can, because of their constitution, have only one position in which the carbon chain is attached. This is the carbon atom adjacent to the nitrogen and is always the linking position. This is not the case with the quinoline and pyridine bases, where the reactive methyl group can be equally well in the α (or 2) position or the γ (or 4) position; there are therefore three possible combinations:

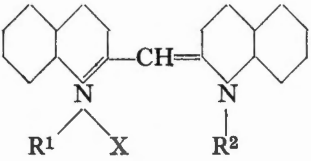
Two nuclei attached in 4: '*true*' *cyanines.*
One nucleus in 4 and the other in 2: *isocyanines.*
Two nuclei in position 2: *pseudocyanines.*



True cyanine



Isocyanine



Pseudocyanine

The alkyl radicals attached to the nitrogen atoms influence the sensitizing properties; thus an ethyl dye may be a powerful sensitizer whilst the same compound, but containing methyl groups, may be devoid of any action. With the carbocyanines, stronger sensitizing action is produced if the alkyl radical is substituted by a *hydroxyalkyl* group such as $—CH_2—CH_2 . OH$. To do this, the heterocyclic base is reacted with 2-iodo-ethanol$I . CH_2—CH_2 . OH$. The fog level of the sensitized emulsion is reduced at the same time.

The nature of the acid radical has a less pronounced effect; this radical affects only the solubility. Cyanines are used as the iodides, chlorides, nitrates, chlorates, methylsulphates and p-toluene sulphonates.

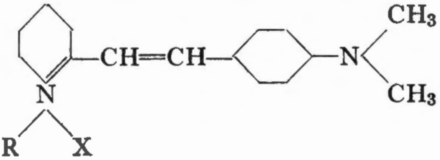
Although the presence of the radicals RX attached to the nitrogen are absolutely essential to the formation of a sensitizer, the lateral linkages introduced into the nucleus are not indispensable; they result, however, in the modification, in one way or another, of the photographic properties. Frequently, an increase in the complexity of the molecule results in a loss of sensitizing properties. This is also the case when the methine chain is substituted.

666. Hemicyanines

A second group of sensitizing dyes related to the cyanines having a single nucleus, generally aromatic, linked *via* a carbon chain of the form $(—CH{=}{=}CH)_n$— (*styryl chain*)

[Heterocyclic nucleus with pentavalent nitrogen] $(—CH{=}CH—)_n$ [Aromatic nucleus]

The *pinaflavols* are hemicyanines with the general structure:



Pinaflavol

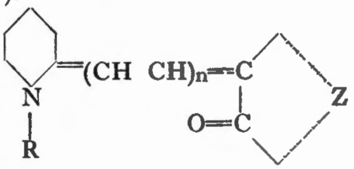
Beside the hemicyanines containing a single nitrogenous heterocyclic nucleus in the α position, is another series of dyes, each of which is formed by the union of two halves of a polycarbocyanine, the two portions of the methylene chain being joined by an auxiliary link $-\mathrm{CO}-$ or $-\mathrm{NH}-\mathrm{C_6H_4}-$ $-\mathrm{NH}-$. In the former case the nuclei have trivalent nitrogen atoms, and in the latter, pentavalent nitrogen:

$$\left[\begin{array}{c}\text{Heterocyclic base}\\\text{with trivalent}\\\text{nitrogen}\end{array}\right]\!=\!\mathrm{CH}-(\mathrm{CH{=}CH})_n-\mathrm{CO}-\begin{array}{c}\\-(\mathrm{CH{=}CH})_n-\mathrm{CH}=\end{array}\left[\begin{array}{c}\text{Heterocyclic base}\\\text{with trivalent}\\\text{nitrogen}\end{array}\right]$$

$$\left[\begin{array}{c}\text{Heterocyclic base}\\\text{with pentavalent}\\\text{nitrogen}\end{array}\right]\!-(\mathrm{CH{=}CH})_n-\mathrm{NH}-\mathrm{C_6H_4}-\begin{array}{c}\\-\mathrm{NH}-(\mathrm{CH{=}CH})_n-\end{array}\left[\begin{array}{c}\text{Heterocyclic base}\\\text{with pentavalent}\\\text{nitrogen}\end{array}\right]$$

667. Merocyanines

If, instead of the heterocyclic base with pentavalent nitrogen, there is a nucleus with trivalent nitrogen, the chain must be of the type $=(\mathrm{CH}-\mathrm{CH})\underset{n}{=}$. The dyes having this structure are called *merocyanines*. The other end of the carbon chain is attached to a nucleus or aliphatic radical which originally contained a reactive methylene group $-\mathrm{CH_2}-$ adjacent to $>\mathrm{C{=}O}$ (see para. 697):

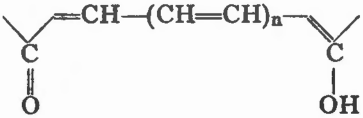


Merocyanine

The most familiar merocyanines are the *rhodacyanines*, derived from rhodanine.

668. Oxanols

Whereas the merocyanines have one nucleus with a nitrogen atom and one nucleus with a CO group, the *oxanols contain a CO group in both nuclei.* One of these keto groups is in enolic form:



669. Azacyanines

The introduction of one or two nitrogen atoms in the methine chain of the cyanines or hemicyanines gives rise to the *azacyanines.*

The azacyanines corresponding to the simple cyanines have the linkage —N= in place of —CH=.

The azacyanines corresponding to the carbocyanines have the chains —N=CH—N= or —CH=N—N= in place of —CH=CH—CH=.

The azacyanines corresponding to the hemicyanines have the chain —N=CH— in place of —CH=CH—.

670. Resonance

The photographic sensitization region of a cyanine corresponds to the region of absorption of coloured light. Thus a blue dye, whose principal absorption band is in the red, sensitizes to the latter colour. The sole difference is that *the sensitization maximum is generally found to be displaced about* 30 $m\mu$ *towards the longer wavelengths* compared with the absorption maximum.

It would therefore be useful to forecast the absorption of a dye, and therefore its sensitization region merely by examining its chemical constitution.

The dyestuff molecule contains two principal auxochromic centres joined by a *chain* of greater or lesser length composed of the chromophoric elements. The positive and negative charges of the atoms of this chain mutually and symmetrically neutralize each other. But the greater the distance between the conjugated atoms, the greater the polarization opposing their neutralization. The electrons of the extreme atoms vibrate at a lower frequency, as the distance between them increases. These frequencies correspond to those of the absorbed radiations. The longer the chain separating the two positive centres, the further towards the longer wavelengths are the absorption bands; by increasing the distance, the compound passes successively through the colours yellow, orange, red, violet, blue, green, complementary to the absorption bands.

The dyestuff molecule can then be likened to an electronic oscillatory system in resonance, whose frequencies of vibration determine the isochronus frequencies of the absorbable radiations. The mobile electrons of the outermost orbit of the atoms are the only ones which take part in this vibratory movement, combined with the rotation of the complete molecules, whose change from one state of activation to another is done by quanta. The frequencies of the atomic vibrations are not pure, as the neighbouring atoms also vibrate.

As the cyanines contain chains of conjugated double bonds, the electrons from a terminal atom travel the length of the molecule by *successive transfer*. Different wavelengths of absorption each correspond to the different lengths of travel through the molecule, the longest wavelength resulting from the longest path. This happens in the most extended form of the molecule. The shorter wavelengths are due to coiled forms or to incomplete migration in the transfer of electrons.

Sheppard, Lambert and Walker have shown(2) that the resonance phenomena necessitate, for their favourable development, a flat form of molecule accompanied by a polar vibration in the plane of the molecule. Under these conditions, the cyanines are considered as linear oscillators, it consequently seems that a plane configuration necessitates a minimum intranuclear distance of 1·6 Å. Thus for an isocyanine this distance is 2·7 Å with an intermediate link at 120°, whilst a planar structure for the pseudocyanines necessitates a deformation of the chain (or mesochrome) to increase this distance from 2·4 to 3·4 Å.

For the resonance system to attain a high degree of perfection it is necessary for a complementary ionic charge to be always available. This is made possible by the mobility of the links in the conjugated chain. The intensity of absorption, and consequently the intensity of colour, are always greater when the resonance is more perfect.

The resonance passes through two extreme molecular states of the same internal energy. If the two structures are not identical, the molecule tends towards a more stable form and the ease of resonance is diminished, which leads to a weakening of the colour. The molecular structures which are favourable for optimum resonance appear when the + and − charges are distributed between the substituents on one hand and the chain on the other; Thus, for example, there is a bathochromic effect (displacement of the colour towards the blue) when the positive charge is on a substituent R_2N— and the negative charge on the chain.

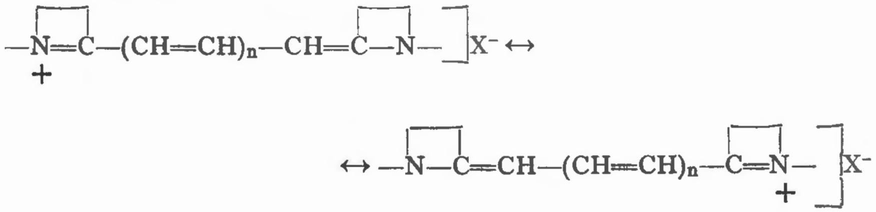
671. Comparative structures of cyanines, oxanols and merocyanines

The difference between cyanines, oxanols and merocyanines is essentially an electric one.

Cyanines are *cations*, therefore basic.
Oxanols are *anions*, therefore acid.
Merocyanines are not externally ionized, they are *neutral.*

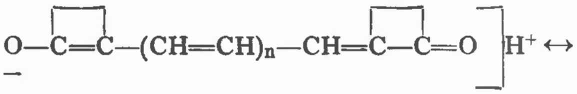
The resonance structures of these three groups can be represented by the following schemes:

Cyanines: two reversible structures of an ammonium ion:

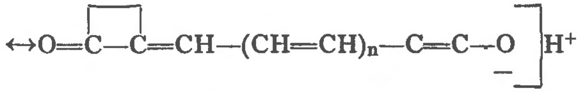


$$\left[-\underset{+}{N}=C-(CH=CH)_n-CH=C-N-\right]X^- \leftrightarrow \left[-N-C=CH-(CH=CH)_n-C=\underset{+}{N}-\right]X^-$$

Oxanols: two structures caused by ketomethylenic nuclei:

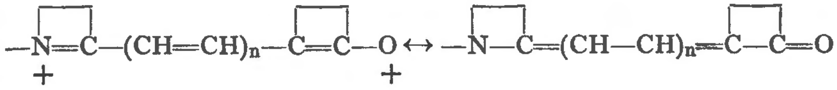


$$\left[\underset{-}{O}-C=C-(CH=CH)_n-CH=C-C=O\right]H^+ \leftrightarrow$$



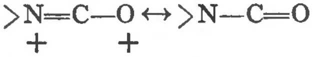
$$\leftrightarrow O{=}C{-}C{=}CH{-}(CH{=}CH)_n{-}C{=}C{-}\overset{-}{O}\Big]H^+$$

Merocyanines: These dyes are hybrids, formed by the above two types; so, they can be considered as '*internal ionoids*', when in one of the two states:



$$-\underset{+}{N}{=}C{-}(CH{=}CH)_n{-}C{=}C{-}\underset{+}{O} \leftrightarrow -N{-}C{=}(CH{-}CH)_n{=}C{-}C{=}O$$

This system is similar to the amide system:



$$>\underset{+}{N}{=}C{-}\underset{+}{O} \leftrightarrow >N{-}C{=}O$$

672. Calculation of the absorption bands

Supposing that the electrons from the atoms of the two positive centres describe elliptical-trajectories round these two centres (Fig. 114), the wavelength λ of the radiation absorbed, is given by the formula $\lambda = 112a^{\frac{3}{2}}$ $(1{\cdot}249{-}0{\cdot}79\ c/a)$ where a represents half the major axis of the ellipse and c half the distance between the two positive centres.⁽³⁾

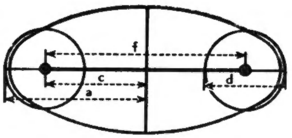


FIG. 114.

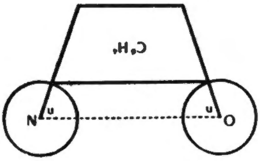


FIG. 115. p-aminophenol.

2. *Examples*. To calculate the position of maximum absorption of *p-aminophenol* OH . C_6H_4 . NH_2 (Fig. 115): the trapezium represents schematically the C_6H_4 group of benzene whose complete configuration is that of a *skew hexagon* formed from two trapeziums. The distance nn′ = 2c which will be 3·82 Å for benzene and 4Å for p-aminophenol. The diameter d of the O and N atoms being 1·3 Å gives: 2a = 2c+d = 4+1·3 Å = 5·3 Å, and a = 2·65 Å. By applying the preceding formula the result is $\lambda = 315$ mμ. The observed absorption maximum is in fact 315 mμ.

Indophenol and indamine are represented by the diagram in Fig. 116; the two benzene rings must have between them an angle of 155 to 160°; one therefore has 2c = 7·85 Å and 2a = 9·26 Å values which can be put in the preceding formula.

To explain the colour of the triphenylmethane dyes, malachite green, crystal violet, or fuchsine, an elliptical orbit identical to that of dihydroxybenzohydrol is assumed.

Indigotine represented by the diagram in Fig. 117, has an observed absorption maximum at 600 mμ. The calculated one is only 550 mμ. This difference appears to be due to the very oblique relative position of the phenyl groups.

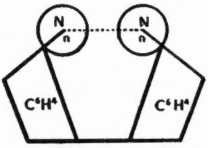


FIG. 116. Indamine.

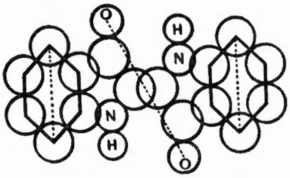


FIG. 117. Indigo.

3. *Graphical representation.* If the dimensions of the diameters of the positive centres are fixed, the wavelength λ depends only on the distance c. The formula then becomes

$$\lambda = 51{\cdot}4\,(c+1{\cdot}77)\sqrt{c+0{\cdot}65}$$

By plotting the curve x = λ and y = 2c a straight line is obtained in practice (Fig. 118) where the marked points correspond to different substances.

The calculation shows that no absorption band lower than 138 mμ is possible, for at this limit there is contact between the two atoms. In the following table are noted the absorptions corresponding to different values of the distance 2c:

2c in Å	λ in mμ	2c in Å	λ in mμ
1·3	138	6·0	469
2·6	218	6·5	509
3·9	308	7·0	550
4·5	352	7·5	596
5·0	390	8·0	641
5·5	429		

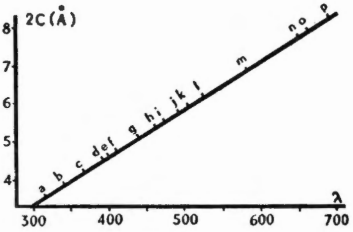


FIG. 118

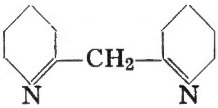
(a) p-aminophenol, p-phenylene diamine;
(b) p-dicetohexamethylene;
(c) quinone-imine;
(d) p-hydroxyazobenzene (ion);
(e) p-nitrophenol (in alkaline medium);
(f) p-nitrosophenol (in alkaline medium);
(g) p-hydroxyazobenzene (alkaline medium);
(h) p-nitrophenylhydrazine (alkaline medium);
(i) p-hydroxyazobenzene (acid medium);
(j) aminoazobenzene (acid medium);
(l) dihydroxyphenazine;
(m) resorufine;
(n) indophenol;
(o) indamine;
(p) quinhydrone.

4. *Absorption of the cyanines.* When the dyestuff molecule contains groups which themselves are inactive, an appreciable bathochromic effect can be produced, the displacement of the absorption band towards the longer wavelength being as much as 10%.

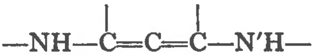
The spectrum of the cyanines generally contains two adjoining absorption bands. The relation between the two maxima is always equal to 1·065.

When passing from a pseudocyanine to an isocyanine then to a true cyanine, a successive deepening of colour is observed, the absorption bands being shifted towards the red. The relationship of the displacement is each time by coincidence 1·065.

Let us examine 2-*dipyridylmethane* which is an almost colourless compound.

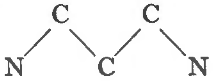


Activated by acetic acid in weak alcoholic solution it has a chain with the following constitution:



$$—NH—\overset{|}{C}=C=\overset{|}{C}—N'H—$$

With a deep yellow colour, its absorption bands are therefore situated at 399 and 422 mμ. The value of λ given to this chain is 415 mμ. Now if this is related to the above graph it is found that 2c = 5·33 Å corresponds to 415 mμ. If the 5 atoms are placed in a straight line the distance between the two active centres N and N′ will be 5·92 Å but with the atoms arranged at an angle of 125° 16′ following the scheme



the distance 2c becomes 5·26 Å which is nearly the value shown above: the central carbon atom is almost in a straight line with the two nitrogen atoms (Fig. 119).

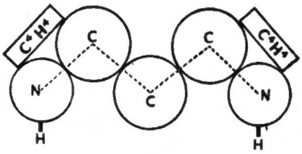


FIG. 119. 2: 2′-dipyridylmethane.

With 2:4′-*dipyridylmethane* the form of the chain is appreciably changed due to the second nitrogen atom being more remote (Fig. 120).

The diagram for the quinolyl cyanines is the same as that of the pyridyl cyanines, the group C_4H_4 being substituted by the group C_8H_6.

The position of the absorption maximum for 2:2′-*diquinolylmethane*, activated by a weak acid, is obtained by multiplying that of 2:2′-*dipyridylmethane* by the factor 1·221.

The absorption maximum of the *pseudocyanines* is almost equal to that of activated 2:2′-diquinolylmethane.

The absorption maximum of the *isocyanines* is equal to the product of that for the pseudocyanines and 1·065.

The weighting of the molecule with aromatic nuclei or with side chains results in a deeper colour. In the other direction, *the substitution of —CH=CH— groups in the nucleus by selenium, sulphur or oxygen produces (in order of increasing action) a hypsochromic effect,* that is to say, a displacement of the absorption towards the shorter wavelengths. In this case it produces a deformation of the chain angles which bring the two positive centres nearer together; the distance 2c therefore becomes about 4·2 Å for a *thiacyanine* instead of 5·3 Å for the corresponding quinolyl cyanine. If the molecule is weighted the angle becomes greater.

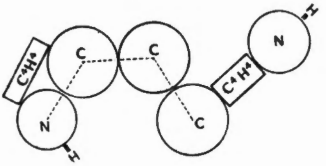
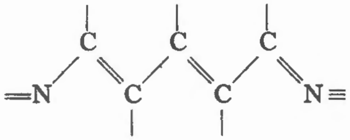


FIG. 120. 2 : 4′-dipyridylmethane.

With the *carbocyanines* and *polycarbocyanines* the chain, which can be long, has a zig-zag structure as with the simple cyanines. The angles are 125° 16′ except for one of them which is smaller:



The distance 2c is about 6 Å for the 2:2′-carbocyanines.

To obtain, approximately, the maximum absorption of a *dicyanine* (or 2:4-carbocyanine) the figure for the 2:2′-carbocyanine must be multiplied by the coefficient 1·08.

The absorption maximum of a *kryptocyanine* (or 4:4′-carbocyanine) is equal to that of the dicyanine multiplied by 1·08.

In fact, the absorption maxima of pinacyanol (2:2′-), dicyanine (2:4′-) and kryptocyanine (4:4′-) are, respectively, 607 mμ, 657 mμ and 711 mμ.

The effect of substituents in the carbon chain is very variable, depending on the nature of the substituent and the position of substitution; frequently the colour is lightened, particularly with alkyl radicals.

5. To sum up, the colour of a cyanine depends upon the following factors.

(*a*) *The length of the chain* between nuclei; the longer the chain, the further is the absorption (and therefore the sensitization) situated towards the longer wavelengths (red and infra red). The displacement is about 100 mμ for each additional —CH=CH— group.

(*b*) *The position of the nucleus* whose effect is to modify the length of the chain between the two nitrogen atoms; the 2:2′ cyanines have absorptions at a shorter wavelength than the 2:4′-cyanines which are themselves lighter than the 4:4′-cyanines.

(*c*) *The nature of the nucleus.* The shorter wavelengths are obtained with the oxazoles, then the selenazoles, the indolines and the thiazoles. The quinolines are the most bathochromic, but the pyridines are less so.

(*d*) *The size of the nucleus.* The hypsochromic effect due to sulphur or oxygen can be offset by the introduction into the molecule of naphthalene nuclei (naphthothiazoles or naphthoxazoles) or even anthracene.

(*e*) *Substitutions of the chain* have a very variable effect (see thiacarbocyanines).

(*f*) *Substitution of the nucleus* has but a slight bathochromic effect. Mainly the sensitizing properties of the dye are affected.

Thus, for example, the introduction of a CH_3 group or an alkoxy group such as CH_3O into one or both nuclei of a thiacyanine is favourable only in positions 4 (or ortho) and 6 (or para). A dialkylamino group such as $(CH_3)_2N$, must, on the contrary, be placed in position 5 (or meta) otherwise the sensitizing power is reduced.

The phenyl group C_6H_5, which is beneficial to sensitizing, must be introduced in the 6- position.

(*g*) *The assymetry of the dye with different nuclei.* The wavelength of maximum absorption is the arithmetic mean of the absorption maxima of the two corresponding symmetrical dyes. However, substituents of different polarities bring about a hypsochromic displacement with respect to this mean. For the carbocyanines this displacement is usually less than 3 mμ. It is 6·5 to 30 mμ if one of the nuclei is an N-ethyl-indoline. The difference is further increased if one of the nuclei is very slightly basic.

Merocyanines. The calculation of the absorption bands of merocyanines can be done, following the mathematical technique of W. T. Simpson.(4)

The position of the absorption maximum depends on the solvent polarity. Brooker(5) has shown that the shift of this maximum is a function of the dye stability. When the dye is slightly stable, due to a weak polarity, the shifts are ample: in water, the maximum is shifted towards the red portion of the spectrum. When the dye is quite stable, there is no appreciable change, except in high polarity solvents, like water. The maximum displacement is increased by long chains. For instance, between a pyridine solution and a water solution of the same dye, there is a difference of 36·5 mμ when $n = 0$, 80 mμ when $n = 1$, and 140 mμ when $n = 2$.

1. See Kaufman and Strubin: *Ber.*, 1910, **44**, 690; Mills and Ordisch: *J.C.S.*, 1928, 81.
2. Sheppard, Lambert and Walker: *Jl. Chem. Phys.*, 1941, 96.
3. See, on this subject: Moir, *J.C.S.*, 1924, **125**, 1134 and 1548; 1925, **127**, 967 and 2338.
4. Simpson W. T.: *J.A.C.S.*, 1951, 5359–5363.
5. Brooker L. G. S. and others: *J.A.C.S.*, 1951, 2332–5350.

Chapter XXXVI

INTERMEDIATES USED IN THE PREPARATION OF SENSITIZING DYES

673. Quinoline bases

The principal quinoline bases used in the preparation of cyanines are quinoline, quinaldine, toluquinaldine, the alkoxyquinolines and quinaldines, naphthoquinoline and quinaldine.

Quinoline is obtained by Skraup's general method, which is to heat aniline with glycerin and sulphuric acid to 140°C in the presence of an oxidizing agent such as arsenic acid or nitrobenzene; the reaction can be catalyzed with vanadium oxide. The glycerin is dehydrated to acrolein $CH_2{=}CH{-}{-}CHO$, which combines with aniline to give β-anilino-acrolein $C_6H_5{-}NH{-}CH{=}CH{-}CHO$, then its anilide, $C_6H_5{-}NH{-}CH{=}CH{-}CH{=}N{-}C_6H_5$. This is cyclized to quinoline with the elimination of aniline.

Lepidine or γ-methylquinoline is obtained by heating aniline with hydrochloric acid and formaldehyde in acetone, the neutralized reaction product being then treated with acetic anhydride. By replacing the aniline by p-toluidine $CH_3{-}C_6H_4{-}NH_2$, tolulepidine or 4:6-dimethyl-quinoline is obtained. Acetone condenses with the formalin to give an ethylene ketone $CH_3{-}CO{-}CH{=}CH_2$, which in turn condenses with the aniline in the presence of HCl giving the compound $C_6H_5{-}NH{-}CH{=}CH{-}CO{-}CH_3$. The latter is dehydrated with aetic anhydride and is cyclized to lepidine.

Quinaldine (2-methylquinoline) is prepared by heating a mixture of aniline and paraldehyde in the presence of hydrochloric acid and nitrobenzene, following the technique of Mikeska, Stewart and Wise,⁽¹⁾ an improvement on that of Dobner and Miller.⁽²⁾

Toluquinaldine (6-methylquinaldine). This quinaldine derivative is obtained by the same method: p-toluidine $CH_3{-}C_6H_4{-}NH_2$, and concentrated hydrochloric acid are heated with paraldehyde. The ether-washed solution is made alkaline with soda. The oil which separates is extracted with ether, and diazotized, the diazonium compound being decomposed by heating. The p-toluquinaldine separates from the solution as a solid when made alkaline. This is washed with ether and distilled at 266°C to give crystals M.Pt. 55°C. Yield 40–45%.

p-ethoxyquinaldine. p. phenetidine, $C_2H_5O{-}C_6H_4{-}NH_2$, is condensed with acetaldehyde in the presence of concentrated hydrochloric acid. The p-phenetidine is obtained by reducing the ether corresponding to p-nitrophenol. Another method is to alkylate hydroxyquinaldine obtained by heating p-aminoquinaldine with concentrated hydrochloric acid. Gategunst and Gray obtained a complete range of homologues.⁽³⁾

6:7-*methylenedioxide-quinaldine*. Nitrated piperonal is condensed with acetone: the resulting lactylketone is reduced with zinc and acetic acid.

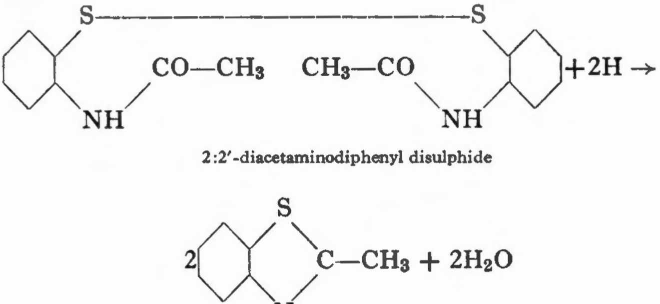
β-naphthoquinoline. Knupel's method:⁽⁴⁾ a mixture of 100 g β-naphthylamine, 215 g glycerin, 100 g arsenic acid and 250 g concentrated sulphuric acid, is heated cautiously in an oil bath for four hours. The mass is diluted with water, filtered and made alkaline. The base separates and is taken up in alcohol, again precipitated by water and recrystallized from alcohol as the hydrochloride, by the action of hydrogen chloride gas. M. Pt. 93°C, yield 92 g.

β-naphthoquinaldine. Preparation similar to that of quinaldine:⁽⁵⁾ one part of β-naphthylamine, one part of paraldehyde and two parts of concentrated hydrochloric acid are heated to 100–110°C. The solution is made alkaline, and the product which separates on cooling is extracted with warm ether; after recrystallizing from alcohol the M. Pt. is 82°C.

674. Benzthiazoles

Benzthiazole is obtained by Molhau's method⁽⁶⁾ which is to heat dimethylaniline with sulphur, or by Reissert's method, via benzthiazole-carbonic acid.⁽⁷⁾

2-*methylbenzthiazole* (or μ-methylbenzthiazole). One method starts from diphenylamine disulphide (or 2:2′-diaminodiphenyl) $NH_2—C_6H_4—S—S——C_6H_4—NH_2$ which is prepared by heating aniline with sulphur.⁽⁸⁾ By boiling this disulphide with acetic acid and anhydride for 5 hours, 2:2′-diacetaminodiphenyl disulphide is produced. This is reduced with sodium hydrosulphite in boiling alcohol and cyclizes as follows:



2:2′-diacetaminodiphenyl disulphide

2-methylbenzthiazole

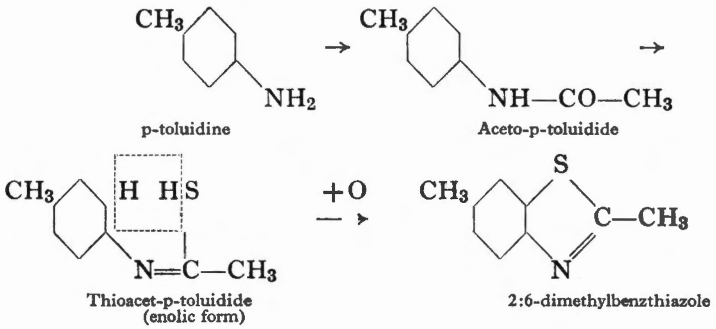
The usual method of preparing 2-methylbenzthiazole is to heat acetanilide $C_6H_5—NH—CO—CH_3$ with phosphorus pentasulphide P_2S_5: this gives the thioacetanilide which is oxidized with potassium ferricyanide, and cyclizes to methylbenzthiazole.⁽⁹⁾

Thioacetanilide. Place 108 g acetanilide and 600 cc benzene in a 3-litre flask. Dissolve by heating on the water-bath and keep the solution boiling gently. Add 66 g powdered phosphorus pentasulphide in five portions at five-minute intervals. A viscous mass is formed. After the final addition, continue heating for a further 20 minutes and cool. The benzene solution is filtered and added slowly to: water 1000 cc, soda lye, 30%, 200 cc. Stir for 15 minutes. Separate the aqueous layer, and filter after adding activated charcoal. The thioacetanilide is precipitated by slowly adding 140 cc acetic acid with cooling and vigorous agitation. It is sucked off, washed with a little water and dried. Yield 57 g.

The formation of a solid mass at the bottom of the flask is avoided by mixing the phosphorus pentasulphide with 47 g powdered calcium carbonate.

Oxidation of the thioacetanilide. 236 g thioacetanilide is dissolved in 1960 cc of 30% soda lye diluted with 6300 cc water. It is cooled by adding 1500 g ice and poured into a solution of: potassium ferricyanide 1160 g, water 4100 cc, ice 4000 g. The temperature is kept below 0°C and stirring is continued for 75 minutes, then 300 cc ether and a paste of filter paper are added. It is filtered on the Buchner and the methylbenzthiazole is extracted with two lots of ether (3000 cc and 1400 cc). The ether solution is evaporated, and the residue is steam distilled for 6 hours. The oily liquid in the receiver is then extracted three times with ether to remove the base which is finally purified by distillation (235–237°C). The steam distillation residue is again treated, and distilled with the low and high distillation fractions.

2:6-dimethylbenzthiazole is obtained by oxidizing thioacet-p-toluidide with potassium ferricyanide following the general method⁽¹⁰⁾



p-toluidine

Aceto-p-toluidide

Thioacet-p-toluidide (enolic form)

2:6-dimethylbenzthiazole

Thioacet-p-toluidide is prepared like thioacetanilide using phosphorus pentasulphide. It can also be obtained by the action of hydrogen sulphide on the imino chloride corresponding to the acetotoluidide⁽¹¹⁾ or by treating aceto-p-tolylamidine with carbon disulphide.⁽¹²⁾

6-ethoxy-2-methyl benzthiazole from p-phenetidine $C_2H_5O—C_6H_4—NH_2$, via the acetophenetidide to the thio derivative with phosphorus pentasulphide and cyclized with ferricyanide.⁽¹³⁾ The methoxy derivative is prepared as follows.

6-methoxy-2-methylbenthiazole: 50 g p-anisidine hydrochloride $CH_3O—C_6H_4—NH_2 . HCl$ and 400 g sulphur chloride are heated to 50–70°C. The reaction product is washed with benzene, placed in alcohol and, at the boil, 120 g concentrated soda lye and 400 cc 50% alcohol are added. Heating is continued for 2 hours with 25 g hydrosulphite and the precipitate is filtered and cyclized with acetic anhydride.

Sometimes *5-ethoxy-2:6-dimethylbenzthiazole* is used, and is prepared from m-ethoxy-p-toluidine.

6-chloro and bromo derivatives. The *p-chloro* or bromothioacetanilide is treated with ferricyanide in the presence of soda. The thioacetanilide is obtained by the action of P_2S_5 on the halogenated acetanilide.

5-chloro and bromo derivatives: 2:2′-dinitro-4:4′-dichlorodiphenyl disulphide obtained by Blanksma's method(14) is treated with acetic anhydride and zinc powder, under reflux: reduction and condensation to 5-chloromethylbenzthiazole takes place.

6-chloro-2:4-dimethylbenzthiazole. o-toluidine $CH_3—C_6H_4—NH_2$ hydrochloride is treated with sulphur chloride, and the reaction product with water, then soda lye: the 5-chloro-3-methylaminothiophenol obtained is cyclized with acetic anhydride.(15)

2-methyl-5-dimethyl (or diethyl) *aminobenzthiazole* is prepared from *p-bromodimethylaniline* (or diethylaniline) by the method given in B.P. 400,951.

2-methyl-7-dimethylaminobenzthiazole is prepared by cyclization with ferricyanide of m-dimethylaminothioacetanilide.(16)

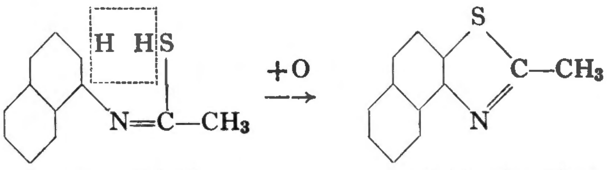
Jacobson's method of oxidation and cyclization in alkaline medium is not always possible in the case of secondary amines, when their thioacetyl derivatives are insoluble in alkali. To do this, Brooker and Cressman used iodine in acetic acid.(17)

675. Methylnaphthothiazoles

These bases are necessary for the preparation of heavy nucleus cyanines. They are prepared from β and α-thioacetonaphthalide, using Jacobson and Sullwald's(18) method of oxidation with ferricyanide in alkali. The thioacetonaphthalides are obtained from the corresponding naphthylamines. The acetonaphthalide is treated with phosphorus pentasulphide:

$$\underset{\alpha\text{-naphthylamine}}{C_{10}H_7—NH_2} + [CH_3—CO—] \rightarrow \underset{\text{Aceto-}\alpha\text{-naphthalide}}{C_{10}H_7—NH—CO . CH_3} + P_2S_5 \rightarrow$$

$$\rightarrow \underset{\text{Thioacet-}\alpha\text{-naphthalide}}{C_{10}H_7—NH—CS—CH_3}$$



Thioacet-α-naphthalide (enolic form)

2-methyl-β-naphthothiazole

It should be noted that the α-compounds give the β-naphthothiazoles, for it is the position of the sulphur, in β, which counts in the latter case for the notation. Similarly, the β-compounds give the α-naphthiazoles.

α-acetonaphthalide. Into a 3-litre flask fitted with a reflux condenser, put 41·5 fused sodium acetate, and 166 g glacial acetic acid. Heat to dissolve the acetate, then add 257·5 g ground α-naphthylamine in small portions without allowing the contents to crystallize by cooling; then, again in small amounts, add 183·6 g acetic anhydride. The contents become hot. After leaving for 10 minutes add slowly, before crystallization, 900 cc of water with stirring. The resulting mass is broken up and sucked off on a buchner. It is washed with 1500 cc cold water and dried in an oven. Yield, 323 g or 97%.

α-thioacetonaphthalide. Introduce an intimate mixture of 148 g crushed α-acetonaphthalide and 66 g crushed phosphorus pentasulphide into a 2-litre flask fitted with a thermometer, heated on the oil bath. The mixture starts to melt at 66°C. The internal temperature is kept at 115°C for 30 minutes (oil bath at 120°C) and the temperature is then raised to 120°C in 15 minutes (bath at 130°C). Heating is stopped. When the oil bath temperature drops to 100°C, fit a reflux condenser and add 500 cc 96% alcohol (in five 100 cc parts every 15 minutes), keeping the bath at 100°C. The mass dissolves while hydrogen sulphide is evolved. The acetonaphthalide is removed on the buchner and washed with alcohol. 200 cc 30% soda lye and 4400 cc water are added to the filtrate. The precipitated mass is stirred for 45 minutes, then filtered off and washed with 600 cc water. The filtrate still contains some sodium salt of α-thioacetonaphthalide. It is treated with carbon dioxide until acid to phenolphthalein. Leave to crystallize for 18 hours. Filter and wash the second crop with 400 cc water. 88+54 g thioacetonaphthalide is obtained, which is 33·5% theory.

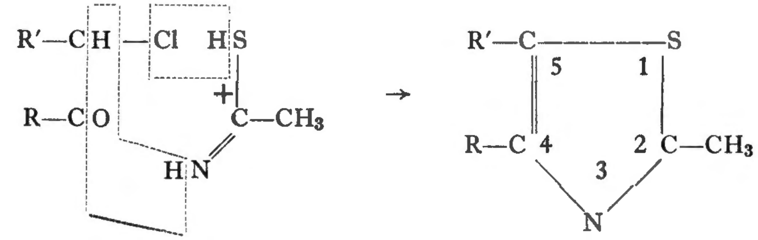
2-methyl-β-naphthothiazole. Grind 90·5 g α-thioacetonaphthalide and dissolve in 574 cc 30% soda lye and 2250 cc water. Stir for 10 minutes then add a further 157 cc soda lye. Continue stirring and add filter paper paste, stirring for a further 5 minutes. Filter, wash with 300 cc water and retain the filtrate. Crushed ice is added and the solution is slowly poured into 2422 cc of 14·4% potassium ferricyanide. Stir for 90 minutes adding further ice as required. Leave for 18 hours. Filter off the 2-methyl-β-naphthothiazole and wash with 400 cc water. Melt the damp product in a beaker and leave to cool slowly. Decant the supernatant water. In this way, 88 g crude methylnaphthothiazole is obtained. This is mixed with 225 cc benzene, which is distilled until the azole vapour reaches the neck of the flask. This can then be distilled, and the portion boiling between 330° and 333°C is collected. Yield 58 g or 64%.

2-methyl-5-ethoxy-β-naphthiazole. 1-amino-4-ethoxy naphthalene is converted to the acetylamino derivative, and then treated with phosphorus pentasulphide. The 4-ethoxythioacetonaphthalide produced in this way is oxidized with alkaline ferricyanide to the corresponding naphthothiazole.

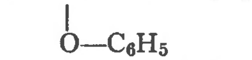
Knott[19] has prepared naphthothiazoles using the method of Hantzch for the thiazoles, then carrying out an intramolecular condensation. For example: β-benzoylpropionic acid is condensed with a thioamide to give 2-substituted 4-phenylthiazolyl-5-acetic acid. This is treated with acetic anhydride and sodium acetate to give 4′-acetoxynaphtho-1′:2′:4:5-thiazole with a 2-substituent.

676. Methylthiazoles

The μ-methylthiazoles, especially *2-methylthiazole, 2:4-dimethylthiazole* and *2-methyl-4-phenylthiazole* are prepared by Hantzch's general method:⁽²⁰⁾ the action of *thioacetamide* on *monochloracetaldehyde, chloracetone* or *α-chlorobenzophenone.* If the chlorinated methyl group is substituted by an R′ group, this is found in the 5-position of the thiazole nucleus.



Chloracetone Thioacetamide (enolic form) R′R′methylthiazole

If the substituent R is a phenyl group, and the substituent R′ is an aryloxy group, an α-chloro or α-bromo α-aryloxy-acetophenone  $Cl—CH(O—C_6H_5)—CO—C_6H_5$ is the starting material. By condensing with thioacetamide, 2-methyl-4-phenyl-4-phenoxythiazole is produced.

2:4-dimethylthiazole. Into a 250 cc flask fitted with a reflux condenser, and heated in an oil bath, place 16 g monochloracetone and 16 g 96% ethanol. Add 13 g thioacetanilide with 22 cc alcohol in four portions. A vigorous reaction takes place. The remaining crystals of thioacetanilide are taken up in 14 cc alcohol. After boiling for 13 minutes, the liquid is cooled and mixed with 21 cc hydrochloric acid diluted with 87 cc water. A crystalline deposit is formed. The filtrate is distilled to 100° and cooled; 45 cc 30% soda lye is added. An oil is produced which is extracted three times with ether (100 cc, 30 cc, 30 cc). The ether extracts are dried over potassium carbonate and distilled. 4·9 g dimethylthiazole is collected between 146 and 148·5°C. The low- and high-boiling portions are fractionated. Yield 25%.

677. Methylthiazoline

2-methylthiazoline can be prepared by several methods:

(*a*) *Glycol monochlorhydrin* is converted to *monoethanolamine* $NH_2—CH_2—CH_2—OH$ by treating with ammonia. Monoethanolamine treated by hydrobromic acid gives *β-bromoethylamine hydrobromide* $HBr . NH_2—CH_2—CH_2—Br$. This is heated with *thioacetamide* $CH_3—C(SH)═NH$ (enolic form) to give 2-methylthiazoline.⁽²¹⁾

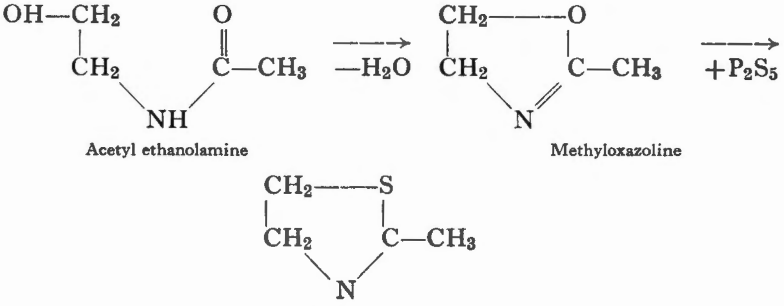
(*b*) *Ethylene bromide* is heated with thioacetamide.⁽²²⁾

(*c*) *Dithioethylamine* hydrochloride is heated with phosphorus pentachloride and acetic anhydride.⁽²³⁾

(*d*) *Monoethanolamine* is converted to *acetylethanolamine*, and treated with phosphorus pentasulphide, following Wenker's method:(24)

$$\underset{\text{Acetic acid}}{CH_3\text{—}CO\,.\,OH}+\underset{\text{Monoethanolamine}}{NH_2\text{—}CH_2\text{—}CH_2\text{—}OH} \rightarrow$$

$$\rightarrow \underset{\text{Acetyl ethanolamine}}{CH_3\text{—}CO\text{—}NH\text{—}CH_2\text{—}CH_2\text{—}OH}$$


Acetyl ethanolamine

Methyloxazoline

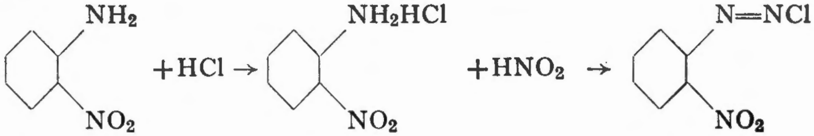
Methylthiazoline

Acetylethanolamine. Into a 500 cc Claisen flask containing 180 cc acetic acid, pour 183 g pure monoethanolamine slowly and with cooling to counteract the reaction heat. Add acetic acid until the mass has an acid reaction, then heat on a gauze from 150 to 210°C. 340 g of crude material is obtained.

Methylthiazoline. The acetylethanolamine is put into a 2-litre flask fitted with a delivery tube with a thermometer and a condenser. 150 g powdered phosphorus pentasulphide is added. The flask is agitated vigorously and then left, cooling if necessary. When the formation of the mass has stopped, heat very slowly and carefully until the mass becomes liquid, then distil at 120–160°C. The yellow oil obtained is dried over caustic potash pellets, then fractionated. The 144–147° fraction is kept. 73 g 2-methylthiazoline is obtained, 23·7%. Wenker gives 25–30%.

678. Methylbenzselenazole

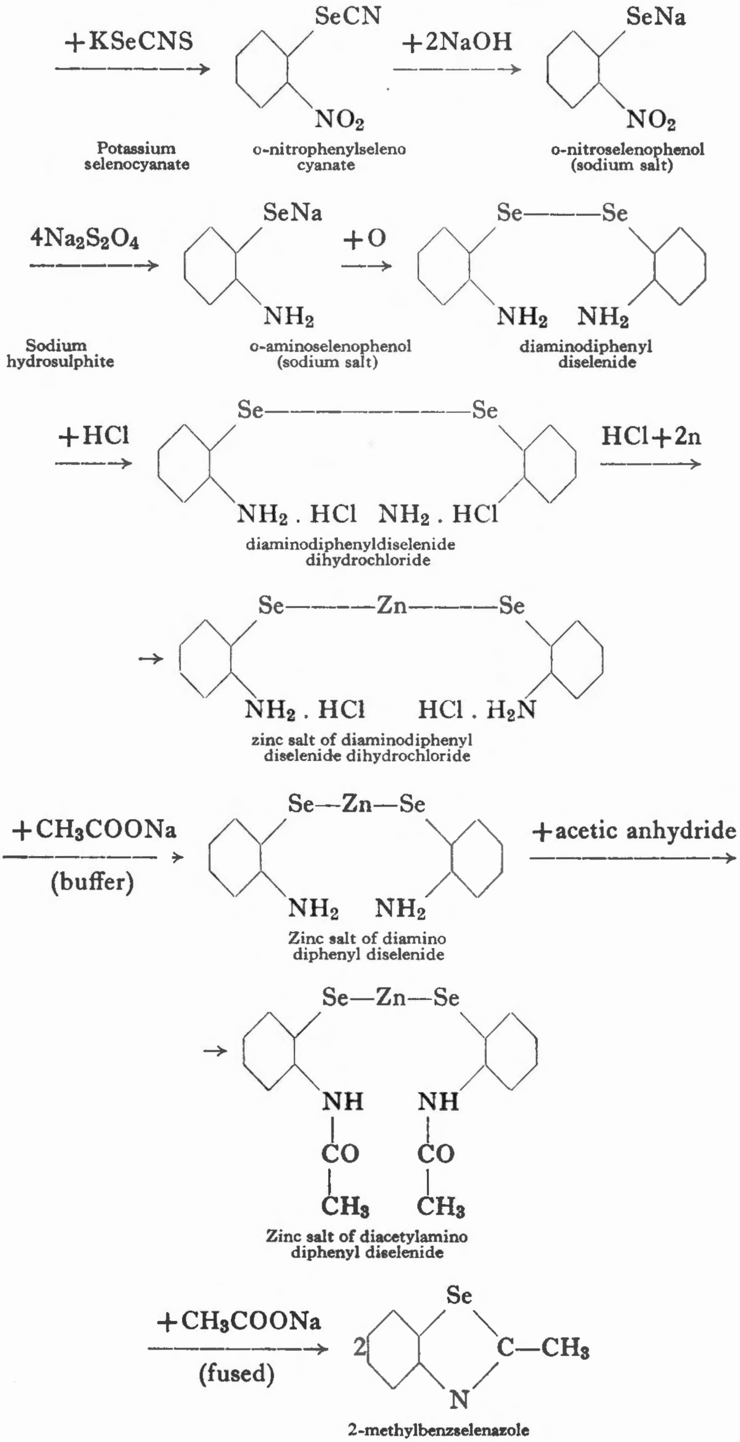
μ- (or 2-) methylbenzselenazole is obtained from *o-nitraniline*. This is diazotized, then treated with *potassium selenocyanate*: this gives *o-nitrophenylselenocyanate* (or selenocyana-2-nitrobenzene) which is converted with caustic soda to 2-nitroselenophenol. By reducing with hydrosulphite, the sodium salt of the corresponding *aminoselenophenol* is obtained. The oxidized o-aminoselenophenol is converted to *o-aminodiphenyl diselenide* whose zinc salt is cyclized to methylbenzselenazole with acetic anhydride or acetyl chloride.(25) The sequence of reactions is as follows:


o-nitraniline

o-nitraniline hydrochloride

Nitrous acid

o-nitrophenyl diazonium chloride


+KSeCNS
SeCN
NO₂
+2NaOH
SeNa
NO₂
Potassium selenocyanate
o-nitrophenylseleno cyanate
o-nitroselenophenol (sodium salt)
4Na₂S₂O₄
SeNa
NH₂
+O
Se——Se
NH₂ NH₂
Sodium hydrosulphite
o-aminoselenophenol (sodium salt)
diaminodiphenyl diselenide
+HCl
Se——Se
NH₂ . HCl NH₂ . HCl
HCl+2n
diaminodiphenyldiselenide dihydrochloride
Se——Zn——Se
NH₂ . HCl HCl . H₂N
zinc salt of diaminodiphenyl diselenide dihydrochloride
+CH₃COONa
(buffer)
Se—Zn—Se
NH₂ NH₂
+acetic anhydride
Zinc salt of diamino diphenyl diselenide
Se—Zn—Se
NH NH
CO CO
CH₃ CH₃
Zinc salt of diacetylamino diphenyl diselenide
+CH₃COONa
(fused)
2
Se
C—CH₃
N
2-methylbenzselenazole

Potassium selenocyanate. Heat 76 g fused potassium cyanide, 500 cc water and 91 g red selenium powder on the waterbath at 70–75°C for 5 hours. Filter to remove the undissolved black selenium powder and keep the solution at 0°C until it is used. Selenocyanate can also be prepared by fusing a mixture of potassium cyanide and selenium. The mass is taken up in hot water for three hours, then a current of CO_2 is passed through to decompose the excess cyanide. A variation is to dissolve the selenocyanate in absolute alcohol before treating with CO_2.(26)

o-nitrophenylselenocyanate. 139 g o-nitraniline, ground up with 1000 cc concentrated hydrochloric acid is placed in a stoneware pot with enough crushed ice to reduce the temperature to −5 to −10°C. It is diazotized by adding slowly, over 15 minutes, 75 g sodium nitrite in 250 cc water. The reaction is followed with starch-iodide paper, and the temperature is kept below 0°C by adding ice. After leaving for 30 minutes the solution should not make the paper blue. Filter, and add the following cooled mixture to the filtrate: glacial acetic acid 690 g, 30% soda lye 1070 cc (this should be alkaline to methyl red). Cool to 0°C as the temperature tends to rise above 10°. Pour into a 20-litre stoneware vessel, and add, with stirring, the selenocyanate solution. After leaving for 18 hours, filter and wash with 900 cc water. 648 g damp o-nitrophenylselenocyanate is obtained.

Diaminodiphenyldiselenide. The preceding damp product is dispersed in 4 litres of water and 635 cc 95% alcohol and the mixture is put in a 10-litre flask. After adding 1 litre 30% soda lye, the liquid becomes violet. It is heated on the water bath between 70° and 75°C with stirring, until the solution is decolorized, which takes 30 minutes. Cool to 38°C and pour into a 20-litre stoneware vessel; add 850 g sodium hydrosulphite in small quantities with stirring. The temperature rises to 58°C. Cool and check that the solution reduces methylene blue. Filter and wash the precipitate, then pass a vigorous stream of air through the filtrate for 8 hours (oxidation can also be carried out with hydrogen peroxide or potassium ferricyanide). Leave and filter off the solid which is washed with water. 195 g damp diselenide is obtained, which gives 175 g of the dry product. Yield, 68%.

Zinc salt of diaminodiphenyldiselenide. 149 g of the diselenide is dissolved on the waterbath in 1050 cc ethanol in a 10-litre flask. After stopping heating, add 435 cc concentrated hydrochloric acid slowly, avoiding a violent reaction. A grey precipitate is formed. Then add 2180 cc water, and with stirring, add 350 g zinc powder over 15 minutes. Filter and wash with water. The solid is suspended in 1600 cc water and 400 cc concentrated hydrochloric acid. The liquid is filtered on a Buchner, then an alkaline (to methyl red) mixture of acetic acid 418 g + soda lye 30% 625 g is added. The precipitate formed is filtered, washed with water and dried, giving 24 g of the product. The zinc filter cake is then suspended in 200 cc hydrochloric acid + 800 cc water. The liquid is filtered and a mixture of 209 cc acetic acid and 326 g soda lye, adjusted to neutral to methyl red, is added. The filtered, washed and dried precipitate weighs 1 g. To the first filtrate, obtained after adding the zinc powder, is added a cooled mixture, neutral to methyl red, of: acetic acid 418 g; 30% soda lye 625 cc. The precipitate is filtered, washed and dried: weight 151 g. The three parts of the zinc salt together weigh 176 g. Yield, 99%.

2-methylbenzselenazole. In a 3-litre Pyrex flask with reflux condenser, place 95 g of the zinc salt and 373 cc acetic anhydride. Reflux for 10 minutes avoiding bumping, then add in 3 minutes 150 g fused powdered sodium acetate. When the reaction has subsided, boil for 1 hour, cool, and add 725 cc water and 895 cc soda lye. Neutralize to phenolphthalein, and steam distil the selenazole. The distillate is cooled in iced water, and sown with a few crystals. 35 g of the dry product is obtained. The liquid contains more base, and 1 g can be recovered by again distilling in steam. The yield of crude methylselenazole varies from 47 to 80%. By fractional distillation, pure methylbenzselenazole is obtained, but the crude compound can be used to prepare quaternary salts. *2-methyl-5-ethoxybenzselenazole* is prepared from 2-nitro-4-ethoxy-1-phenylamine.

679. Methylnaphthoselenazoles

The α- and β-methylnaphthoselenazoles are prepared from the nitronaphthylamines.(27) They can also be prepared by the method described by Knott, using the *selenoureas.*(28)

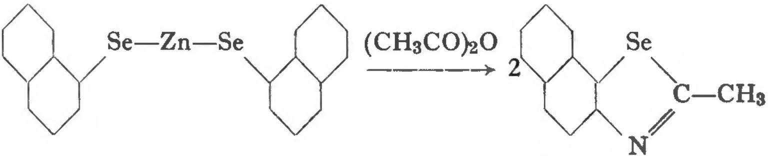
2-methyl-α-naphthoselenazole. 1-amino-2-nitronaphthalene is first diazotized to *1-diazo-2-nitronaphthalene chloride.* The diazonium compound is then treated with potassium selenocyanate KCNSe to give *1-selenocyano-2-nitronaphthalene.* This is converted to *2-nitroselenonaphthol* with soda, and reduced to *2-aminoselenonaphthol,* which gives *2:2′-diamino-1:1′-dinaphthyl diselenide* by boiling with an oxidizing agent. The diselenide is treated with zinc and acetic anhydride, to give successively, the zinc salt of *o-aminoselenonaphthol* and *2-methylnaphthoselenazole.* The reactions are as follows:

$$\underset{\text{1-amino-2-nitro naphthalene}}{NH_2\text{—}C_{10}H_6\text{—}NO_2} + HCl + \underset{\text{Sodium nitrite}}{NO_2Na} \rightarrow \underset{\text{2-nitronaphthalene-1-diazonium chloride}}{ClN{=}N\text{—}C_{10}H_6\text{—}NO_2} \;\; \underset{\longrightarrow}{+KCNSe}$$

$$\underset{\text{2-nitro naphthalene 1-selenocyanide}}{CNSe\text{—}C_{10}H_6\text{—}NO_2} \xrightarrow{+NaOH} \underset{\text{2-nitroseleno naphthol (sodium salt)}}{NaSe\text{—}C_{10}H_6\text{—}NO_2} \xrightarrow{+3H_2} \underset{\text{2-aminoseleno naphthol}}{HSe\text{—}C_{10}H_6\text{—}NH_2}$$

$$2[HSe\text{—}C_{10}H_6\text{—}NH_2] \rightarrow \underset{\text{2:2′-diamino-1:1′-dinaphthyldiselenide}}{NH_2\text{—}C_{10}H_6\text{—}Se\text{—}Se\text{—}C_{10}H_6\text{—}NH_2} \xrightarrow{+2n}$$

$$\rightarrow \underset{\text{Zinc salt of o-aminoselenonaphthol}}{NH_2\text{—}Cl_{10}H_6\text{—}Se\text{—}Zn\text{—}Se\text{—}C_{10}H_6\text{—}NH_2}$$



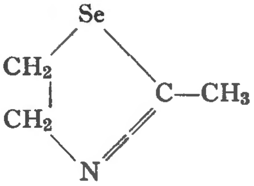
Zinc salt of o-aminoselenonaphthol 2-methyl-α-naphthoselenazole

Dinaphthyldiselenide can also be prepared in the following way: 8 g bromine in 10 cc carbon disulphide is added to 8 g selenium in 30 cc carbon disulphide. The flask of bromine solution is rinsed with 5 cc carbon disulphide, which is poured into the mixture. It is refluxed for 5 minutes and 14·3 g β-naphthylamine dissolved in 50 cc carbon disulphide is added a little at a time. A further 50 cc carbon disulphide is added, and refluxing is continued for 10 minutes. On cooling, the solid product is filtered, washed with 50 cc CS_2 and dried: 28 g diamino dinaphthyldiselenide hydrobromide is obtained.

Zinc salt of o-aminoselenonaphthol: 50 cc hydrochloric acid in 240 cc water, then 66·5 g zinc are added to a suspension of 28·2 g of diselenide in 120 cc 96% alcohol. The mixture is gently heated, and then the solid is filtered off and added to 50 cc hydrochloric acid in 200 cc water. The solution obtained is filtered and a mixture of 46 cc acetic acid and 93·5 cc soda lye (neutral to methyl or Congo red) is added. It is left, and the solid is filtered off, washed and dried. For the sequence of operations, see the preparation of methylbenzselenazole in the previous paragraph.

680. Methylselenazoline

The preparation of methylselenazoline, with the formula:



is comparable with that of 2-methylthiazoline. The 2-methylselenazoline is prepared by the action of phosphorus pentachloride on the diselenide of diacetamidoethane(29)

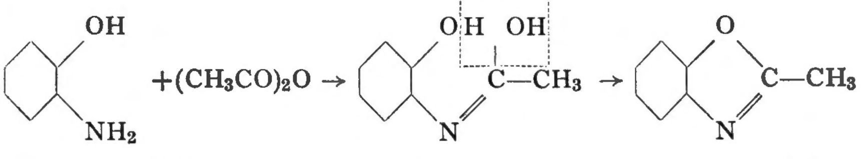
$$(CH_3—CO—NH—CH_2—CH_2—Se—)_2$$

A second method of preparation is to condense selenoacetamide CH_3——C(SeH)═NH with β-bromoethylamine hydrobromide Br—CH_2—CH_2——NH_2 . HBr.(30) Selenoacetamide is itself obtained by the action of hydrogen selenide H_2Se on acetonitrile $CH_3—C\equiv N$.

Third method: application of Wenker's thiazoline technique (para. 677)(31) action of phosphorus pentaselenide on acetylethanolamine.

681. Methylbenzoxazoles

The simplest benzoxazole base is *2-methyl benzoxazole*. It is obtained by Ladenburg's method(32) by condensing *o-aminophenol* with acetic anhydride: acetylation takes place first, then cyclization



o-aminophenol

2-methylbenzoxazole

Add 300 g o-aminophenol to 750 g acetic anhydride slowly and with stirring. During the addition, cool in a bath of iced water. Then reflux for 30 minutes and distil up to 200°C. The residue is washed with 4 litres of a saturated solution of potassium carbonate until the aqueous layer has an alkaline reaction. The base is extracted with ether and the ether solution is dried over anhydrous sodium sulphate. The ether is distilled off, and the residue is fractionated. The colourless liquid boiling from 200 to 204° is collected. Yield 290 g or 79%.

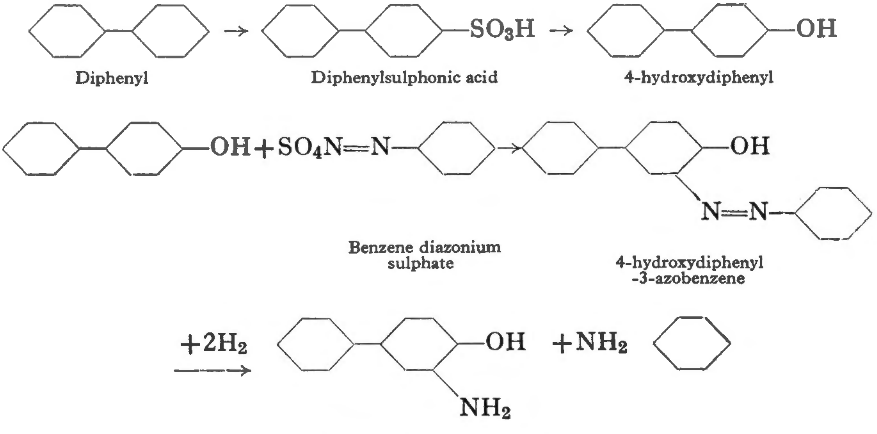
2-methyl-5-phenylbenzoxazole is prepared by cyclizing 3-amino-4-hydroxydiphenyl with acetic anhydride. Diphenyl $C_6H_5—C_6H_5$ is first converted to 4-hydroxydiphenyl $C_6H_5—C_6H_4 . OH$ by one of the following methods:

(*a*) Sulphonation then alkali fusion.(33)

(*b*) Nitration of diphenyl by a mixture of concentrated nitric acid and fuming nitric acid in acetic acid. Separation of the ortho and para compounds. Reduction of the para compound, then decomposition of the latter with conversion to the corresponding phenol by boiling.(34)

(*c*) Conversion of phenylazobenzene $C_6H_5—N{=}N—C_6H_4—OH$ to hydroxydiphenyl $C_6H_5—C_6H_4 . OH$ with elimination of nitrogen.(35)

To prepare the *3-aminohydroxydiphenyl*, either the 4-hydroxydiphenyl can be nitrated with nitric acid in acetic acid, then reducing the nitro compound, or by a simpler process, which is to couple the 4-hydroxydiphenyl with diazobenzene. The azo dye produced is then split by hydrosulphite reduction.



3-amino-4-hydroxydiphenyl

Diphenylsulphonic acid. In a 500 cc flask with reflux condenser, stirrer, thermometer and dropping funnel, place 100 g diphenyl. Melt to 90°C and add 290 g concentrated sulphuric acid slowly, keeping the temperature between 100 and 115°C. The mixture begins to solidify, so is kept liquid by heating over an open flame, continuing to stir for 15 minutes (T = 115–120°C). After cooling, it is slowly poured into 600 cc water and ice, and left overnight in a cold place. Filter and dry: 43 g of the sulphonic acid is obtained. Sodium chloride is added to the filtrate to precipitate some of the less soluble sodium salt.

3-hydroxydiphenyl. Fuse 30 g dry diphenylsulphonic acid with 35 g caustic potash dissolved in the minimum quantity of water, in a nickel crucible, taking care to avoid spitting. Pour the mass into 500 cc water, and heat until dissolved. Add 50 cc HCl to neutralize the excess alkali, then some activated charcoal, and filter warm. The residue is washed with 200 cc boiling water and the combined filtrate are left to cool overnight. Filter and recrystallize from 40% alcohol. M. Pt. 165°C.

3-amino-4-hydroxydiphenyl. Two solutions are prepared: (*a*) the phenate with 70 cc water, 12 g caustic potash and 10 g hydroxydiphenyl; (*b*) the diazobenzene sulphate with water 30 cc, concentrated sulphuric acid 6 cc, aniline 5·4 g, then, when dissolved, ice 60 g and 4·4 g sodium nitrite in 18 cc water. Stir whilst the latter is added, and check with starch-iodide paper that there is an excess of nitrite. The phenate solution is then cooled with 60 g crushed ice and placed in an ice and salt bath. The diazo solution is then added slowly with stirring. The deep red solution is left for 30 minutes cold, and then 30 minutes at room temperature. Filter off the precipitate and wash with water before dissolving in 1000 cc alcohol + 160 cc water. Then reduce with 53 g sodium hydrosulphite at the boil for 15 minutes. Cool, and distil the alcohol, then the water, on the water bath at 40–45°C at a pressure of 40–45 mm. The residue is dissolved in 300 cc hot water. A yellowish product is obtained which is dissolved in 400 cc 10% HCl at the boil. Add activated carbon, boil for 5 minutes, filter, neutralize and finally filter. 10·2 g of dry 3-amino-4-hydroxy diphenyl is obtained.

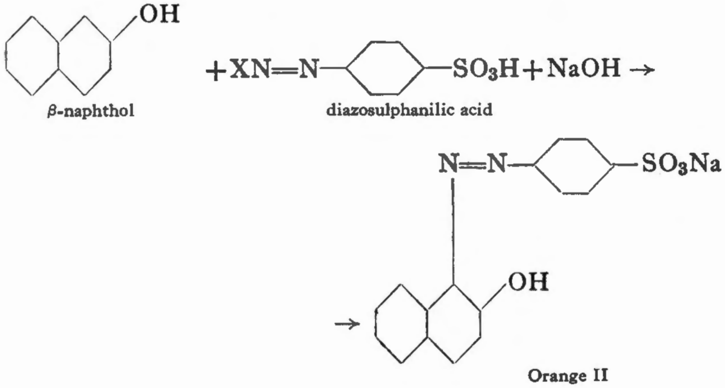
682. Methylnaphthoxazoles

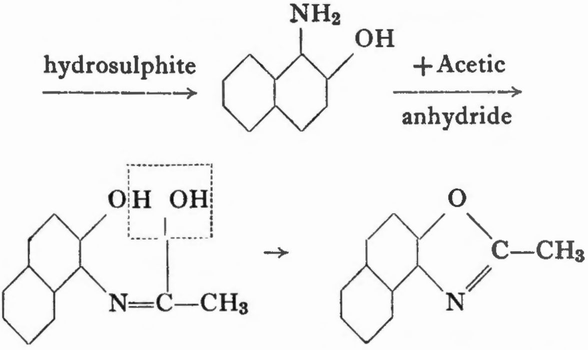
The 2-methylnaphthoxazoles are obtained from the *aminonaphthols.* To obtain 2-methyl-α-naphthoxazole, *α-naphthol* is converted to nitrosonaphthol with sodium nitrite,⁽³⁶⁾ then oxidized to *2-nitro-1-naphthol* with hydrogen peroxide in alkaline solution.

$$\mathrm{OH-C_{10}H_7 \xrightarrow{+NiNO_2} OH-C_{10}H_6-NO \xrightarrow{+O} OH-C_{10}H_6-NO_2}$$

2-amino-1-naphthol is obtained by reducing 2-nitro-1-naphthol with powdered tin and hydrochloric acid.(37) It is then cyclized by heating with acetic anhydride.

2-methyl-β-naphthoxazole is similarly prepared.(38) It can also be prepared by cyclizing aceto-α-amino-β-naphthol. $\mathrm{OH-C_{10}H_6-NH-CO-CH_3}$, according to Böttcher.(39) *β-naphthol* is coupled with *diazosulphanilic acid* and the azo dye is split to 1-amino-2-naphthol and sulphanilic acid.





2-methyl-β-naphthoxazole

2-nitro-1-naphthol. To a well-stirred mixture of 2·5 litre water, 50 g ice, 15 cc concentrated sulphuric acid, and 10g sodium nitrite, add a solution of 20 g pure α-naphthol and 10 g caustic soda in 200 cc water. The greenish precipitate which is produced is left overnight and taken up in very dilute soda (1 part of nitroso compound to 200 parts solution, and reprecipitated from the filtered solution with dilute HCl. These precautions are necessary to prevent resin forming. A mixture of 2- and 4-nitroso-1-naphthols is obtained. Yield, 80%.

A paste of 10 g of the nitrosonaphthols, 35 cc 100 vol. hydrogen peroxide and 2 drops of 10% ferrous sulphate is treated with 8 cc 20% caustic soda. The mixture becomes hot and the solid swells slightly. When the reaction slows down, add a further 15–20 cc of soda solution. After leaving for 12 hours, dilute the mixture with 300 cc water, and dissolve by boiling. Filter, cool, acidify and steam distil the *2-nitro-1-naphthol* with superheated steam. Yield, 38%.

Another method of preparing 2-nitro-1-naphthol is to heat 30 g *α-naphthylamine* for 5 minutes at 100°C with 27 cc acetic anhydride and 200 cc acetic acid. Aceto-α-naphthalide $C_{10}H_7$—NH—CO—CH_3 separates on cooling. The paste product is treated at 14–16°C with stirring, with 21·5 cc of a nitric-sulphuric acid mixture for 30 minutes. The solid is recrystallized from alcohol, the mother liquor containing mostly the 4-compound. By hydrolysis with boiling 5% caustic soda, a mixture of the 2- and 4-nitro-1-naphthols is obtained. The 2-nitro derivative is distilled with superheated steam.

2-amino-1-naphthol. Heat an intimate mixture of 60 g powdered tin, 20 g 2-nitro-1-naphthol and 160 cc concentrated hydrochloric acid until it is completely decolorized. Continue to heat for a further 30 minutes. Redissolve the tin salt of 2-amino-1-naphthol hydrochloride, which separates on cooling, in boiling water. Treat the filtered solution with hydrogen sulphide to precipitate tin sulphide. Concentrate the filtrate in a current of hydrogen sulphide. A brown solid separates. Filter hot, and cool. The aminonaphthol is precipitated with HCl as a whitish solid. Filter and dry. (Yield, 56%.)

2-methyl-α-naphthoxazole. Grind together 57 g 2-amino-1-naphthol hydrochloride and 24 g anhydrous sodium acetate, and heat to 150–160°C with 55 cc acetic anhydride for 8 hours. Distil off the excess acetic anhydride and add water to the residue, and neutralize with crystalline sodium carbonate. The base is extracted with ether, and the ether solution is dried over anhydrous sodium sulphate before the solvent is evaporated. The 2-methyl-α-naphthoxazole is distilled at reduced pressure, B. Pt. 178–201°C at 18–20 mm. White crystals M. Pt. 36–37°C.(40)

2-methyl-β-naphthoxazole.(41) First prepare the *diazonium compound of sulphanilic acid* in the following way: dissolve 42 g of sulphanilic acid ($2H_2O$) in 200 cc distilled water containing 11 g anhydrous sodium carbonate. Heat until completely dissolved, and check the neutrality. Cool to 15°C when the sodium salt starts to precipitate. Add, with stirring, 15 g sodium nitrite dissolved in 40 cc water. Pour the mixture into a 1-litre vessel containing 237 g crushed ice and 42 cc pure hydrochloric acid. Stir and leave in a salt-ice bath for 30 minutes. A yellowish-white product is obtained.

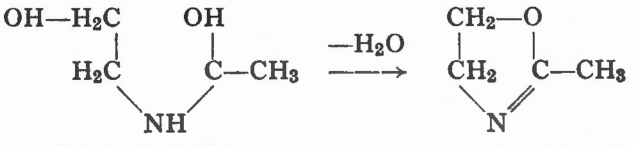
Then dissolve 43 g caustic soda in 240 cc water in a 3-litre flask and add 28·5 g β-naphthol to the hot solution. When dissolved, cool to 15°C, add 160 g crushed ice and pour in the previously obtained diazonium compound. Stir for one hour at room temperature. A suspension of *Orange II* is obtained.

The suspension of Orange II is dissolved by heating to 45–50°C and 10 g freshly made sodium hydrosulphite is added. A small amount of gas is given off from the foam. Then add 83 g more hydrosulphite and heat until a further foam is produced. Filter, wash with water and dry. 32 g of yellow-orange 1-amino-2-naphthol is obtained.

This is put into a 250 cc flask with reflux condenser after mixing with 14 g fused and ground sodium acetate, then 32 cc acetic anhydride is added. The mixture is refluxed for 8 hours to cyclize the aminonaphthol. The excess anhydride is distilled off, and the residue is dissolved in water and neutralized with carbonate. The base is extracted with ether and the ethereal layer is dried with anhydrous sodium sulphate before removing the ether. The residue is distilled at 10 mm and the fraction boiling between 152 and 154° is collected. 22 g 2-methyl-β-naphthoxazole, M. Pt. 27°C, is obtained. Yield, 60%.

683. Oxazolines

These have a similar structure to the thiazolines (para. 677) and are prepared by Wenker's general method(24) which is to dehydrate the *N-acetylethanolamines*.



N-acetylethanolamine 2-methyloxazoline

Acetylethanolamine, heated to between 260 and 280°C cyclizes to 2-methyloxazoline. The base is then distilled, dried over caustic potash and fractionated. Yield 30%; B. Pt. 110°C. Dehydration can also be carried out with phosphorus pentoxide (violent reaction).

684. Indoline bases

These bases (which are sometimes called indolenines) are *indole* derivatives. They are formed by cyclizing ortho-amines, particularly o-aminoketones. They are also formed by combining *phenylhydrazine* C_6H_5—NH—

—NH_2 with ketones (phenylhydrazones). Thus with methylisopropylketone and phenylhydrazine:

$$C_6H_5—NH—NH_2+CH_3—CO—CH : (CH_3)_2 \rightarrow$$

Phenylhydrazine Methyl isopropyl ketone

$$\rightarrow C_6H_5—NH—N{=}C(CH_3)—CH{=}(CH_3)_2$$

Methyl isopropylketone phenyl hydrazone

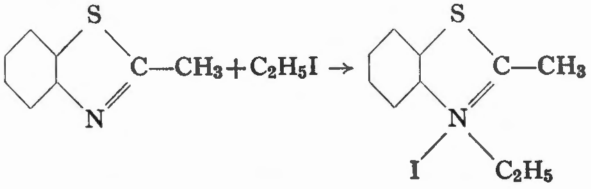
When the phenylhydrazones are fused with zinc chloride, they lose ammonia and cyclize into indoline bases.(42) The preceding phenylhydrazone gives *2:3:3-trimethyllindoline*. To obtain *1:3:3-trimethyl-2-methyleneindoline*, or Fischer's base, *phenylmethylhydrazine* $C_6H_5—N(CH_3)—NH_2$ and butyraldehyde $(CH_3)_2{=}CH—CHO$ are used, whose phenylhydrazone has the formula $C_6H_5—N(CH_3)—N{=}CH—CH{=}(CH_3)_2$.

The nuclear substituted indoline bases such as the dimethylamino indolines are prepared from the substituted phenylhydrazines.

CONVERTED BASES

685. Cyclammonium quaternary bases

The heterocyclic bases containing a trivalent nitrogen atom combine readily with the alkyl or aryl salts to give quaternary ammonium salts with pentavalent nitrogen. For example:



2-methylbenz thiazole Ethyl iodide 2-methylbenzthiazole ethiodide

The bases are used in the form of these cyclammonium salts, for the preparation of the cynanines.

The principal organic salts are *methyl iodide* CH_3I, *ethyl iodide* C_2H_5I, *methyl sulphate* $(CH_3)_2SO_4$, ethyl sulphate $(C_2H_5)_2SO_4$ and *ethyl p-toluene sulphonate* $CH_3—C_6H_4 . SO_3 . C_2H_5$; and more rarely, *ethylchlorocarbonate* $Cl—CO—O—C_2H_4$, *p-toluyl bromide* $CH_3—C_6H_4—CO—Br$, *p-carboxybenzyl bromide* $COOH—C_6H_4—CH_2—Br$ and *glycol monoiodhydrine* $I—CH_2—CH_2 . OH$ which gives a hydroxyalkyl group.

The iodine is sometimes replaced by *bromine*, which gives more soluble salts, or by *perchloric* or *thiocyanic* acid. These compounds can be obtained by adding the corresponding sodium salt to the alkyl p-toluenesulphonate of the base, or by boiling the alkiodide with the silver salt (silver bromide for example). An alkyl nitrate is similarly obtained by treating the alkiodide with a solution of silver nitrate.

The alkiodides and the alkyl p-toluene sulphonates of the bases are prepared by *prolonged heating of equimolecular parts* of the reagent and the base under reflux or in an autoclave. Frequently the reaction is slow, but sometimes it is violent and spontaneous as with quinoline methiodide.

The methiodides and ethiodides of quinoline, lepidine, quinaldine and toluquinaldine are prepared by heating under reflux on the oil bath, one molecule of methyl or ethyl iodide with one mol. of the base. For example: 152 g methyl iodide and 157 g p-toluquinaldine. Heat for several hours until a completely solid cake is formed, cautiously at first, to avoid a violent reaction. The cooled mass is recrystallized from 95% alcohol. Yield, 65–75%.

p-toluquinaldine methiodide: pale yellow needles; M. Pt. 246°C.

p-ethoxyquinaldine ethiodide; M. Pt. 182°C.

l-phenylquinaldine perchlorate(42b)

Quinoline dimethylsulphate. Put 129 g quinoline in a 1-litre flask. Add 130 g dimethyl sulphate in 15 min., keeping the temperature between 50° and 70°C and stirring continuously. The mixture solidifies. Leave for 15 mins. and dissolve the mass in water to purify it.

686. Benzthiazole quaternary salts

Benzthiazole ethiodide. Heat equimolecular quantities of the base and ethyl iodide at 100°C for 24 hours. Recrystallize from methanol or ethanol.

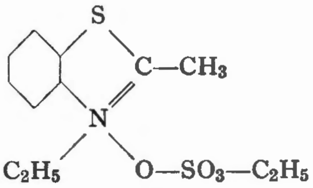
2-methylbenzthiazole methiodide. Heat 67 g base and 65 g methyl iodide for 20 hours at 90°C in a 1-litre flask. Recrystallize from methanol. The addition of ether to the filtrate precipitates more of the product. Yield 84 g + 14 g, which is 75%.

2-methylbenzthiazole ethiodide. Heat 298 g of the base with 312 g ethyl iodide for 20 hours at 105–110°C in a flask with reflux. Recrystallize from 720 cc methanol. A further amount can be obtained by adding ether to the filtrate. Yield, 478 + 48 g. It is advisable to recrystallize the recovered product.

2-methylbenzthiazole propyliodide. Heat 14·9 g of base and 17 g of n-propyl iodide for 20 hours at 105–110°C. Grind the solid with 60 cc ether. Filter and wash with 180 cc ether. 27·7 g of product is obtained. Yield, 87%.

2-methylbenzthiazole p-toluene-sulphonate. Heat 7·5 g of base and 10 g ethyl p-toluene-sulphonate for 6 hours at 120°C. The mass is removed from flask with the help of a little acetone. 17·5 g of the crude product is obtained (97·5%). Brooker and White heated for 6 days at 100°C, dissolved the mass in methanol and precipitated with acetone, with stirring and cooling. M. Pt. 164°C.

2-methylbenzthiazole diethyl-sulphate



Heat 16·5 g base and 17 g diethyl sulphate for 15 hours at 90–100°C. The mass becomes viscous and deposits crystals on cooling. Wash with acetone and dry. 27 g of crude material is obtained which is suitable for use. Yield, 81%.

2-methylbenzthiazole ethyl-chlorocarbonate. Heat 2·17 g ethyl chlorocarbonate with 3 g of base for 3 hours, at 110°C, after leaving for 3 days at room temperature. Grind the solid with ether, and filter and wash with ether. 1·3 g of the product melting at 179°C is obtained. Yield, 25%.

2-methylbenzthiazole N-p-toluyl-bromide. Leave 1·4 g p-toluyl bromide and 1·05 g base in contact for 14 hours, then bring to 110° for 2 hours. Grind with 100 cc ether and filter. 1·35 g of product is obtained. Yield, 55%. M. Pt., 202–205°C.

2:6-dimethylbenzthiazole ethiodide. Heat equimolecular quantities of base and ethyl iodide for 2 days at 100°C. Recrystallize from alcohol. Colourless needles, M. Pt. 138°C.

687. Naphthothiazole quaternary salts

β-naphthothiazole ethyl-p-toluene sulphonate. Heat an equimolecular mixture of 2-methyl-β-naphthothiazole and ethyl-p-toluene sulphonate for 3 weeks at 115–120°C. After the first week, assist crystallization by rubbing the inside of the container. Grind with ether, filter and wash with acetone (Brooker and White). Another more rapid method is to heat for 7 hours at 185°C. After cooling, pour in 600 g benzene (for 169 g base and 169 g sulphonate), reflux for 30 mins. with stirring to disperse the viscous mass and dissolve the excess base. Decant the benzene layer and repeat three times. Distil the residual benzene to obtain the crude p-toluene-sulphonate of the base. This can be ground with 200 cc petroleum ether, or purified in the way given above. Recrystallize from boiling acetone.

2-methyl-β-naphthothiazole p-carboxybenzylbromide. Heat 4 g of base with 4·3 g of ω-bromo-p-toluic acid for 3 hours at 130°C then for 15 mins. at 200°C. Cool and grind with 60 cc ether. 3·5 g of the product is obtained. Yield, 42%.

2-methyl-β-naphthothiazole ethiodide. A hot aqueous solution of crude 2-methyl-β-naphthothiazole ethyl-p-toluene-sulphonate is prepared and a solution of potassium iodide is added to it: the ethiodide crystallizes on cooling; it is washed with water, treated with ether and recrystallized from alcohol.⁽⁴³⁾

2-methyl-α-naphthothiazole ethyl-p-toluene-sulphonate. Heat equimolecular quantities of 2-methyl-α-naphthothiazole and ethyl p-toluene-sulphonate to 120–130°C for 45 hours. The resulting mass is ground up in the presence of acetone and dissolved in boiling methanol from which it is precipitated by adding an equal quantity of acetone and cooling. Yield 77% + 19% recoverable from the filtrate. Colourless crystals M. Pt. 200–206°C with softening at 190°C (Brooker and White).

688. Thiazole quaternary salts

2:4-dimethylthiazole ethiodide.(44) Heat 3 g of 2:4-dimethylthiazole with 4·2 g ethyl iodide at 90°C for 14 hours. Grind with 25 cc ether, filter and wash with ether. 3·2 g of the crude compound is obtained (44%). Recrystallize from alcohol. The yield is higher if 1 mol base is heated with 1·2 mol ethyl iodide in a sealed tube at 100°C. The mass is dissolved in water and, after filtration and evaporation, is washed with ether and recrystallized from dry alcohol.(45) The *methiodide* is similarly prepared.

The *methiodide* and *ethiodide* of *2-methyl-4-phenyl thiazole* are prepared by the same method. In sealed tubes, heat for 34 hours at 80°C.

2-methylthiazoline ethiodide. Heat an equimolecular mixture of the reactants for 24 hours at 80°C, for example 78 g of the base and 124 g ethyl iodide. The mass is washed with acetone and recrystallized from a mixture of acetone and methanol. 168 g of crude product is obtained. Yield, 81%. Brooker and White, working at the boil, had a yield of 63°. M. Pt. 190–193°C.

2-methylthiazoline methiodide. Heat 1 mol base with 1 mol methyl iodide as above for 12 hours. Yield of crude product: 77%. Recrystallize from methanol. M. Pt. 241–242°C (Brooker and White).

2-methylthiazoline ethyl-p-toluene-sulphonate. Heat 1 mol base (1 part) with 1 mol ethyl p-toluene-sulphonate (2 parts) for 24 hours at 100°C. Grind the mass with a little acetone: it slowly crystallizes. Filter, wash with 12 cc benzene to remove the excess base, then twice with acetone and dry the white product which is suitable for use. Yield of crude product: about 40%. For the methyl derivative, one hour's heating is enough.

689. Benzselenazole quaternary salts

2-methylbenzselenazole ethiodide. Heat 133 g of the selenazole base with 106 g ethyl iodide to 90–100°C for 36 hours. The solid mass is ground up with 800 cc ether. Filter, wash with 200 cc ether and dry. Yield 214 g of crude product (89%). Recrystallize from alcohol.

2-methylbenzselenazole ethyl-p-toluene-sulphonate. 3·9 g of base and 4 g of sulphonate are heated to 100°C for 50 hours. Grind the cooled mass with 12 cc benzene to remove the excess base, then twice with 12 cc petroleum ether. Decant and add 48 cc petroleum ether (80–100°C). The mass solidifies. Filter, wash with petroleum ether and dry. The product is soluble in warm alcohol.

2-methyl-α-naphthoselenazole diethyl-sulphate. Heat equimolecular quantities of the two reactants until the mass solidifies. Use as it is.

690. Benzoxazole quaternary salts

2-methylbenzoxazole methiodide. Heat 13·5 g of the oxazole base with 17 g methyl iodide for 8 hours at 100°C. The yellow mass is washed with ether and the residue is recrystallized from acetone as colourless needles which turn brownish with damp. M. Pt. 196°C with decomposition.(46)

2-methylbenzoxazole ethiodide. Heat 24 g of the oxazole base with 24 ethyl iodide for 11 hours at 110°C. Make up for the loss of ethyl iodide by evaporation. Cool in ice and filter, retaining the filtrate, and wash first with acetone, then with ether. 14·3 g of crude product is obtained. Add ethyl iodide to the initial filtrate and heat for 20 hours. Cool, filter, and wash with acetone and ether. A further crop of 12·5 g is obtained. Repeat the operation with the new filtrate. Total yield, 29 g (55%).

2-methylbenzoxazole ethyl p-toluene-sulphonate. Heat 2·7 g of the oxazole base and 3·9 g of ethyl p-toluene-sulphonate for 6 hours at 100°C.

2-methylbenzoxazole p-carboxybenzylbromide. Heat 2·35 g of 2-methylbenzoxazole and 3·75 g ω-bromotoluic acid for 20 mins. at 190°C. Grind the product with 15 cc ether. Filter and dry. Yield 90%.

691. Naphthoxazole quaternary salts

2-methyl-β-naphthoxazole methiodide. 10 g of base and 4 cc methyl iodide are heated (preferably in a sealed tube) at 100°C for two days. The mass is extracted with ether, and the residue is recrystallized from 400 cc absolute alcohol. M. Pt. 212–213°C. Yield, 38%.

2-methyl-β-naphthoxazole ethiodide. Method as above. Yield, 11%. 33% of the unreacted base can be recovered.

Another method is to prepare *2-methyl-β-naphthoxazole p-toluene-sulphonate* first, as with the naphthothiazole compound, and to precipitate from the aqueous solution with a solution of potassium iodide.

2-methyl-α-naphthoxazole methiodide. The product recrystallized from absolute alcohol melts at 202°C. Yield, 65%.

2-methyl-α-naphthoxazole ethiodide. M. Pt. 215°C. Yield, 62%.

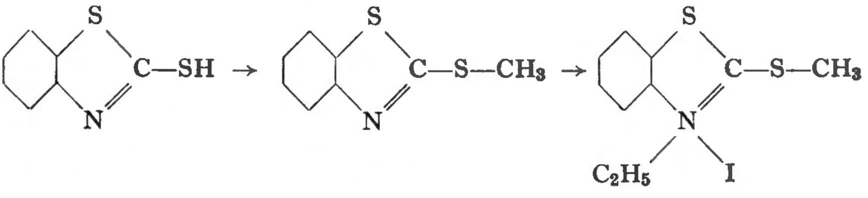
2-methyl-β-naphthoxazole diethyl sulphate. Heat 13·8 g of 2-methyl-β-naphthoxazole and 11·6 g of diethyl sulphate for 5 hours at 120–130°C. Use the crude product.

692. Trimethylindoline quaternary salts

2:3:3-trimethylindoline ethiodide. Heat 1 mol 2:3:3-trimethylindoline with 1 mol ethyl iodide at 100°C in a sealed tube for 48 hours according to König and Muller.(47) Good results are obtained, however, by simple heating of 6·3 g of base with 6·3 g ethyl iodide for 8 hours at 90°C, at normal pressure. Grind and wash the product with ether. Yield, 19·6 g or 92%.

693. Methylmercaptobenzthiazole

2-methylmercaptobenzthiazole, whose quaternary salts are used, is a derivative of the commercially available *mercaptobenzthiazole* obtained by the action of carbon disulphide and sulphur on aniline.



Mercaptobenzthiazole

Methylmercapto benzthiazole

2-methylmercapto benzthiazole ethiodide

2-methylmercapto-β-naphthothiazole has a similar structure. To obtain *mercaptonaphthothiazole*, α-naphthylamine is treated with carbon disulphide CS_2. This produces α-dinaphthylthiourea $C_{10}H_7$—NH—CS—NH—$C_{10}H_7$ which is converted by phosphoric acid to α-naphthyl isothiocyanate $C_{10}H_7$—N=C=S. The latter, under the action of sulphur and carbon disulphide, then soda lye followed by a current of CO_2, gives 2-mercapto-β-naphthothiazole (the sulphur being in β). The excess isothiocyanate is removed by steam distillation.

Conversion of mercaptobenzthiazole to 2-methylmercaptobenzthiazole. Pour 60 cc of dimethyl sulphate (80 g), in 4 portions, into a mixture of 84 g mercaptobenzthiazole, 200 cc distilled water and 95 cc 30% caustic soda lye. When the reaction subsides, heat for 30 mins. at 130°C. On cooling, the oily mass solidifies. Filter and wash with water. Melt, and allow to set slowly and decant the supernatent water. The filtrate is washed three times with ether (300, 200 and 130 cc) and dry the ether solution with $CaCl_2$. Distil the ether and add the residue to the main product. Total, 84 g. Purify by distillation collecting the 294–297°C fraction. Yield, 57 g or 63%. Fractionate the low and high fractions.

The methylmercaptans of α- and β-naphthothiazole, benzoxazole, etc., can be prepared in the same way.

2-methylmercaptobenzthiazole ethiodide. Heat 20 g (1 mol) of 2-methylmercaptobenzthiazole with 21·7 g (1·25 mol) ethyl iodide for two days, refluxing gently. Grind with ether, filter and wash with ether. Yield, 90%.

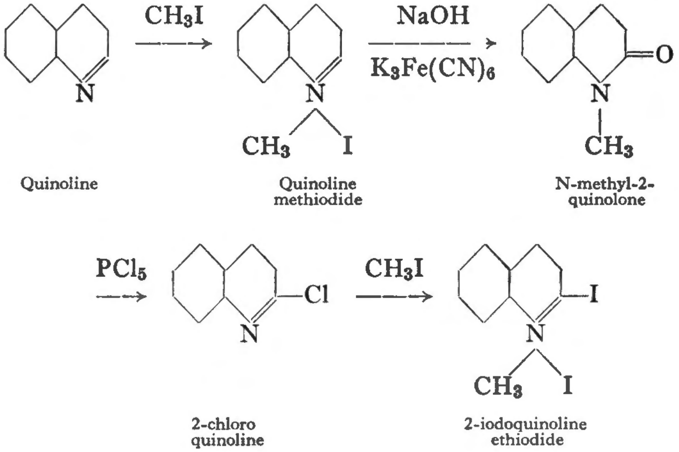
2-methylmercaptobenzthiazole ethyl-p-toluene-sulphonate. Heat 18 g of the mercapto base with 20 g of ethyl p-toluene-sulphonate for 5 hours at 185°C. Dissolve the product in water and wash the solution with ether. Distil the water to obtain the crude product.

2-methylmercaptobenzthiazole dimethyl-sulphate. Heat 8·9 g of the mercapto base with 6·2 g dimethyl sulphate for 4 hours at 100°C. After cooling, grind the product with 60 cc ether, filter and wash with 50 cc ether. 14·8 g of the product is obtained. Yield, 98%.

2-methylmercaptobenzthiazole diethyl-sulphate. Heat 3·6 g of the mercapto base with 3·1 g diethyl sulphate for 9 hours at 105°C. The liquid mass is poured into 25 cc acetone and is precipitated as a white powder. Filter and wash with 25 cc acetone. 3·35 g of the product M. Pt. 76–77°C is obtained. Yield, 55%.

694. 2-iodoquinoline

Quinoline methiodide or dimethyl-sulphate, oxidized with potassium ferricyanide in the presence of caustic soda at 0–7°C gives a product which, when extracted with chloroform and recrystallized from benzene, corresponds to the structure of *1-methyl-2-quinolone*. This is converted to *2-chloroquinoline* by heating with phosphorus pentachloride for several hours at 150–160°C. 2-chloroquinoline, heated for 10 days with methyl iodide gives *2-iodoquinoline methiodide*, which is extracted with ether and recrystallized from water.(48)



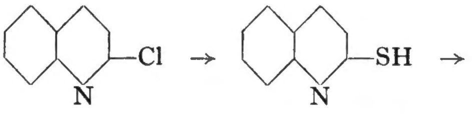
N-methyl-2-quinolone. Heat 118 g of pure quinoline to 50–65°C and add 97·5 g dimethyl sulphate over 25 minutes. The resulting mass should be water soluble. 600 cc water is added, and in 10 mins. the quinoline dimethyl-sulphate solution is added to a solution of: 30% caustic soda lye 822 cc, 14·4% potassium ferricyanide 4300 cc, crushed ice to reduce the temperature to below 0°C, with vigorous stirring. This is continued for 1 hour with cooling, and 2 kg potassium carbonate is added. An oil forms and is separated. The aqueous layer is extracted four times with 2 litres ether. The ether layer is steam distilled to remove the ether, and then superheated steam removes excess quinoline. The oily layer remaining in the flask is decanted. Potassium carbonate, added to the aqueous layer produces more oil. In all, 115 g of crude quinolone is obtained which is dried at 150°C. By distilling between 322 and 328°C pure quinolone is obtained.

2-chloroquinoline. 100 g N-methyl-2-quinolone and 250 g crushed dichlorobenzene are put into a flask fitted with a reflux condenser, and 147 g of phosphorus pentachloride is added carefully. The mixture is heated on the oil bath to 160–165°C for 5 hours, controlling the amount of gas given off. The solution, still warm, is poured into 950 cc of distilled water. It is left overnight, and the 2-chloroquinoline is distilled in steam. It is then melted and the water is separated before distillation. The 274–276°C fraction is separated. Yield, 79%.

2-iodopyridine. Pyridine is converted to the p-toluene-sulphonate, and oxidized with ferricyanide in alkaline solution to N-methyl-2-pyridone. When heated with phosphorus pentachloride this gives 2-chloropyridine, which gives 2-iodopyridine methiodide with methyl iodide.⁽⁴⁹⁾

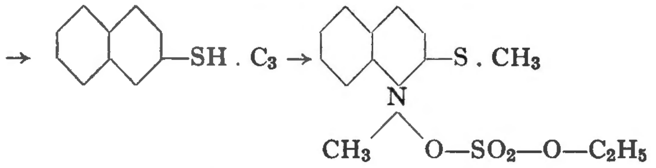
695. Methylmercaptoquinoline

2-chloroquinoline, treated with sulphur and hydrogen sulphide in pyridine gives mercaptoquinaline or 2-quinolinethiol, the quinoline corresponding to mercaptobenzthiazole. The 2-quinolinethiol is in turn treated with dimethyl sulphate to give *2-methylmercaptoquinoline,* which combines with a second molecule of dimethyl sulphate to give *2-methylmercaptoquinoline methyl-sulphate.*



2-chloroquinoline

2-quinolinethial
(mercaptoquinoline)



2-methylmercaptoquinoline

2-methylmercaptoquinoline
methyl-sulphate

2-quinolinethiol (mercaptoquinoline). Heat a mixture of 81·7 g 2-chloroquinoline, 160 g sulphur and 300 cc anhydrous pyridine to 115–130°C. Pass a current of H_2S, washed and dried with $CaCl_2$ and P_2S_5 through it. Oil bath temperature 146°C. After 40 mins. the reaction is complete. Pour the warm mass into 250 cc distilled water. Filter and wash with water. 136 g of the crude product is obtained. The precipitate of quinolinethiol and sulphur is suspended in 1250 cc boiling water. 160 cc 30% caustic lye is added, and after 4 mins. the liquid is filtered hot. The sulphur remains on the filter. The filtrate is cooled, and 125 cc acetic acid is added with stirring, which precipitates the thiol as a yellow powder: 160 g of damp purified product is obtained.

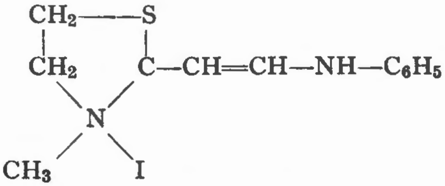
2-methylmercaptoquinoline. 143 g quinolinethiol, 180 cc water and 75 cc 30% caustic lye are put into a flask, then 60 cc of dimethylsulphate is added in 3 parts. The mixture becomes hot, and when the reaction has subsided, boil for 25 mins. The methylmercaptoquinoline is steam distilled. 69 g of fused dry product is obtained, which can be fractionated at 296–300°C.

2-ethylmercaptoquinoline is similarly obtained.

2-methylmercaptoquinoline diethyl-sulphate. Mix 45 g of 2-methylmercaptoquinoline with 39·6 g diethyl-sulphate. Leave to react cold for 45 mins. Then heat in an oil bath at 135°C for 2 hours 15 mins.

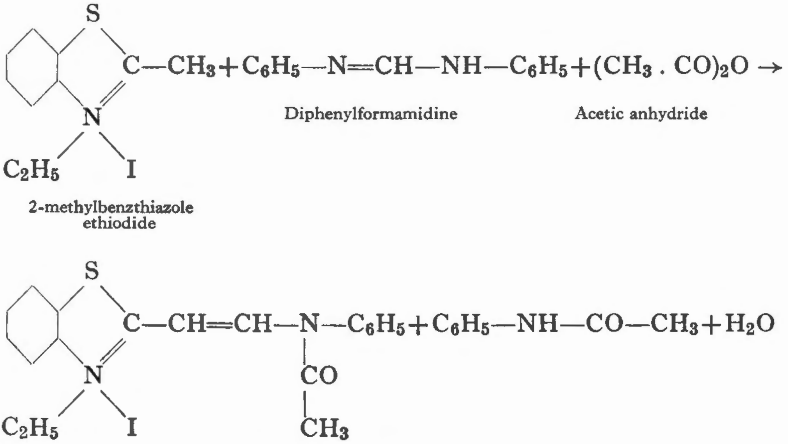
696. Formamidine derivatives

Diphenylformamidine $C_6H_5—N{=}CH—NH—C_6H_5$ combines with the heterocyclic base quaternary salts to give compounds with an *anilidovinyl* chain. For example, 22·2 g of 2-methylthiazoline methiodide, 18 g diphenylformamidine and 30 cc acetic acid are heated for an hour on the waterbath. On cooling, *2-β-anilidovinylthiazoline* precipitates. The product is washed with acetone and dried and recrystallized from acetic acid (2 cc for g). Yield, 40%.



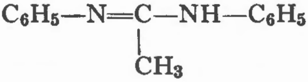
2-β-anilidovinylthiazoline

If the condensation is carried out in the presence of *acetic anhydride*, a quaternary salt of the *2-ω-acetanilidovinyl heterocyclic base* is obtained. With 2-methylbenzthiazole ethiodide the reaction is:



2-ω-acetanilidovinylbenzthiazole ethiodide

The diphenylformamidine can be replaced by *diphenylacetamidine*



$$C_6H_5\text{—}N\text{=}\underset{\displaystyle CH_3}{\underset{|}{C}}\text{—}NH\text{—}C_6H_5$$

to give the *acetanilidomethylvinyl* derivatives.

The derivatives of diphenylformamidine and its homologues are used to prepare *assymmetrical carbocyanines and merocyanines.*

Diphenylformamidine is prepared by heating 186 g (2 mol) of pure aniline with 148 g (1 mol) of ethyl orthoformate for 2 hours on an open flame.(50) The temperature rises to 185°C. The alcohol produced is distilled as it forms. Pour the molten mass into a mortar or it will crystallize. Grind with 50 cc benzene. Filter and wash with 20cc benzene. 183 g of crude product is obtained. This is recrystallized from 650 cc alcohol to give 136 g of pure product (70%) M. Pt. 141°C.

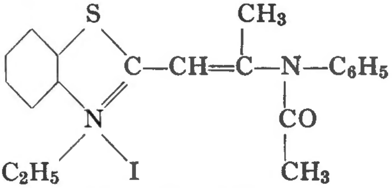
Diphenylacetamidine. 56 g aniline (0·6 mol), and 81 g acetanilide (0·6 mol) are placed in a 500 cc flask with a reflux condenser fitted with a calcium chloride tube. 172 g (1·3 mol) phosphorus trichloride is slowly added. Hydrogen chloride is evolved. Heat for 3 hours on the oil bath at 110°C, and cool in ice. Dissolve the hard mass which is formed in four lots of 250 cc cold distilled water. The filtered aqueous solution is treated with 525 cc 0·960 ammonia. Cool the warm liquid and filter. Wash with 500 cc water, then 150 cc ethanol. 92 g of crude product is obtained. This is crystallized from 200 cc boiling ethanol. Filter and wash with 60 cc alcohol. Yield 70 g or 55%. M. Pt. 134·5–138·5°C.

2-ω-acetanilidovinylbenzthiazole ethiodide. Heat a mixture of 6·11 g (0·02 mol) 2-methylbenzthiazole ethiodide, 4·55 g (0·023 mol) diphenylformamidine and 40 cc acetic anhydride under reflux in an oil bath at 140°C for 50 mins. Cool for 3 hours and filter. Wash successively with 12 cc acetic acid, 30 cc alcohol, and 30 cc ether. 6·8 g of product is obtained (75·5%).

2-ω-acetanilidovinylbenzoxazole N-p-carboxybenzylbromide. Heat 3·48 g 2-methylbenzoxazole N-p-carboxybenzylbromide (0·01 mol), 5·88 g diphenylformamidine (0·03 mol) and 1·1 g acetic anhydride (0·01 mol) on an oil bath at 110°C for 30 mins. Dissolve the product in warm alcohol and precipitate with ether. Decant the ether solution; redissolve the viscous product in warm alcohol and re-precipitate with ether. 1·82 g of the product is obtained. Yield, 44%.

2-ω-acetanilidovinyl-1:3:3-trimethylindoline iodide. Heat 1·44 g (0·048 mol) 2:3:3-trimethylindoline methiodide with 1·11 g (0·057 mol) diphenylformamidine and 10 cc acetic anhydride on the oil bath at 150°C for 30 mins. Concentrate to half volume and cool. The crystals obtained are filtered and washed successively with 4·5 cc acetic acid, 3 cc 96% alcohol and 10 cc ether. 1·56 g of product is obtained. Yield, 73%.

2-ω-acetanilidomethylvinylbenzthiazole ethiodide. Heat 3·05 g of 2-methylbenzthiazole ethiodide (0·01 mol) with 2·5 g *diphenylacetamidine* (0·012 mol) and 20 cc acetic anhydride, for 40 mins. on an oil bath at 145°C. Leave overnight when crystals are formed. Filter and wash successively with 10 cc acetic acid, 10 cc 96% alcohol and 20 cc ether. 0·74 g of the product is obtained. Yield, 16%.



2-ω-acetanilido*methyl*vinylbenzthiazole ethiodide

2-ω-acetanilidomethylvinylbenzthiazole ethyl-p-toluene sulphonate. Heat 3·5 g 2-methylbenzthiazole ethyl p-toluene-sulphonate with 2·1 g diphenylacetamidine and 10 cc acetic anhydride for 30 mins. on the oil bath at 160°C.

No crystallization occurs. The solution is poured into 120 cc ether. The oily precipitate is separated and dried and 150 cc water is added. The viscous residue is dissolved in 50 cc alcohol and re-precipitated with 60 cc ether. Filter and wash with ether. Only 0·18 g of the product is obtained, which is a yield of 3·55%.

2-ω-acetanilidomethylvinylbenzselenazole ethiodide. Heat 3·25 g 2-methylbenzselenazole ethiodide, 2·5 g diphenylacetamidine and 20 cc acetic anhydride for 40 mins. on the oil bath at 145°C. Crystals form after leaving overnight. Filter and wash successively with 5 cc acetic acid. 5 cc 96% alcohol and 10 cc ether. 0·48 g of product is obtained. Yield, 9·4%.

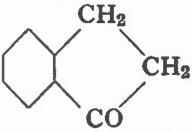
2-ω-acetanilidomethylvinylbenzoxazole methiodide. By heating 6 g of 2-methylbenzoxazole ethiodide, 4·2 g diphenylacetamidine and 20 cc acetic anhydride for 30 mins. in an oil bath at 160°C only a 2% yield is obtained. 20 cc alcohol is added to the solution and when poured into 250 cc ether gives an oily precipitate, which is separated and treated with 120 cc water to which a little potassium iodide has been added. The separated product is taken up with a little alcohol and crystallized. It is filtered and washed with ether.

KETOMETHYLENE HETEROCYCLIC COMPOUNDS

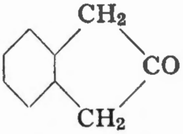
697. Constitution of ketomethylene heterocyclic compounds

Cyclic compounds having a nuclear methylene group —CH_2— linked to a keto group —CO— have a great affinity for heterocyclic compounds containing a reactive methyl group. They are the starting point in the preparation of the merocyanines. The colouring properties of the compounds thus obtained are related to the presence, in the same nucleus, of oxygen, sulphur and nitrogen atoms.

Simple ketocyclic nuclei

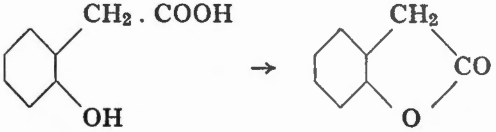


α-hydrinolone



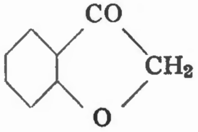
β-hydrinolone

Oxygen containing ketomethylene nuclei. A γ-phenolic acid, such as o-hydroxyphenylacetic acid cyclizes with heat to a lactone, losing a molecule of water. The product obtained is *α-coumaranone* isomeric with *β-coumaranone.*



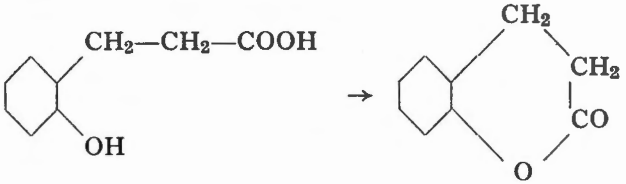
o-hydroxyphenyl-acetic acid

α-coumaranone

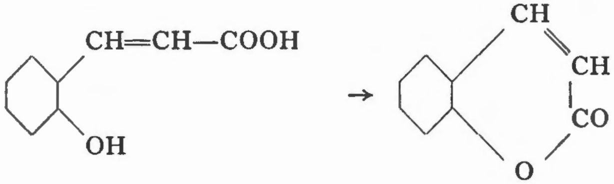


β-coumaranone

A δ-phenolic acid cyclizes to a hexa-atomic nucleus: o-hydroxyhydrocinnamic acid is converted to *hydrocoumarin*. If o-hydroxycinnamic acid is used, coumarin is produced by heating.

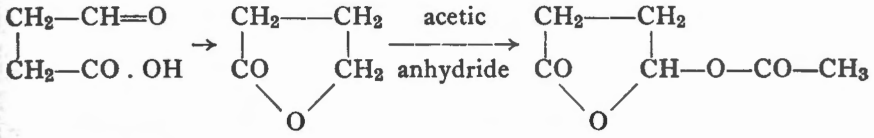


o-hydroxyhydrocinnamic acid — Hydrocoumarin



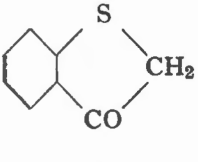
o-hydroxycinnamic acid — Coumarin

The aliphatic carboxylic aldehydes cyclize to *hydroxylactones* which are stable if the CH_2 next to O is substituted:

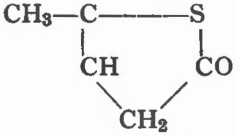


γ-aldehyde acid — Butyrolactone

Sulphur ketomethylene nuclei. The most important is *thioindoxyl*, used in the preparation of thioindigo:



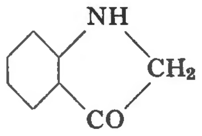
Thioindoxyl
(or oxithionaphthene)

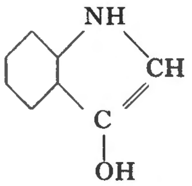


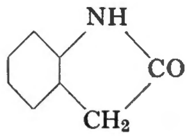
Oxythiotolene

Thioindoxyl is prepared by condensing chloracetic acid with thiophenol-o-carboxylic acid HS—C_6H_4—COOH. This gives phenylthioglycine-o-carboxylic acid, CO . OH—CH_2—S—C_6H_4—COOH, which cyclizes in the presence of fused potash to thioindoxyl-carboxylic acid. The latter gives thioindoxyl by elimination of CO_2.

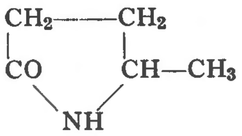
Mononitrogen ketomethylene nuclei. Indoxyl, the starting material for the synthesis of indigo, corresponds to thioindoxyl. Indoxyl is isomeric with *oxindole* obtained by cyclizing o-aminophenylacetic acid $NH_2—C_6H_4—CH_2—COOH$.

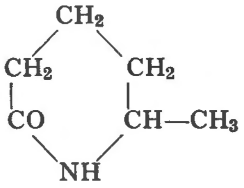

(Keto form)

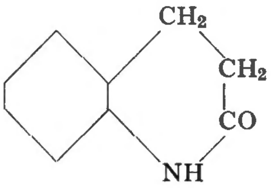

Indoxyl
(Enol form)


Oxindole

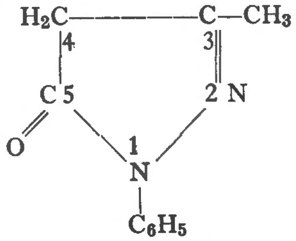
Cyclization of the γ-aminoacids such as $NH_2—CH(CH_3)—CH_2—CH_2—COOH$ gives the γ-lactones or *pyrrolidones.* The δ-aminoacids give the *piperidones* whilst the cyclization of o-aminohydrocinnamic acid $NH_2—C_6H_4—CH_2—CH_2—COOH$ gives hydrocarbostyryl (hydrogenated α-hydroxyquinoline).

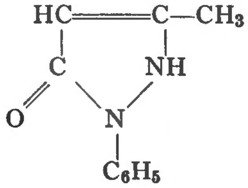

Pyrrolidone

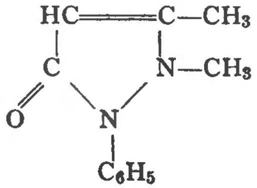

Piperidone


Hydroxycarbostyryl

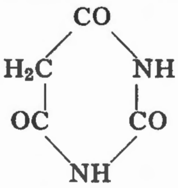
Ketomethylene nuclei with two nitrogen atoms. The β-keto esters such as acetoacetic ester $CH_3—CO—CH_2—CO—OC_2H_5$, especially in their enol forms $CH_3—C(OH){=}CH—$, react with phenylhydrazine to give *phenylmethylpyrazolones.* Phenylmethylpyrazolones, treated with dimethyl sulphate, are converted to *antipyrin* which is a pyrazolone with its second N substituted.


1-phenyl-3-methyl-5-pyrazolone

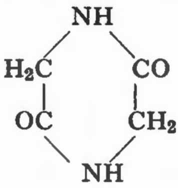

1-phenyl-3-methyl-isopyrazolone


Antipyrin

A ketomethylene nucleus in current use is *malonylurea* (or *barbituric acid*) which is a triketo derivative of hexahydropyrimidine, and which can be compared with diketopiperazine obtained by condensing two α-aminoacids.

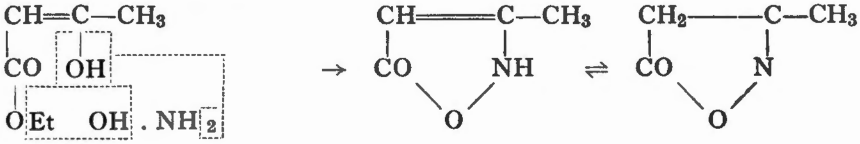


Barbituric acid
(malonylurea)



Diketopiperazine

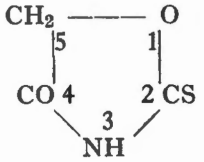
Ketomethylene nuclei containing a nitrogen and an oxygen atom. The representative of this family is *isooxazolone* obtained by condensing a β-keto ester with hydroxylamine NH_2OH.



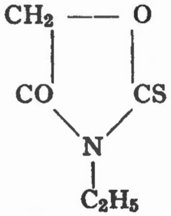
Enol acetoacetate hydroxylamine
(enol form)

Isooxazolone

In the *oxazolediones*, the nitrogen atom is next to the CO, and to a thioketo group CS (or $>C{=}S$)



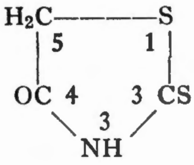
2-thio-2 : 4(3 : 5)-oxazoledione



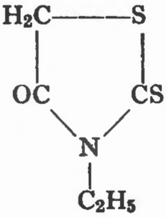
3-ethyl-2-thio-2 : 4(3 : 5)-oxazoledione

2-thio-2:4-(3:5)-oxazoledione and its 3-ethyl and 3-phenyl derivatives are prepared by Ahlquist's method.(51)

Ketomethylene nuclei containing an atom of nitrogen and an atom of sulphur. The rhodanines correspond to the oxazolediones. The nitrogen atom is situated between a keto $>C{=}O$ and a thioketo $>C{=}S$ group



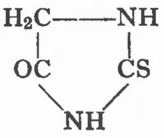
Rhodanine



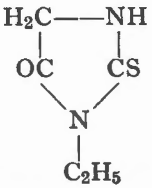
3-ethylrhodanine

The rhodanines are very important in the preparation of the merocyanines.

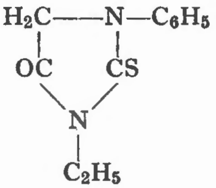
Ketomethylene nuclei containing two nitrogen atoms and a sulphur atom. These are represented by *thiohydantoin* and *isothiohydantoin* (or pseudothiohydantoin). Their substituted derivatives are generally used:



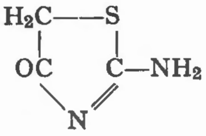
Thiohydantoin



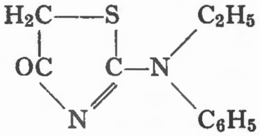
3-ethylthiohydantoin



1-phenyl-3-ethyl thiohydantoin



Isothiohydantoin



Ethylphenylisothiohydantoin

698. Preparation of the thiohydantoins

1-phenyl-3-ethylthiohydantoin⁽⁵²⁾ is prepared by heating 17 g (1 mol) of phenylaminoacetic acid ethyl ester and 8·7 g (1 mol) of ethyl isothiocyanate for 72 hours on the waterbath under reflux. The resulting viscous liquid is poured into methanol which precipitates the thiohydantoin, or the solid cake is ground up with alcohol. This is recrystallized from methanol using 10 cc per gram. Yield of crude product, 63% and after crystallizing, 50%. M. Pt. 125·5–128°C.

3-phenylthiohydantoin: Wheeler and Brautlecht's method.(53)

3-methylthiohydantoin: Markwald, Neumark and Stelzer.(54)

1-acetylthiohydantoin: Johnson and Nicolet.(55)

4-thiohydantoin. All of the above thiohydantoins are the 2-thiohydantoins (thioketo group in the 2- position). There is also 4-thiohydantoin prepared by Johnson and Chernoff(56) in which the CO and CS groups are reversed.

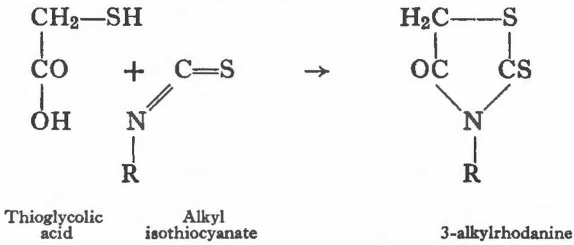
Methylphenylisothiohydantoin: prepared by Dixon.(57)

Ethylphenylisothiohydantoin: Andreasch.(58)

Diphenylisothiohydantoin: Dixon and Taylor.(59)

699. Preparation of rhodanines

The rhodanines are prepared by condensing *thioglycolic acid* HS—CH$_2$——CO . OH with an *isothiocyanate* R—N═C═S.



The isothiocyanates are prepared from the alkylamines R—NH_2 using the method disclosed by Holmberg.⁽⁶⁰⁾

Thioglycolic acid. Saturate a solution of 11·2 g (0·2 mol) of caustic potash in 100 cc water with hydrogen sulphide. Add 10 g monochloracetic acid dissolved in 30 cc water in 10 mins. without agitation. Heat for 15 mins. at 100°C and cool. Add 24·5 g barium chloride $2H_2O$ and 18 cc ammonia S.G. 0·950 (0·125 mol). After leaving for 12 hours in a refrigerator, the crystals which are formed (8 g) are filtered and washed with water, alcohol and ether. They are dissolved in 10 cc hydrochloric acid (S.G. 1·17) in 18 cc water. Fresh crystals separate, and are extracted with ether. After evaporating the ether, a crystalline residue is left M. Pt. 128–129°C. However, it would seem preferable to decompose the barium salt with dilute sulphuric acid and filter off the precipitated barium sulphate.

Ethyl isothiocyanate. Prepare a solution of 14 g (0·183 mol) carbon disulphide CS_2 in 25 g 30% caustic soda (0·183 mol) and cool to 10–15°C. Add 22 g *ethylamine* as a 33% aqueous solution with stirring (0·161 mol). Heat to 80–90°C on the waterbath stirring continuously. Allow to cool to 35°C and add 19·8 g (0·183 mol) *ethyl chlorocarbonate* in one hour. Stir for a further 30 mins. and separate the crude product. Purify by steam distillation. The distillate is extracted 3 times with 20 cc ether. Remove the ether by distillation and remove the last traces by raising the temperature to 120°C, and distil, collecting the fraction boiling between 130° and 137°C. 6·2 g of the product is obtained. Yield, 44%. A further quantity can be obtained by fractionating the low and high boiling fractions.

3-ethylrhodanine: heat 0·8 g ethylisothiocyanate, 1 g thioglycolic acid, 1 g alcohol and 3 cc water for 4 hours at 100°C. Cool, separate the lower oily layer and wash it with water. 1 g dry ethylrhodanine is obtained. Yield, 67%.

3-naphthylrhodanine. Heat 1·85 g (0·01 mol) of α-naphthyl isothiocyanate and 1·1 g (0·012 mol) of thioglycolic acid, for 6 hours, at 100–105°C. Grind the solid obtained with 50 cc ether. Filter and wash successively with 6 cc alcohol and 20 cc ether. 2 g of a product melting at 169°C is obtained. Yield, 77%. *Phenylrhodanine* is similarly obtained.

3-methylrhodanine: see Andreasch and Zizsser.⁽⁶¹⁾

3-allylrhodanine: Andreasch and Zizsser.⁽⁶²⁾

3-β-hydroxyethylrhodanine: from ethanolamine. Holmberg.⁽⁶⁰⁾

3-n-propylrhodanine: B. Pt. 123°/2 mm.

3-isopropyl rhodanine: M. Pt. 58–61°C.

3-phenylthiorhodanine.⁽⁶³⁾ Heat 10g 3-phenylrhodanine in 200 cc dry toluene to 110–120°C and add 5·3 g (0·5 mol) of phosphorus pentasulphide mixed with an equal volume of sand. Heat for a further 15 minutes. The toluene layer is decanted and poured on to crushed ice and 10 cc of 40% caustic soda is added. Separate the aqueous layer; add acetic acid, filter, redissolve the residue in caustic soda, filter, cool the filtrate and filter again. Recrystallize from acetic acid then from petroleum ether. Yield, 4%. M. Pt. 114–116°C.

CONDENSING AGENTS

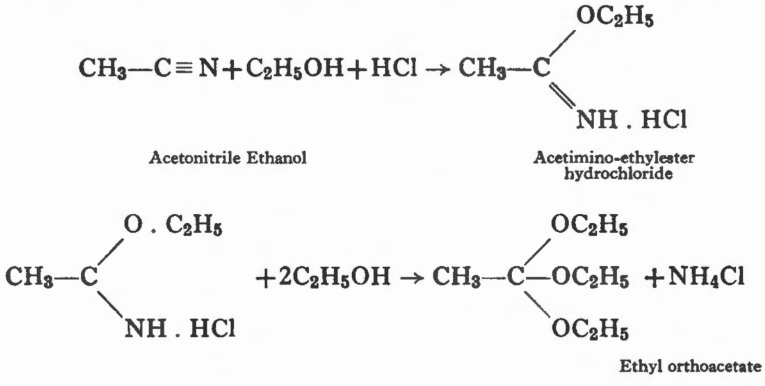
700. Ethyl orthoformate

The hypothetical organic acids with the formula $R.C{\equiv}(OH)_3$ are derived from the normal acids, and correspond to orthophosphoric acid $O{=}P{\equiv}{\equiv}(OH)_3$. Thus the unisolated orthoformic acid $HC{\equiv}(OH)_3$ corresponds to formic acid $H.CO.OH$. Between these two compounds there is the same difference as there is between metaphosphoric acid $O.P.O.OH$ and orthophosphoric acid. The esters of these ortho-acids have been isolated, such as *ethyl orthoformate* $HC(OC_2H_5)_3$ obtained by the action of chloroform on sodium ethoxide⁽⁶⁴⁾ or by the action of ethanol on the formoimino ester hydrochlorides using Pinner's process.⁽⁶⁵⁾ Ethyl orthoformate boils at 142–146°C.

701. Ethyl orthoacetate

The esters of the ortho acids homologous with orthoformic acid are prepared by Pinner's general method, simplified by Reitter and Hess⁽⁶⁶⁾ and used by Sah,⁽⁶⁷⁾ Sigmund and Herschdorfer,⁽⁶⁸⁾ then by Brooker and White.⁽⁶⁹⁾

The preparation takes place in two stages: the formation of the imino-ester by the addition of alcohol and hydrochloric acid to the corresponding nitrile, then conversion of the imino ester to the orthoacid ester by the action of an alcohol (which finally occurs in the ester groups). Thus *ethyl orthoacetate*, which is made from *acetonitrile* is prepared according to the scheme:



$$CH_3{-}C{\equiv}N + C_2H_5OH + HCl \rightarrow CH_3{-}C\begin{matrix}OC_2H_5\\ NH.HCl\end{matrix}$$

$$CH_3{-}C\begin{matrix}O.C_2H_5\\ NH.HCl\end{matrix} + 2C_2H_5OH \rightarrow CH_3{-}C\begin{matrix}OC_2H_5\\ {-}OC_2H_5\\ OC_2H_5\end{matrix} + NH_4Cl$$

Ethyl iminoacetate (hydrochloride). Place 270 g of acetonitrile (dried over sodium sulphate), 400 cc absolute ethanol and 240 cc ether (dried over sodium) in a 2-litre flask. It is important to exclude all moisture. Cool the mixture to 5–10°C with an ice-bath, and pass a slow current of dry hydrogen chloride through until saturated, that is, when a washing flask placed after the flask shows a considerable amount of gas passing through. This takes about 4 hours.

The current of hydrogen chloride gas is generated in a 3-litre flask fitted with a pressure tube and containing 500 g of sodium chloride into which is poured a cool solution of 500 cc sulphuric acid and 300 cc water. The gas evolution is achieved by progressive warming over a gauze which can be regulated at will. The hydrochloric acid is passed through a washing bottle filled with sulphuric acid, then through a large tube filled with pumice stone impregnated with sulphuric acid(70) before being passed into the acetonitrile solution.

After the absorbing flask is an empty flask, followed by a further flask containing sulphuric acid to check the amount of gas passing through and then a flask filled with water to absorb the excess HCl. The exit tube must only be immersed a few mm. The exhausted sulphuric acid mixture must be emptied while it is still warm otherwise the flask will be difficult to clean.

The vessel containing the imino ester is carefully stoppered and placed in ice for 24 hours. The liquid solidifies with a hard cake formed of white crystals. The supernatant ether is decanted and the crystalline product is ground up and placed in a dessicator, containing soda lime and phosphorus pentoxide to absorb the excess hydrogen chloride, for at least 48 hours, finishing by exhausting the dessicator. In this way 678 g of ethyl iminoacetate hydrochloride is obtained. Yield, 80–95%.

The imino esters are unstable compounds and must be converted to the ortho esters as soon as possible.

Ethyl orthoacetate. Place 630 g of ethyl imino acetate (HCl) and 1350 cc absolute ethanol in a flask with a ground in stopper. The mixture is agitated once or twice a day and left standing the rest of the time for *two weeks*. Some ammonium chloride separates which is removed by filtration. 4 g of fused potassium carbonate is added to the filtrate to remove the last traces of free HCl, then it is distilled at 50°C. The fraction boiling between 55 and 75°C is collected and redistilled at normal pressure. The pure product boils at 144–146°C. It is a colourless liquid, insoluble in cold water and miscible with alcohol, ether and chloroform. 493 g of crude orthoacetate giving 225 g of pure orthoacetate plus 73 g recoverable from the other fractions, giving a total of 308 g is obtained. (Yield, 29% based on the acetonitrile.) The forerun from the reduced pressure distillation is mainly absolute alcohol.

After 5 months' keeping, one-third of the orthoacetate is decomposed and it must be redistilled.

702. Other ortho esters

The following ortho esters have been prepared by Brooker and White⁽⁷¹⁾ by the general method given for ethyl orthoacetate.

Preparation of the imino esters (hydrochlorides)

Imino-ester	*Nitrile*	*Alcohol*	*Days in Contact*	*Days Drying*	*Yield %*
Methyl imino propionate	C_2H_5CH	Methyl	2	3	88
Methyl imino-n-butyrate	n-C_3H_7CN	Methyl	3	3	67
Methyl imino-n-valerate	n-C_4H_9CN	Methyl	2	3	63
Methyl imino-n-caproate	n-$C_5H_{11}CN$	Methyl	4	2	75
Methyl imino isocaproate	iso-$C_5H_{11}CN$	Methyl	3	3	71
Ethyl imino phenoxyacetate	$C_6H_5OCH_2CN$	Ethyl	2	2	82
Ethyl imino benzoate	C_6H_5CN	Ethyl	20	8	90

Preparation of the ortho esters

Ortho ester	*Days*	*Yield %*	*Boiling Point*
Methyl ortho propionate	6	69	126–128°C
Methyl ortho n-butyrate	28	13	145–147°C
Methyl ortho n-valerate	28	12	167–170°C
Methyl ortho n-caproate	5	40	187–190°C
Methyl ortho iso-caproate	35	9	178–181°C
Ethyl ortho phenoxyacetate	28	30	99–100°C (1·5 mm)
Ethyl ortho benzoate	42	20	239·5–240°C

Ethyl orthobenzoate, distilled at 130–140°C at 8·5 mm is ground up with water to dissolve the amide. Benzene is added. The benzene solution is washed with water, dried over anhydrous sodium sulphate and fractionated.

Ethyl orthophenylacetate—see Staudinger and Rathsam.⁽⁷²⁾

703. p-dimethylaminobenzaldehyde

p-dimethylaminobenzaldehyde $(CH_3)_2N—C_6H_4—CHO$ is obtained by the action of chloral hydrate on dimethylaniline following Boessneck's technique.⁽⁷³⁾ The aldehyde is purified by vacuum distillation. By replacing the dimethylaniline by diethylaniline, p-diethylaminobenzaldehyde is produced.

1. Mikeska Stewart and Wise: *Ind. and Eng. Chem.*, 1919, 456.
2. Döbner and Miller: *Ber.*, 1883, **16,** 2465.
3. Gatekunst and Gray: *J.A.C.S.*, 1922, **44,** 1741.
4. *Ber.*, **29,** 703.

5. Seitz: *Ber.*, 1889, **22,** 254; Bamberger and Miller: *Ber.*, 1891, **24,** 2846; Doebner and Miller: *Ber.*, 1884, **17,** 1711.
6. Molhau: *Ber.*, 1888, **21,** 59.
7. Reissert: *Ber.*, 1904, **37,** 3731.
8. Hofmann: *Ber.*, 1894, **27,** 2808; Clark L. M.: *J.C.S.*, 1928, **131,** 2313.
9. Jacobson P.: *Ber.*, 1886, **19,** 1072.
10. Jacobson and Ney: *Ber.*, 1889, **22,** 907.
11. Wallach O.: *Ber.*, 1880, **13,** 529.
12. Bernthsen: *Ann. d. Chemie*, **184,** 359; Bernthsen and Trompetter: *Ber.*, 1878, **2,** 1859.
13. Fries and Engelbertz: *Ann. d. Chemie.*, 1915, **407,** 207.
14. Blanksma: *Rec. Tr. Chim. Pays Bas*, 1902, **20,** 399.
15. G.P. 360,690.
16. Levkoev and Portnaya: *Zh. Obsh. Khimii*, Nov. 1951, 2050.
17. Brooker and Cressman: *J.A.C.S.*, 1945 Dec., 2046.
18. Jacobson and Sullwald: *Ber.*, 1888, **25,** 2624; Jacobson and Schwartz: *Ann. d. Chemie*, 1893, 257; Rupe and Schwartz: *Z. Farb. Textilchem*, 1904, 397.
19. Knott E. B.: *J.C.S.*, 1945, 455.
20. Hantzch: *Ann. der Chemie*, 1889, **250,** 257–269; Banerji, J. C. and Banerji K.: *Jl. Ind. Chem. Soc.*, 1954, 509.
21. *Ber.*, 1896, **29,** 2610.
22. *Ber.*, 1891, **24,** 787.
23. *Ber.*, 1891, **24,** 1117.
24. Wenker H.: *J.A.C.S.*, **57,** 1079.
25. Bauer: *Ber.*, 1913, **46,** 92; Clark L. M.: *J.C.S.*, 1928, **131,** 2313.
26. Muthmann and Schroeder: *Ber.*, 1900, 1765.
27. B.P. 389,969 (1933).
28. Knott E. B.: *J.C.S.*, 1945 (Sept.), 628.
29. *Ber.*, **25,** 3048.
30. U.S.P. 1,957,870 (1934).
31. Van Dormael A. and Ghys T.: *Bull. Sco. Chim. Belge.*, 1948 (Sept.), 341.
32. Ladenburg: *Ber.*, 1876, **9,** 1523; Theilaker: *Jl. f. Prakt. Chem.*, **153,** 54.
33. *Gazz. Chim. Ital.*, 1948, 78, 435.
34. Raiford-Colbert L.: *J.A.C.S.*, **47,** 1456.
35. Norris: *J.A.C.S.*, 1903, **29,** 123.
36. Hodgson and Kilner: *J.C.S.*, 1924, **125,** 807.
37. Liebermann: *Ann. d. Chemie*, **183,** 225; Liebermann and Dittler: *Ber.*, 1874, **7,** 240; Grandmougin and Michel: *Ber.*, 1892, **25,** 972; Liebermann and Jacobsen: *Ann. d. Chemie*, 1882, **211,** 36; Hamer and Fisher: *J.C.S.*, 1934, 962.
38. Linemann, Konitzer and Romanoff: *Ann. d. Chemie*, 1927, **456,** 284; Grandmougin and Michel: *Ber.*, 1892, **25,** 3429.
39. Böttcher: *Ber.*, 1883, **16,** 1933.
40. Hamer and Fisher: *J.C.S.*, 1934, 962; Brooker L. G. S.: U.S.P. 1,939,201 (1932).
41. Also known as 1-methyl-β-naphthoxazole.
42. Fisher: *Ber.*, **19,** 1563 and **22R,** 14; *Ann. d. Chemie*, 1887, 353. See also *Ber.*, **31,** 1488; **19,** 2448 and **22R,** 664.

42b. Pilyugin G. T. and Kainer Z. Y.: *Doklady Ak. Nauk. S.S.S.R.*, 1951, 609.

43. Hamer F. M.: *J.C.S.*, 1929, 2598; Jacobson P.: *Ber.*, 1887, p. 1898.
44. Also known as 1 : 3-dimethylthiazole.
45. Hamer and Fisher: *J.C.S.*, 1933, 2502.
46. Clark L. M.: *J.C.S.*, 1926, **129,** 232.
47. König and Muller: *Ber.*, 1924, **57,** 114.
48. Perkin and Robinson: *J.C.S.*, 1913, **103,** 1937; Roser: *Ann. der Chemie*, 1894, **282,** 373.

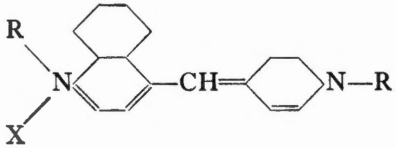
49. Hamer F. M. and M. I. Nelly: *J.C.S.*, 1931, **134,** 777.
50. Walther: *Jl. Prakt. Chem.*, **53,** 3116; Heller: *Ber.*, **37,** 473.
51. Ahlquist: *Jl. Prakt. Chem.*, 1919, **99,** 45.
52. Kodak: F.P. Add., 48,226 (1937) U.S. Priority 1935.
53. Wheeler and Brautlecht: *J.A.C.S.*, 1911, **45,** 466.
54. Markwald, Neumark and Stelzer: *Ber.*, 1891, **24,** 3278.
55. Johnson and Nicolet: *J.A.C.S.*, 1911, **33,** 1937.
56. Johnson and Chernoff: *J.A.C.S.*, 1912, **34,** 1208.
57. Dixon: *J.C.S.*, 1897, **71,** 629.
58. Andreasch: *Ber.*, 1895, **31,** 137.
59. Dixon and Taylor: *J.C.S.* 1908, **93,** 689.
60. Holmberg: *Jl. Prakt. Chem.*, 1910, **81,** 451.
61. Andreasch and Zizsser: *Monatsch.*, 1904, **25,** 167.
62. Andreasch and Zizsser: *Monatsch.*, 1903, **24,** 504.
63. Kodak: F.P. Add., 48,226 (1937) U.S. Prior., 1935, p. 15.
64. Williamson and Kay: *Ann. d. Chemie.*, **92,** 346.
65. Pinner: *Ber.*, 1883, **16,** 1645.
66. Reitter and Hess: *Ber.*, 1907, **40,** 3020; Hill and Rabinowitz: *J.A.C.S.*, 1926, **48,** 732.
67. Sah: *J.A.C.S.*, 1928, **50,** 516.
68. Sigmund and Herschdörfer: *Monatsh.*, 1931, **58,** 280.
69. Brooker and White: *J.A.C.S.*, 1935, **57,** 2480–2488.
70. *Sulphuric treated pumice:* granular pumice stone is baked and impregnated with sulphuric acid, drained for 15 minutes, then heated until white sulphuric acid vapour is given off. Put into a flask before cooling.
71. *Loc. cit.*
72. Staudinger and Rathsam: *Helv. Chem. Acta.*, 1922, **5,** 645; Sah, Ma and Kao: *J.C.S.*, 1931, 305.
73. Boessneck: *Ber.*, **18,** 1516; **18,** 1886; **19,** 365.

Chapter XXXVII

CYANINES

704. True cyanines

The true cyanines are the 4:4′-cyanines with the general formula



They are only of theoretical interest as their sensitizing properties are weak. Their sensitization region is in the orange-red; they are in fact blue dyes having their absorption maximum in the orange.

The 'true' cyanines were the first known cyanines: Williams' *'cyanine'* was an iodoamylate (1856), Von Babo's *irisin* was a methylsulphate whilst *ethylirisin* was an ethylsulphate (1857). Schnitzer later prepared *quinoline blue* (1861) identical with Williams' cyanine. These dyes were obtained from an impure quinoline, extracted from cinchonine.

It was in 1883 that Hoogewerff and Van Dorp found that the cyanines can be readily prepared by treating a mixture of the *alkyl iodides of quinoline and lepidine with caustic potash.*

1:1-diethyl-4:4′-cyanine (iodide) is prepared by boiling a mixture of 15 g of lepidine ethiodide (1 mol) 28 g quinoline ethiodide (2 mol) in 375 cc 95 % alcohol with 100 cc normal alcoholic soda. After 20 minutes' boiling the deep blue liquid is cooled and deposits crystals which are recrystallized from alcohol.

Dull green needles slightly soluble in water. Absorption maximum 595 mμ. Weak sensitization to 650 mμ with maxima at 560 and 620 mμ.

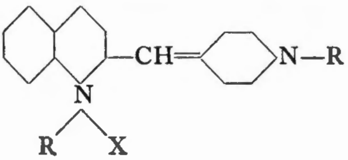
Ethylcyanine T from Hoechst, was 1:1′-diethyl-2′:6′-dimethyl-4:4′-cyanine prepared from p-toluquinaldine and lepidine. A slightly more powerful sensitizer than the preceding one.

In the preparation of cyanines, an isocyanine is always formed simultaneously.

ISOCYANINES

705. Quinoline isocyanines

The isocyanines derived from quinoline have the general formula



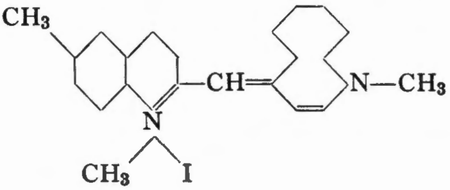
These are the 2:4′-cyanines. Discovered in 1883 by Spalteholtz, Hoogewerff and Van Dorp, they are red dyes which have green sensitizing properties.

The *isocyanines* are formed when a mixture of the alkyl iodides of quinoline and quinaldine (α-methylquinoline) are treated with a caustic alkali: the iodine of quinoline methiodide, for example, is replaced by an OH group with loss of potassium iodide giving 1-methylquinoline hydroxide. This is converted to 1-methyl-γ-quinolone CH_3—N . C_9H_6=O which reacts with the quinaldine methiodide to produce an isocyanine.

Another method is to condense lepidine with itself which also gives an isocyanine. The isocyanines derived from quinoline are medium power sensitizers. They were widely used at one time for the preparation of orthochromatic emulsions but have now been surplanted by the thia-, selena-, and oxa-cyanines which are much more powerful. A very large number of isocyanines have been prepared, the most important of which were *pinaverdol*, *orthochrome T*, and *pinachrome*.

706. Preparation of quinoline isocyanines

Pinaverdol. This isocyanine was also known by the names *sensitol green* and *chlorochrome.* It was prepared by reacting an alkali with a mixture of the methiodides of p-toluquinaldine and quinoline.(1) It is therefore 1:1′:6-trimethylisocyanine iodide.



p-toluquinaldine methiodide anh.	17·5 g
Quinoline methiodide anh.	32·2 g

are dissolved in 500 cc 95% alcohol in a flask fitted with a reflux condenser.

The solution is heated to boiling point and 96·5 cc of a 0·7N alcoholic solution of caustic potash (3·75 g) are slowly added through a dropping funnel. Boiling is continued for 5 minutes and 62 cc alcohol is added; the coloured solution is allowed to cool: it deposits a mass of blackish granular crystals. These are filtered off on a buchner and dried. 6·8 g of crude dye are obtained (yield, 25 %). The product is ground up and extracted with ether in a soxhlet until the extract is no longer coloured. This operation is repeated with absolute methanol until the extract has a faint pink colour. The brick red powder remaining in the extraction flask is the isocyanine. A little more isocyanine can be obtained by concentrating the methanol extract. Overall yield, 13·14 %.

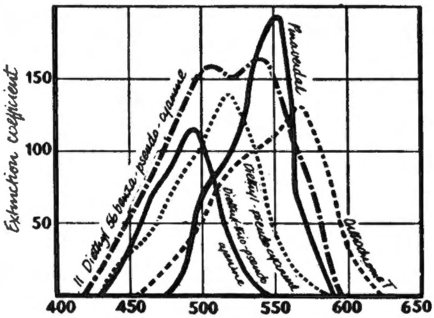


FIG. 121. Absorption curves of isocyanines and pseudocyanines.

Pinaverdol crystallizes in the monclinic system as pleochroic prisms. Absorption maxima at 522 and 562 mμ (Fig. 121). Sensitization to 650 mμ with maxima at 535 and 583 mμ; minima at 500 and 558 mμ.

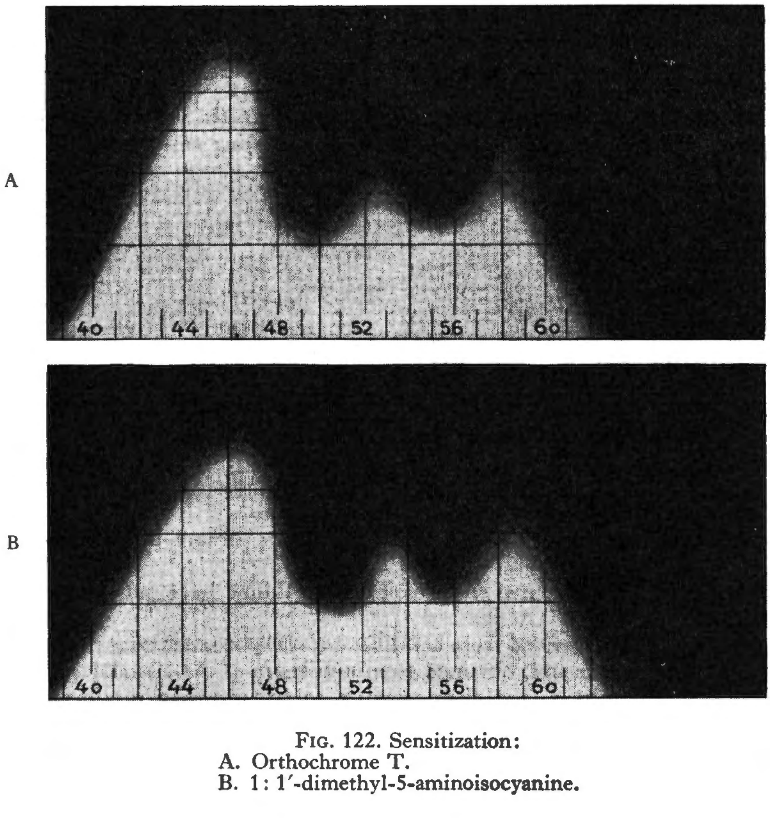


FIG. 122. Sensitization:
A. Orthochrome T.
B. 1 : 1′-dimethyl-5-aminoisocyanine.

Orthochrome T. (1:1′-diethyl-6:6′-dimethylisocyanine) was obtained from the ethiodides of toluquinoline and toluquinaldine. It crystallizes from methanol in rectangular tablets with a metallic lustre. Sensitizing action to 635 mμ with maxima at 530 and 583 mμ (Fig. 64).

Pinachrome (1:1′-diethyl-6-ethoxy-6′-methoxyisocyanine bromide) was prepared by condensing the ethobromides of p-methoxyquinoline and p-ethoxyquinaldine in the presence of caustic soda in alcohol. In the same way the diethoxy derivative was obtained. Pinachrome gives violet solutions, it sensitizes to 640 mμ with maxima at 540 and 615 mμ.

A large number of isocyanines have been prepared. The principle ones were:

(*a*) Simple derivatives.

1:1′-dimethylisocyanine (iodide) obtained from a mixture of the methiodides of quinoline and quinaldine. Sensitization maxima at 535 and 585 mμ.

1:1′-diethylisocyanine (iodide) or ethyl red, weaker sensitization.

1:1′:6′-trimethylisocyanine (iodide), isomeric with pinaverdol: obtained from toluquinoline and quinaldine. Sensitization maxima at 533 and 585 mμ.

1:1′-di-n-propyl-6-methylisocyanine (iodide). Sensitization maxima at 540 and 590 mμ.

1:1′:4:6:6′-pentamethylisocyanine (iodide). Weak sensitizer like all the polymethyl derivatives.

(*b*) *Alkyl sulphate isocyanines* obtained from the alkyl sulphates of the heterocyclic bases; for example, 1-methylquinaldine dimethylsulphate. *Homocol, isocol* and *pericol* from Bayer were alkyl sulphate isocyanines.

(*c*) *Acetylamino-isocyanines*: the presence of acetylamino groups $CH_3 . CO . NH—$ generally tend to suppress sensitization except the 6′ derivative whose action is equal to the simple cyanine.

Cinnamoylamino-isocyanines containing the group $C_6H_5 . CH = CH . CO . NH—$ substituted in the nucleus. Analogous to the acetylaminoisocyanines, their sensitizing power is even weaker (except the 6 derivative).

(*d*) *Aminoisocyanines* contain the group $NH_2—$ substituted in the nucleus, which often increases the sensitizing power. The most interesting aminoisocyanine of the series is *5-amino-1:1′-dimethylisocyanine* whose action is almost uniform from blue to orange up to 660 mμ, with maxima at 535 and 585 mμ (Fig. 64). The aminoisocyanines are obtained by hydrolysis of the acetylaminoisocyanines.

The introduction of an active auxochrome group such as $—N(CH_3)_2$ gives a new series which are good sensitizers.

1:1′-diethyl-6:6′-tetramethyldiaminoisocyanine (iodide). This was the main constituent of Koenig's *pinachrome violet*, and Lumière and Barbier's *cyanine B*. It sensitizes up to 700 mμ with maxima at 578 and 635 mμ. It was obtained by condensing a mixture of the ethiodides of p-dimethylaminoquinoline and quinaldine with soda. Dimethylaminoquinoline and p-dimethylaminoquinaldine are prepared from dimethyl-p-phenylenediamine, $(CH_3)_2N—C_6H_4—NH_2$.⁽²⁾

1:1′-diethyl-6-methyl-6′-dimethylaminoisocyanine, a constituent of Lumière and Barbier's *cyanine A*, is prepared from toluquinaldine and dimethylaminoquinoline. Sensitizes up to 685 mμ with maxima at 548 and 612 mμ.

(*e*) *Halogenated isocyanines* obtained from chloro or bromo bases. Weak sensitizers.

(*f*) *Benzoisocyanines*, prepared from naphthoquinaldine, have only a weak sensitizing action.

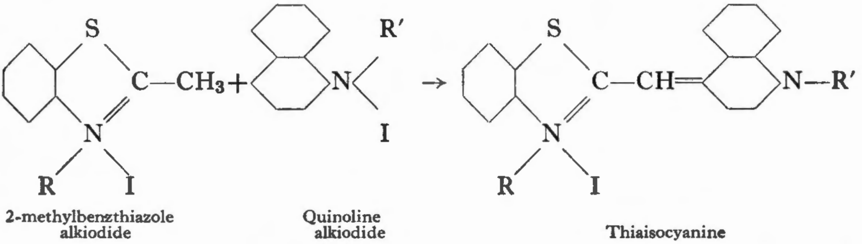
(*g*) *Acridoisocyanines*, derived from acridine, are without sensitizing properties.

(*h*) *Acenaphthenoisocyanines*, obtained from a mixture of the alkiodides of quinoline and methylacenaphthenopyridine, sensitize to 680 mμ with maxima at about 540 and 610 mμ.⁽³⁾

(*i*) *Isoquinoline isocyanines*. These are derived from isoquinoline, in which the second ring (benzene) is in the 3:4 position with reference to the nitrogen. They are obtained by condensing the salts of 1-iodo-isoquinoline with those of lepidine. Mediocre sensitizers.⁽⁴⁾

707. Thiaisocyanines

The thiaisocyanines contain a quinoline nucleus and a benzthiazole nucleus. They are prepared by the action of alcoholic soda on a mixture of the alkiodides of quinoline and 2-methylbenzthiazole:



A thiaisocyanine is an isocyanine in which the —CH=CH— of one of the nuclei is replaced by —S—. The formation of the thiaisocyanines is due, as with the isocyanines, to the activity of the methyl groups of the 2-methyl base.

The thiaisocyanines are red compounds which crystallize well from alcohol. Their orange-red solutions have two unequal, overlapping absorption bands in the green and blue-green. *Compared with the isocyanines, the thiaisocyanines have their absorption and sensitization maxima shifted about 50 mμ towards the shorter λ.* These sensitizers are superior to the quinoline isocyanines and can sensitize up to 580 mμ.

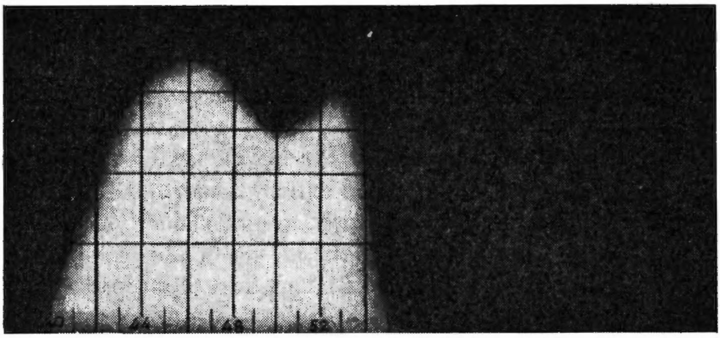


FIG. 123. Sensitization: 3: 1′-diethylthiaisocyanine.

708. 3:1′-diethylthiaisocyanine

14·4 g of quinoline ethiodide and 15·4 g 2-methylbenzthiazole⁽⁵⁾ are dissolved in 200 cc boiling alcohol. A solution of 1·38 g sodium in 80 cc absolute alcohol is added. A deep red colour develops immediately. After 15 minutes' boiling, the solution is allowed to cool. Red needles separate, and are recrystallized from methanol, and dried at 80°C.11 mm. Yield, 2–3 g.

Another method is to heat lepidine ethylnitrate with di-o-formylethylaminodiphenyl disulphide H . CO . $N(C_2H_5)—C_6H_4—S—S—C_6H_4—N(C_2H_5)COH$ in pyridine. A *kryptocyanine* is formed simultaneously, and is isolated from the filtrate by precipitating with potassium iodide.(6)

Properties: Absorption maxima at 489 and 503 mμ.

Fairly powerful sensitizing action, extending to 580 mμ with a maximum at 525 mμ (Fig. 123).

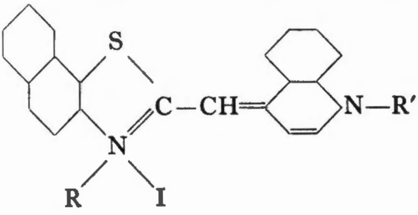
6-methyl-3:1′-diethylthiaisocyanine is a similar sensitizer to the preceding one with a maximum at 530 mμ. Absorption at 492 and 508 mμ. It is obtained by heating in alcohol a mixture of the ethiodides of quinoline and *2:6 dimethylbenzthiazole* in the presence of sodium alkoxide. Crystallizes from alcohol in brilliant red needles. M. Pt. 269–270°C (decomp.).

The following thiaisocyanines have also been prepared: 1′:6′-dimethyl-3 ethyl thiaisocyanine (iodide) (methylbenzthiazole + p-toluquinoline), 6:1′:6′-trimethyl-3-ethylthiaisocyanine (iodide) (2:6-dimethylbenzthiazole + p-toluquinoline), 6′-ethoxy-3:1′-diethylthiaisocyanine, (iodide) (6-ethoxyquinoline and 2-methylbenzthiazole or p-ethoxylepidine + di-o-formylethyldiaminodiphenyldisulphide) 6′-ethoxy-5-methyl-3:1′-diethylthiaisocyanine (p-ethoxyquinoline + 2:6 dimethylbenzthiazole).

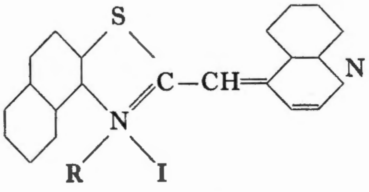
709. Benzothiaisocyanines

These thiaisocyanines are obtained from naphthothiazole. They are prepared by the general method: condensation of a quinoline alkyl iodide with *methylnaphthothiazole* alkyl iodide, or better, ethyl p-toluene-sulphonate, in the presence of alkali.

The *benzothiaisocyanines* are sensitizers for the green and yellow-green. Compared with the simple thiaisocyanines, their absorption and sensitization maxima are shifted towards the red.



α-benzothiaisocyanine



β-benzothiaisocyanine

α-benzothiaisocyanines:

1′:3-diethyl-6:7-benzothiaisocyanine (iodide) (quinoline ethiodide + 2-methylnaphthothiazole ethyl p-toluene sulphonate in alcoholic solution in the presence of potash. The dye is precipitated with potassium iodide, and recrystallized from alcohol.)(7)

1′:3-diethyl-6′-methyl-6:7-benzothiaisocyanine (iodide) (p-toluquinoline ethiodide + 2-methylnaphthothiazole ethiodide). Similar cyanines are obtained using methoxy, ethoxy, dimethylamino or acetamino quinolines.

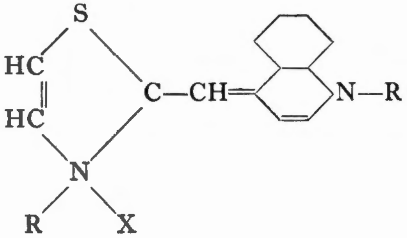
β-benzothiaisocyanines

1′:3-diethyl-4:5-benzothiaisocyanine (iodide) quinoline methiodide (2 mol) + 2-methyl-β-naphthothiazole p-toluene-sulphonate (1 mol) + sodium ethoxide (1·2 mol). After 20 minutes' boiling, the dye is precipitated with a concentrated solution of potassium iodide.

1′:3-dimethyl-6′-methoxy-4:5-benzothiaisocyanine (bromide) obtained by condensing 2-methyl-β-naphthothiazole p-toluene-sulphonate with p-methoxy-quinoline p-toluene-sulphonate. Precipitated as bromide by adding ammonium bromide. Sensitizes from the blue to 560 mμ.

710. Thiazoisocyanines

The thiazoisocyanines are derived from 2-methylthiazole (alkyliodide or alkyl-p-toluene-sulphonate). They have the general formula



1′:3-dimethyl-4-phenylthiazoisocyanine (iodide). 2-methyl-4-phenylthiazole methiodide is condensed with quinoline ethiodide. The precipitate, recrystallized from methanol, gives deep red solutions which sensitize up to 600 mμ with a maximum at 530 mμ.

1′:3-diethylthiazoisocyanine (iodide). Quinoline ethiodide and 2-methylthiazole.(8) The alkyl p-toluene-sulphonates can be used. In this case the method is the same as for benzoisocyanines, precipitation with an alkali halide. Green sensitizer.

Thiazolinoisocyanines. These are obtained from 2-methylthiazoline. An alkyliodide of 2-methylthiazoline is condensed with an alkyliodide of quinoline in alkaline alcoholic solution. Sensitizers for the blue-green and green.(8)

Thiaisocyanines with heavy nuclei. Sensitizers for the green and yellow-green, with absorption and sensitizing maxima shifted 10–20 mμ towards the red compared with the simple thiaisocyanines, are obtained by condensing quaternary salts of heterocyclic bases with heavy nuclei such as *2-methylanthrathiazole*, *2-methylacenaphthothiazole*, *2-methyldiphenyleneoxidethiazole*, *2-methylcarbazothiazole*, with the quaternary salts of quinoline.(9)

711. Selenaisocyanines

The selenaisocyanines are similar to the thiaisocyanines with the exception that the starting bases are selenazole. For example, to obtain 3:6′-dimethyl-1′-diethyl-6:7-benzoselenaisocyanine,(10) 2-methyl-γ-naphthoselenazol dimethylsulphate is boiled with p-toluquinoline ethyl bromide in the presence of sodium ethoxide in alcohol (1 mol of the selenazole base, 2 mols of the quinoline base and 1·2 mols sodium). After 20 minutes' boiling and cooling the dye is precipitated with potassium bromide and recrystallized from methanol followed by washing with ether. Sensitizing action in the green and yellow-green.

The quinoline ring can carry substituents such as CH_3O—, C_2H_5O—, $(CH_3)_2N$—, etc.

The *telluraisocyanines* could be prepared in a similar way.

712. Oxaisocyanines

The oxaisocyanines are prepared from methylbenzoxazole or the methyl-α or β-naphthoxazoles. They sensitize chloride emulsions to blue. Their sensitization maxima are shifted towards the shorter λ compared with the thiaisocyanines.

The oxaisocyanines are obtained by the general preparation method.

PSEUDOCYANINES

713. Quinoline pseudocyanines (or 2:2′ cyanines)

The pseudo cyanines were discovered by Kaufmann ⁽¹¹⁾ in 1912, then studied by Fisher and Scheibe⁽¹²⁾ in 1919. These dyes have their principle absorption in the region of 490–525 mμ. They sensitize in the blue-green and the green.

The pseudocyanines are prepared by heating a *2-iodoquinoline alkyliodide* (para. 694) with a *quinaldine alkyliodide* in the presence of caustic potash in water or absolute alcohol.

A second method of preparation is to condense a quinaldine quaternary salt with a quaternary salt of *quinoline 2-methylmercaptan* (see para. 695). We will return to this method in connection with the selenapseudocyanines.

1′-methyl-1-ethylpseudocyanine (iodide) sensitizes in the yellow-green with a maximum at 580 mμ. It is prepared in the following way:

20 g of 2-iodoquinoline methiodide is added to 1 litre of boiling water. Into the filtered solution 15 g of quinaldine ethiodide is poured, then, when boiling, 6 g of caustic potash dissolved in 150 cc of water is added. After 15 minutes it is allowed to cool when the dye precipitates; it is recrystallized

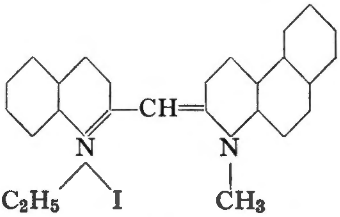
from alcohol (yield 21%). With absolute alcohol as the solvent the yield is 52%: in this case, a mixture of 24 g 2-iodoquinoline methiodide, 17·5 g quinaldine ethiodide in 1200 cc absolute alcohol to which 8 g of caustic potash dissolved in 120 cc absolute alcohol is added, is boiled for half an hour. The product which precipitates on cooling is crystallized from alcohol and dried at 100–120°C. Bronze crystals with green reflex. M. Pt. 261°C (decomp.)

Among the similar pseudocyanines we would mention *1:1'-dimethylpseudocyanine* (maximum at 560 mμ), *1:1':6-trimethylpseudocyanine* (maximum at 550 mμ), *1:6:1':6'-tetramethylpseudocyanine* (maximum at 550 mμ), *1:1'-diethylpseudocyanine* (maximum at 570 mμ), *1:1'-diethyl-6-methylpseudocyanine* (maximum 580 mμ).

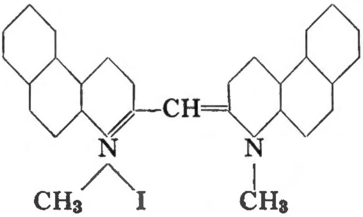
714. Benzopseudocyanines

The benzopseudocyanines are cyanines with naphthalene nuclei. Compared with the simple pseudocyanines, their absorption and sensitization maxima are shifted towards the red.

Depending on whether the dye contains one or two naphthalene nuclei it is a *monobenzopseudocyanine* or a *dibenzopseudocyanine.* The base itself can be either an α- or *β-naphthoquinoline.*



Monobenzopseudocyanine
(1-ethyl-1'-methyl-5' : 6'-benzopseudocyanine)



Dibenzopseudocyanine

1-ethyl-1'-methyl-5':6'-benzopseudocyanine is a sensitizer for the yellow-green with a maximum at 570 mμ. It is prepared by condensing 2-iodo-β-naphthoquinoline ethiodide with quinaldine ethiodide in aqueous solution following the general method. The resulting product is washed with water, then with ether, and is recrystallized from methanol and dried *in vacuo.* M. Pt. 275°C (decomp.)

1-methyl-1'-ethyl-5':6'-benzopseudocyanine sensitizes to 620 mμ with a maximum at 570 mμ. It is prepared from 2-iodo-β-naphthoquinoline and quinaldine. M. Pt. 277°C (decomp.).

1:1'-diethyl-5:6-benzopseudocyanine, weak sensitizer.

1:1'-dimethyl-5:6:5':6'-dibenzopseudocyanine.(13) 25 g of β-naphthoquinaldine methiodide and 33·5 g of 2-iodo-β-naphthoquinoline methiodide in 800 cc of absolute alcohol boiled for 1 hour. After cooling, the solid which is deposited is washed with water then with ether. The residue is dissolved in 8 litres of warm methanol and the solution is concentrated to one-third. Finally the cyanine is obtained as a dark green powder. M. Pt. 286°C (decomp.). Absorption maxima at 530 and 515 mμ.

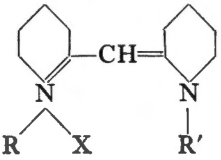
Almost uniform sensitization to 630 mμ with maxima at 520 and 590 mμ.

1-ethyl-1'-methyl-5:6:5':6'-dibenzopseudocyanine obtained in the previous way as the above compound from 13 g of β-naphthoquinaldine ethiodide and 10·5 g of 2-iodo-β-naphthoquinoline methiodide. M.Pt. 300°C with decomposition. Absorption maxima at 510 and 545 mμ. Sensitizing maxima at 520 and 590 mμ.

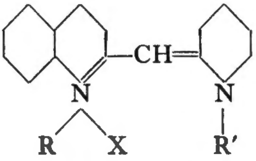
1:1'-diethyl-5:6:5':6'-dibenzopseudocyanine sensitizes to 630 mμ with a maximum at 570 mμ.

715. Pyridopseudocyanines

The pyridine pseudocyanines are divided into two groups: the *protocyanines* containing 2 pyridine nuclei and the *mesocyanines* which contain a single pyridine nucleus.



Protocyanine



Mesocyanine

These are very weak sensitizers and have only a theoretical interest.

The *protocyanines* were obtained by Moir by condensing the alkyliodides of α-picoline with 1-methylpyridone in the presence of phosphorus pentachloride.

The *mesocyanines* are prepared by condensing 2-iodopyridine alkyl iodide with a quinaldine alkyl iodide.

The absorption of the mesocyanines is shifted from 27 to 50 mμ to the blue compared with the quinoline pseudocyanines.

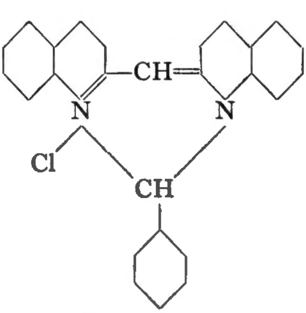
Acenaphthopyridopseudocyanines are derivatives of 2-methylacenaphthopyridine whose alkyl iodides are condensed with those of 2-iodoquinoline.

These are average sensitizers whose maximum is shifted 15 mμ towards the red compared with the corresponding simple pseudocyanines. Their action extends to 640 mμ with maxima at 510 mμ and 540 mμ.

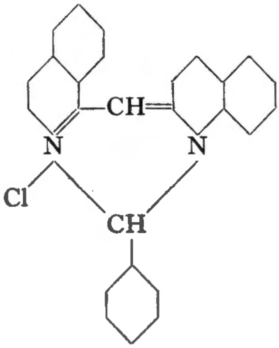
716. Quinoline red

Quinoline red, which must not be confused with *isoquinoline red,* is a pseudocyanine derivative obtained by Jacobsen in 1882.

It is a very weak sensitizer with no practical interest. Its constitution is as follows compared with that of *isoquinoline red*:



Quinoline red



Isoquinoline red

It is obtained by condensing quinoline with quinaldine in the presence of phenylchloroform $C_6H_5C . Cl_3$, or benzylchloride $C_6H_5CH . Cl_2$, or by treating diquinolyl-2-methane with benzyl chloride.(14)

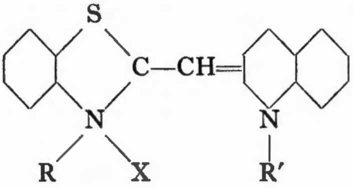
Isoquinoline red was obtained by Jacobsen by heating crude quinoline with zinc chloride and phenylchloroform. A better yield is obtained when equimolecular quantities of quinaldine and isoquinoline are heated. The formula of this pseudocyanine was established by Von Gerichten. Vogel used isoquinoline red as a green sensitizer.

Methyl and ethyl isoquinoline reds also have sensitizing properties although they are weak.

An alkyl iodide of 1-iodoisoquinoline will condense with quaternary salts of heterocyclic bases to give pseudocyanines. Iodoisoquinoline is prepared from 1-chloroisoquinoline which in turn is obtained from 2-alkyl-1-isoquinoline.(15)

717. Thiapseudocyanines

The thiapseudocyanines are pseudocyanines which contain a quinoline and a benzthiazole nucleus. They have the following general structure.



There are two general methods of preparation:

(*a*) A quaternary salt of 2-iodoquinoline is condensed with a quaternary salt of 2-methylbenzthiazole. For example, a mixture of 2 g of 2-iodoquinoline ethiodide (1 mol) and 1·5 g of 2-methylbenzthiazole ethiodide (1 mol) is added to 10 cc of boiling absolute alcohol containing 0·7 g of caustic potash (2·2 mol). After half an hour it is cooled. The solid which is deposited is recrystallized from alcohol (yield 30%). The yield is increased if condensation is carried out in the presence of 1 g of triethylamine.(16)

(*b*) A quaternary salt of *quinaldine* is condensed with an equimolecular quantity of a quaternary salt of 2-methylmercaptobenzthiazole (para. 693) in pyridine (1000 cc per g mol). It is heated under reflux for 6 hours; the dye crystallizes on cooling. It is washed with pyridine, alcohol, water, and ether. The mother liquors poured into water containing 10% potassium iodide give a certain extra amount of dye.

Mills and Braunholtz obtained thiapseudocyanines by reacting *di-ortho-formylalkylamino-diphenyl-disulphide* with *quinaldine ethyl nitrate* in pyridine; at the same time a carbocyanine is formed which is less soluble in cold alcohol.

The use of benzothiazolone-imines has also been disclosed(17) for reacting with the quaternary salts of quinaldine.

The *thiapseudocyanines* have absorption bands shifted towards the blue compared with the corresponding pseudocyanines. They are green sensitizers.

1′-3-diethylthiapseudocyanine sensitizes to 560 mμ with a maximum at 528 mμ and a minimum at 500 mμ (Fig. 124).

1′:ethyl-3-methylthiapseudocyanine; sensitization maxima at 530 and 580 mμ.

3-methyl-1′-ethyl-5′:6′-benzothiapseudocyanine, prepared from 2-methylbenzthiazole and 2-iodo-β-naphthoquinoline sensitizes to 600 mμ with a maximum at 530 mμ.

By replacing the quinoline with isoquinoline, isoquinoline thiapseudocyanines are obtained which are weak sensitizers.

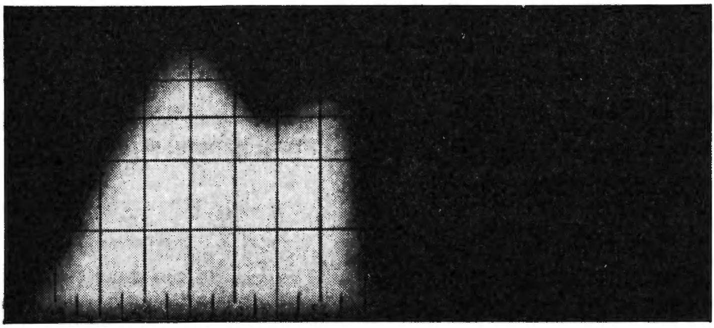
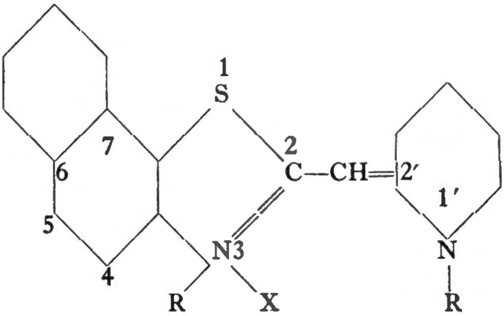


FIG. 124. Sensitization: 1′: 3-diethyl thiapseudocyanine.

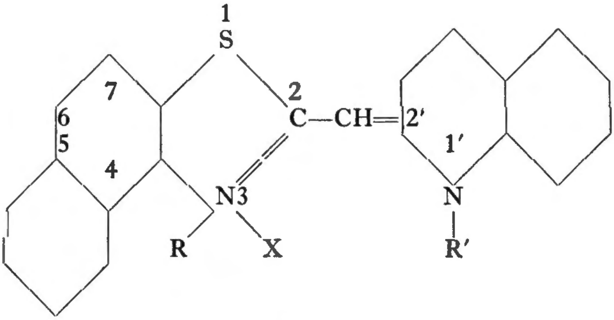
Aminothiapseudocyanines$^{(18)}$ are prepared from aminoquinoline bases. These cyanines have an absorption maximum at about 520 mμ. They are good sensitizers for the green up to 570 mμ with a maximum at 530 mμ, they do not fog emulsions and can be slightly activated with a normal thiapseudocyanine.

718. Benzothiapseudocyanines

These dyes, sometimes called naphthopseudocyanines, are prepared in the same way as the simple thiapseudocyanines, with the difference that the benthiazole base is replaced by an α or β naphthothiazole base.



α or 6 : 7-benzothiapseudocyanine



β or 4 : 5-benzopseudocyanine

The α dyes are less soluble than the β ones in methanol but the yield is higher. The sensitization maxima are displaced about 15 mμ towards the red compared with the simple thiapseudocyanines.

1′:3-dimethyl-4:5-benzothiapseudocyanine: absorption maximum at 500 mμ. Sensitizes to 600 mμ with a maximum at 550 mμ.

1′-methyl-3-ethyl-4:5-benzothiapseudocyanine: identical action with the preceding cyanine.

3-methyl-1′-ethyl-6:7-benzothiapseudocyanine: maximum at 550 mμ.

Anthrathiapseudocyanines obtained from α- or β-anthrathiazole,⁽¹⁹⁾ sensitize in the green and yellow-green.

Acenaphthothiapseudocyanines obtained from methyl α- and β-acenaphthothiazole, sensitize in the green and yellow-green.

In the same way the *carbozolethiapseudocyanines* and the *diphenylene-oxide-thiapseudocyanines* can be obtained.

The naphthalene nucleus can be attached to the quinoline base instead of to the thiazole base. If in the preparation method (*b*) naphthoquinoline-methylmercaptan and a benzthiazole base are used in place of a naphtho-thiazole methylmercaptan and a quinoline base, good results are obtained. Schouwenaars(20) obtained *3-methyl-1′-ethyl-2:2′-α-naphthoquinothiapseudocyanine* bromide by heating 0·87 g of α-naphthoquinoline-2-methylmercaptan dimethylsulphate with 0·65 g of 2-methylbenzthiazole ethylbromide in 10 cc of absolute alcohol with 0·35 cc triethylamine for 10 minutes. The dye crystallizes on cooling. It sensitizes to 590 mμ with a maximum at 548 mμ. Using the same method, *dimethyl-α-naphtho-β-naphthoquinopseudocyanine*, which is a quinoline pseudocyanine sensitizing to 640 mμ with maxima at 540 and 600 mμ can be obtained.

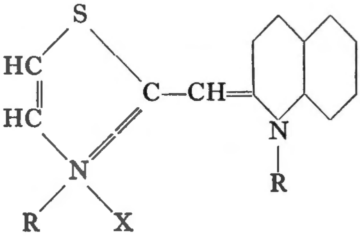
719. Thiazo and thiazolinopseudocyanines

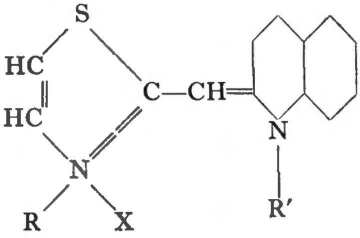
These are sensitizers for the green and blue-green. Compared with the corresponding thiapseudocyanines their sensitization maxima are shifted towards the short wavelengths.

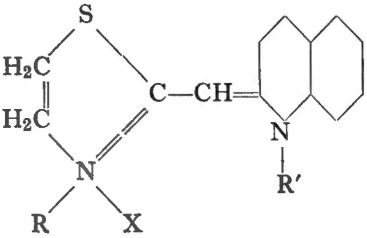
The *thiazopseudocyanines* are obtained by heating 2-methylthiazole alkyl iodides and 2-iodoquinoline in the presence of sodium ethoxide.(21) With methyl thiazoline, a thiazolinopseudocyanine⁽²²⁾ is formed which is recrystallized from alcohol.

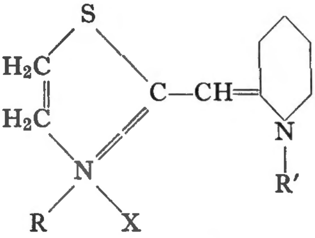
By replacing the 2-iodoquinoline by 2-iodopyridine (para. 694) the *thiazo* and *thiazolinopyridopseudocyanines* are obtained which are sensitizers for the blue and blue-green (particularly for silver chloride).⁽²³⁾

The substitution of thiazole and thiazoline for benzthiazole, and pyridine for quinoline shifts the sensitization maximum more and more towards the blue.


Thiazopseudocyanine

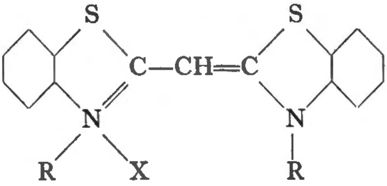

Thiazopseudopyridocyanine


Thiazolinopseudocyanine


Thiazolinopseudopyridocyanine

720. Thiacyanines

The thiacyanines have two thiazole nuclei whilst the thiapseudocyanines have only one, the second being the quinoline nucleus.


Thiacyanine

The thiacyanines are more yellow than the thiapseudocyanines. They sensitize silver chloride emulsion to blue and blue-green.

The thiacyanines isolated by Hoffmann in 1887 were prepared by Mills who condensed the alkyl iodides of benzthiazole with those of methyl benzthiazole in pyridine. A carbocyanine was formed simultaneously. They have also been prepared from the reaction product of o-aminothiophenol and ethylmalonate. The resulting dibenzothiazolylmethane gives with ethyl iodide a monoethyliodide which, when treated by an alkali, loses HI and forms 2-ethylbenzothiazolenylbenzothiazolmethane which under the action of ethyl iodide gives the thiacyanine.

Preparation of the thiacyanines. First method:(24) a 2-methylbenzthiazole alkyliodide in alcoholic solution, boiled with silver chloride is converted to the *ethyl chloride.* Two molecules of this product are then condensed in the presence of amyl nitrite and acetic anhydride: 10 g of the ethyl chloride added to 150 cc of acetic anhydride then 4·8 cc of amyl nitrite are refluxed for 15 minutes. After cooling, the yellow chloride is filtered, washed with ether and dried. (Yield, 18–33%.) The thiacyanine is converted to the iodide or bromide by treating its boiling alcoholic solution with potassium iodide or bromide.

Second method: a 2-methylbenzthiazole alkyliodide is condensed with a benzthiazole-2-methyl-mercaptan alkyl iodide (para. 693), in pure anhydrous pyridine. For example: 6·1 g of 2-methylbenzthiazole ethiodide (0·02 mol) is heated with 6·7 g of benzthiazole 2-methylmercaptan ethiodide (0·02 mol), in 76 cc of dry pyridine for 15 minutes at the boil (oil bath at 145°C). The dye crystallizes on cooling. It is filtered and successively washed with 25 cc pyridine, 20 cc 96% ethyl alcohol, 40 cc distilled water, 20 cc 96% ethyl alcohol and 50 cc ether. 3·54 g of crude diethylthiacyanine (iodide) is obtained: yield, 38%. By recrystallizing from 900 cc of boiling ethyl alcohol and washing with 10 cc of alcohol, then 10 cc of ether, 3 g of pure dye is obtained (total yield 32·5%). Using the methylmercaptan process, *assymetrical thiacyanines* can be prepared.

The condensation of a benzthiazole quaternary salt with a 2-iodobenzthiazole quaternary salt(25) is not possible, as the latter are insoluble in organic solvents.(26)

3:3'-diethylthiacyanine has two absorption bands with maxima at 400 and 423 mμ in the violet. Sensitizes silver chloride to 490 mμ with maxima at 450 and 460 mμ.

3:3'-dimethylthiacyanine. Similar action.

6-methyl-3:3'-diethylthiacyanine. Absorption at 400 and 427 mμ. Sensitizing action equal to the simple diethyl compound.

Dibenzothiacyanines are obtained by the general method from *methyl α- or β-naphthothiazole.*

3:3'-diethyl-6:7:6':7'-dibenzothiacyanine: absorption maximum at 445 mμ. Sensitizes silver chloride to 530 mμ with a maximum at 480 mμ. Stains the gelatin yellow.

3:3'-dimethyl-6:7:6':7'-dibenzothiacyanine. Sensitizing action to 520 with maximum at 475 mμ.

3:3'-diethyl-4:5:4':5'-dinaphthothiacyanine: obtained from β-methylanthrathiazole.(27) Sensitizing action to 605 mμ with maximum at 540 mμ.

Thiazinocyanines. Beilenson obtained thiazinocyanines by condensing *benzothiazole-methylmercaptans* with methylbenzthiazole p-toluene-sulphonates in pyridine. These dyes sensitize in the blue-green and prevent chemical fog.

Quinorhodine thiacyanines. Brooker prepared cyanines containing a benzthiazole nucleus and a quinorhodine nucleus (formed from a nucleus of quinoline fused to a nucleus of thiazole) which is obtained by condensing o-aminobenzaldehyde with a rhodanine substituted in the 3-position. The quinorhodine cyanines sensitize silver chloride to 525 mμ.(29)

CYANINES FROM SELENAZOLE, OXAZOLE, AND INDOLINE

721. Selenacyanines

The cyanines derived from *selenazole*: *pseudoselenacyanines* and *selenacyanines* have a similar structure to the thiazole derivatives. These are lighter dyes than the quinocyanines but darker than the thiacyanines.

The selenazole cyanines are prepared by the same methods as the thiacyanines.(30)

1′:3-diethylselenapseudocyanine. The dimethyl sulphate of quinoline methylmercaptan is first prepared by condensing 14 g (0·08 mol) of *quinoline*-2-*methylmercaptan* (para. 695) with 13·32 g (0·08 mol) of *diethyl sulphate.* After 45 minutes in the cold the mixture is heated on the oil bath to 135°C for 2½ hours. After cooling, 128 cc of pyridine and 28·17 g (0·08 mol) of *2-methylbenzoselenazole ethiodide* are added and heating under reflux on an oil bath at 140–145°C is continued for 5 hours. It is left in ice overnight. The crystals are filtered off and successively washed with 15 cc pyridine, 20 cc ethyl alcohol, 100 cc ether, 50 cc distilled water, 20 cc ethyl alcohol, and 100 cc ether. 18·6 g of crude selenapseudocyanine are obtained.

The *selenapseudocyanines* sensitize in the green. The *benzoselenapseudocyanines* sensitize as far as the orange-red. The *selenapyridopseudocyanines* sensitize silver chloride to blue.(31)

The *selenacyanines* with two selenazole nuclei sensitize silver chloride to 480 mμ. The naphthoselenazole derivatives sensitize into the blue-green.(32)

722. Oxacyanines

The oxapseudocyanines and the oxacyanines have a similar structure to the hiapseudocyanines and the thiacyanines except that the sulphur atoms are replaced by oxygen atoms. They are prepared in the same way from methylbenzoxazoles and methylnaphthoxazoles. *1′:3-diethyloxapseudocyanine*: 2·9 g of 2-methyl-benzoxazole ethiodide and 4·1 g of 2-iodoquinoline ethiodide are heated under reflux in 20 g absolute ethanol with 2·1 g triethylamine. Heating is continued for 10 minutes longer than it takes the dye to precipitate. This is filtered and washed with methanol.(33) Sensitizes silver chloride to blue.

1′:3-diethylbenzooxapseudocyanines prepared from α- or β-naphthoxazoles and 2-iodoquinoline ethiodide or quinoline methylmercaptan diethyl sulphate. Sensitize silver chloride to the blue-green.(34)

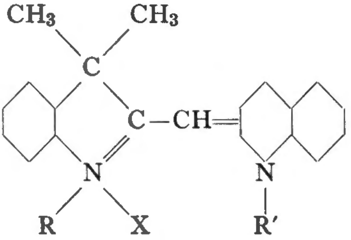
The absorption bands of the oxacyanines are nearer the ultra-violet than any other cyanine; these are pale yellow giving colourless alcoholic solutions. The simplest of them have no practical value, for their absorption is in the region of the intrinsic sensitivity of silver chloride. On the other hand the dibenzo oxacyanines derived from the naphthoxazoles sensitize silver chloride as their sensitizing maximum is displaced from 395 to 430 mμ.

3:3′-dimethyl-6:7:6′:7′-dibenzo oxacyanine. Obtained by the action of amyl nitrite and acetic anhydride on 2-methyl-α-naphthoxazole methiodide (see para. 720). The solid obtained is ground up with water, then extracted with ether. The residue is suspended in methanol and treated with a current of SO_2 to reduce the periodides which are often produced. The dye is finally recrystallized from methanol. Absorption maxima at 395, 295 and 240 mμ. The corresponding β-naphthoxazole derivative has its absorption maximum at 405 mμ.

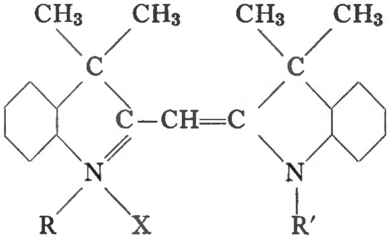
It is possible to prepare *benzo-oxa-benzothiacyanines* and *benzo-oxa-benzoselenacyanines.* Their absorption maxima are higher than those of the symmetrical benzo-oxacyanines.

723. Indocyanines

The *indocyanines* contain 1 or 2 indoline nuclei derived from 2:3:3-trimethylindoline. They comprise the *indopseudocyanines* and the correctly named *indocyanines*.



Indopseudocyanine



Indocyanine

The absorption maxima of the indoline cyanines are near to those of the thiazole cyanines. They have no special properties as sensitizers.

The *indopseudocyanines* such as *1:1′:3:3-tetramethyl indopseudocyanine* are obtained by the general method of condensing 2-iodoquinoline methiodide with 2:3:3-trimethylindoline methiodide.

The *indocyanines* were prepared by Kuhn, Winterstein, and Balser(35) by condensing 2:3:3-trimethylindoline alkyliodide with an *indolinone*, a compound corresponding to quinolone.

Indoline yellow is 1:1′:3:3:3′:3′-hexamethylindocyanine obtained by treating 1:3:3 trimethyl-2-methyleneindoline (Fischer's base) with perchloric acid and sodium nitrite and condensing the resulting oxime with a second molecule of base, in the presence of acetic anhydride.

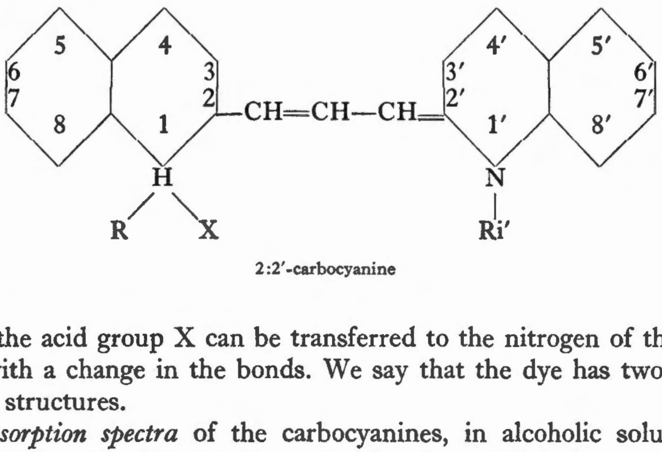
1. Wise, Adams, Stewart and Lund: *Ind. Eng. Chem.*, 1919, **II,** 460; Wise and Adams U.S.P. 1,338,346.
2. Barbier: *Bull. Soc. Chim. Fr.*, 1920, **27,** 427.
3. Hamer F. M.: *J.C.S.*, 1928, 206.
4. Fisher N. I. and Hamer F. M.: *J.C.S.*, 1934, 1905.
5. Braunholtz W. T. K. and Mills W. H.: *J.C.S.*, 1922, **121,** 2004.
6. Mills W. H. and Braunholtz W. T. K.: *J.C.S.*, 1923, **123,** 2804.
7. B.P. 380,140 (1932) and 378,455 (1930); F.P. 713,486 (1931) and 713,047 (1931).
8. F.P. 718,471 (1931) and B.P. 385,332 (1930).
9. F.P. 742,930 (1933).
10. F.P. 729,617 (1932).
11. *Ber.*, 1912, **45,** 1917.
12. *Jl. Prakt. Chem.*, 1919, **100,** 86.
13. B.P. 370,388 (1930).
14. Scheibe and Fisher: *Ber.*, 1926, **59,** 502; Scheiber and Rossner: *Ber.*, 1921, **54,** 756 and 1920, **53,** 2064.
15. Gabriel and Colman: *Ber.*, 1900, **33,** 980; Fisher N. I. and Hamer F. M.: *J.C.S.*, 1934, 1905.
16. F.P. 757,813 (1932).
17. Oksengendler G. M.: *Zh. Obsh. Khimii*, 1953, 135.
18. Meyer K. and Kriebsch: *Zeits. Wiss. Phot.*, July 1953, 126–136.
19. F.P. 742,930 (1933).
20. Schouwenaars: *Naturw. Tidschr.*, July 1940, 112.
21. F.P. 741,023 (1932) and B.P. 386,903 (1933).
22. F.P. 718,471 (1931).
23. F.P. 769,753 (1934).
24. Hamer and Fisher: *J.C.S.*, 1930, 2502.
25. Also note: 1-iodobenzthiazole.
26. Kendall J. D. and Suggate H. G.: *J.C.S.*, 1949, 1503.
27. F.P. 742,930 (1931).
29. F.P. 864,570.
30. B.P. 386,791 (1932) and F.P. 729,634 (1932).
31. F.P. 769,753 (1934).
32. B.P. 380,702 (1931).
33. F.P. 757,813.
34. F.P. 729,617 (1932).
35. *Ber.*, 1930, **63,** 3176.

Chapter XXXVIII

CARBOCYANINES

724. Characteristics of the carbocyanines

The carbocyanines are made up of two nitrogenous heterocyclic nuclei (quinoline, benzthiazole, benzselenazole, benzoxazole, etc.) linked by a chain of *three methine* —CH= groups. Between the two nitrogen atoms is a total of five carbon atoms joined by three alternate double bonds. The 'true' quinoline carbocyanines are 2:2'-carbocyanines: their constitution is represented by the following formula:



2:2'-carbocyanine

in which the acid group X can be transferred to the nitrogen of the second nucleus with a change in the bonds. We say that the dye has two extreme resonance structures.

The *absorption spectra* of the carbocyanines, in alcoholic solution, are generally distinguished by two absorption bands, to which the two sensitization bands correspond (Fig. 125).

The *quinoline carbocyanines* are *blue* dyes which sensitize photographic emulsions to the red. When the quinoline nuclei are replaced by selenazole, thiazole, indoline or oxazole nuclei, carbocyanines are obtained which become less and less blue, that is, whose absorption bands are shifted more and more towards the short wavelengths, and which consequently sensitize not in the red, but in the orange, green or blue-green, as shown in the following table:

In each series, the absorption (and sensitization) bands are shifted towards the red by substitution of heavy groups; phenyl, naphthyl, diethylamino, etc. The absorption spectrum can be modified slightly by substituting the central methine group of the chain. This substitution has a considerable influence on the sensitizing power of the dye: it is very beneficial with carbocyanines other than the quinoline derivatives.

Cyanine	*Heterocyclic base*	*Absorption maximum mμ*	*Main sensitization region*
Carbocyanine	Quinoline	607	Red
Benzthiacarbocyanine	β-naphthiazole	600	Orange-red
Selenacarbocyanine	Benzselenazole	569	Orange
Thiacarbocyanine	Benzthiazole	559	Yellow
Indocarbocyanine	Indoline	547	Yellow-green
Benziminocarbocyanine	Benziminazole	500	Green
Oxacarbocyanine	Benzoxazole	485	Blue-green
Thiazolinocarbocyanine	Thiazoline	442	Blue

725. Quinoline carbocyanines

The quinoline carbocyanines were widely used at one time for sensitizing emulsions, but today have only an historical interest. Their two disadvantages are a general reduction in sensitivity of the emulsion and a tendency to fog. Chain substitutents do not increase their sensitizing power.

The quinoline carbocyanines are blue dyes which are produced by the action of alkali and *formaldehyde* on a mixture of the quaternary salts of quinoline and *quinaldine*: only the quinaldine takes part in the reaction—the quinoline behaving as a catalyst. The formaldehyde can be replaced by *iodoform, chloroform, trihydroxymethylene, glyoxylic acid* or *ethyl orthoformate*. In another method, *diphenylformamidine* is used.

General preparation methods. Example: *1:1'-diethylcarbocyanine* (pinacyanol, sensitol red).

A. A mixture of 90 g quinaldine ethiodide, 85·5 g quinoline ethiodide and 3 litre alcohol is boiled under reflux. When the air from the flask has been expelled by the alcohol vapour, a solution of 90 cc water, 14·4 g caustic soda and 60 cc 40% formalin is added. The solution becomes a reddish blue. 600 cc warm water is added, and heating is continued for 15 minutes. After cooling slowly, a mass of blue-green needles is deposited. This is filtered off and washed with small amounts of ice-cold alcohol, then with ether. (Yield, 23–27 g.) If the flask contains any air, an isocyanine is also formed. The formalin can be replaced by iodoform (yield 20–25%).(1)

B. 50 g quinaldine ethiodide (2 mol), 55 cc ethylorthoformate (4 mol) and 200 cc pyridine (dried over baryta) are boiled for 3 hours under reflux. The product which separates on cooling is recrystallized from dilute alcohol, and the crystals are dried at 100–120°C in vacuo (yield, 70%) (F. M. Hamer). König used ethyl orthoformate with acetic anhydride, and the yield was lower.

C. Quinaldine ethiodide is condensed with trihydroxymethylene in the presence of sodium in absolute alcohol.(2) (Yield, 75%.)

D. The ethiodide of the quinoline base is heated with sodium sulphide (or any other compound containing labile sulphur which is displaced by alkalis), in the presence of chloroform. This method is particularly applicable to the preparation of the kryptocyanines. The thiazoles and the pyridines do not react.⁽³⁾

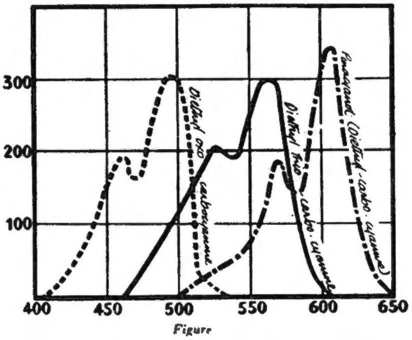


FIG. 125. Absorption curves of carbocyanines.

E. Diphenylformamidine method:⁽⁴⁾ the quaternary salt of the heterocyclic base is treated with diphenylformamidine $C_6H_5—NH—CH=N—C_6H_5$, a reaction which has already been described in para. 696. For example, quinaldine ethiodide, heated with diphenylformamidine at 100°C forms 2-phenylaminoethenylquinoline or 2-β-anilidovinylquinoline ethiodide: [Et I] [Quinoline]—$CH=CH—NH—C_6H_5$. In the presence of a further molecule of base and acetic anhydride (4 mol) and sodium acetate (1 mol) 1:1′-diethylcarbocyanine is formed by heating for 30 minutes at 100°, aniline and hydriodic acid being eliminated. The resulting product is crystallized from methanol.

Simple carbocyanines 1:1′-diethylcarbocyanine (or pinacyanol): dark green lustrous needles M. Pt. 287°C (decomp.), almost insoluble in water. Absorption maxima (alcoholic solution) at 565 and 607 mμ, the second band being more pronounced. Moderate sensitizing action ending at 695 mμ with a maximum at 640 mμ and a minimum at 510 mμ (Fig. 68). The chloride is more soluble than the iodide, but it tends to produce fog. It is prepared by treating the iodide with silver chloride in hydrochloric acid solution.

Contrary to the results with the isocyanines, the dimethylcarbocyanines are much weaker sensitizers than the diethyl compounds.

1:1′-di-isopropylcarbocyanine. Similar sensitizer to the preceding one.

1:1′-diethyl-6:6′-dimethylcarbocyanine. Obtained from toluquinaldine. Fairly good sensitizing up to 710 mμ.

1:1′:6:6′-tetraethylcarbocyanine. Sensitizes to 700 mμ with maxima at 575 and 640 mμ and minima at 510 and 615 mμ. Prepared from ethylquinaldine.

1:1′-diallyl-6:6′-dimethylcarbocyanine. Sensitizes up to 730 mμ but produces fog.

1:1′-diethyl-6:6′-diethoxycarbocyanine or ‘pinachrome blue’. Mediocre sensitizer obtained from ethoxyquinaldine.

1:1′-diphenoxyethylcarbocyanine. Prepared from quinaldine phenoxyethyl-iodide. Sensitizing action up to 695 mμ with a maximum at 620 mμ.

1:1′-diethyl-6:7:6′:7′-methylenedioxide-carbocyanine: the group —O—CH_2 —O— is located in the 6:7 position of the nucleus.(5) A much weaker sensitizer whose action extends to 695 mμ; maxima at 598 and 663 mμ.

1:1′-diethyl-4:4′-diphenylcarbocyanine: weak sensitizer.

Diacetylamino derivatives. Weak sensitizers.

Amino derivatives, obtained by hydrolysis of the acetylamino derivatives: mediocre sensitizers as far as the extreme red, with a maximum at 670 mμ.

Halogenated derivatives: weak sensitizers.

Carbocyanines with naphthoquinoline nuclei. The best known is *1:1′-diethyl-5:6:5′:6′-dibenzocarbocyanine* (naphthocyanol or pinacyanol blue). This dye has a relatively strong sensitizing action in the *extreme red* with a maximum at 690 mμ and a pronounced depression in the green (Fig. 126). Absorption maxima at 635 and 588 mμ. It is prepared by condensing 20 g of *β-naphthoquinaldine ethiodide* in the presence of 20 g of quinoline ethiodide in 2 litres of alcohol, using 16 cc of formalin then 240 cc of a 10% alcoholic potash solution. The dye separates on cooling. It is converted to the nitrate by suspending it in acetic acid and adding 800 cc of 1% nitric acid. After half an hour, the filtrate is stirred with 1 cc of 10% silver nitrate. The resulting silver iodide is separated by filtering and the carbocyanine, precipitated from the filtrate with ammonia, is recrystallized from alcohol.

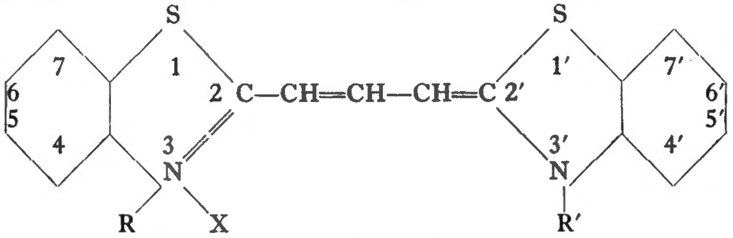
Asymmetrical carbocyanines are obtained by the general methods described in para. 732.

1:1′-diethyl-6-methylcarbocyanine. Relatively active sensitizer up to 695 mμ with maxima at 550 and 640 mμ.

Pyridocarbocyanines. Obtained from α-picoline ethiodide(6) sensitizes in the yellow-orange.

726. Thiacarbocyanines with a simple chain

The thiacarbocyanines are produced by the union of two benzthiazole or naphthiazole nuclei via a trimethine chain —CH=CH—CH=:



Thiacarbocyanine

The first thiacarbocyanine was obtained by Hofmann in 1887, at the same time as a thiacyanine, by the action of ammonia on an aqueous solution of benzthiazole amyl iodide and 2-methylbenzthiazole.

The thiacarbocyanines are less deeply coloured than the quinoline carbocyanines; they are red whilst the latter are blue. (We have already seen that the thiapseudocyanines are yellow whilst the quinoline pseudocyanines are red.) Their sensitization region is therefore situated in the green and the yellow-orange.

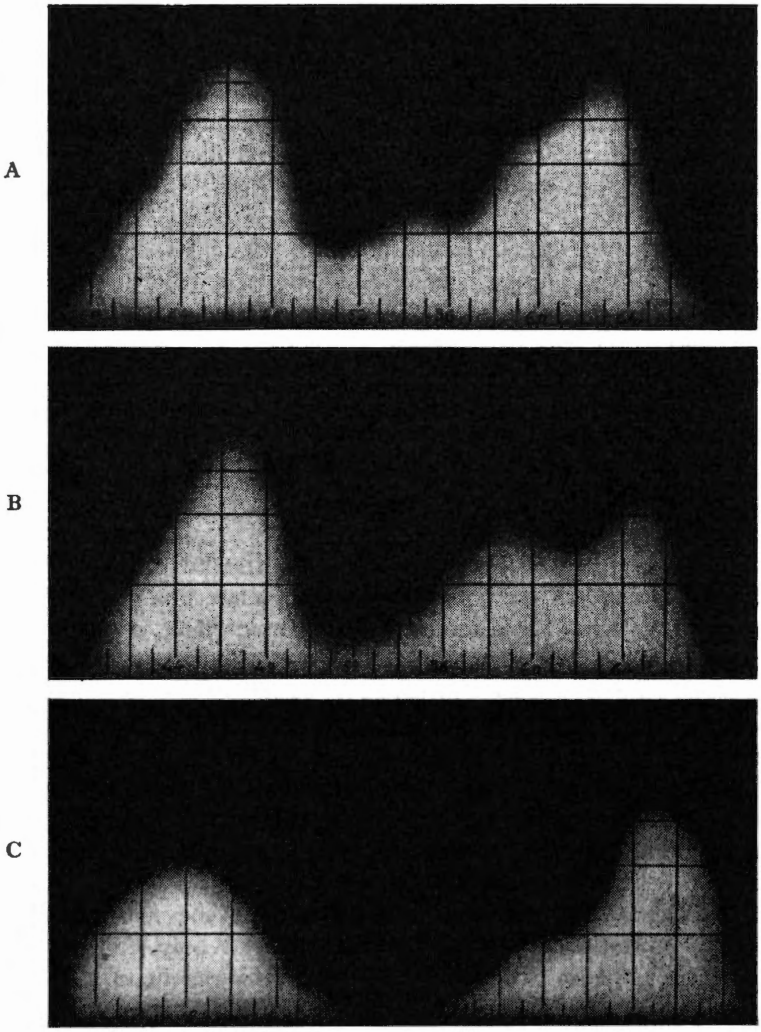


FIG. 126. Sensitization
(A) Pinacyanol; (B) 1: 1′di-n-propyl-6: 6′-dimethylcarbocyanine;
(C) Naphthocyanol (scale shifted to the left) Max. at 690 $m\mu$.

The thiacarbocyanines are much more active sensitizers than the quinoline carbocyanines. Those with a simple chain, however, are less efficient than the corresponding compounds with a meso substituent. They are not therefore widely used, the latter being preferred.

The *3:3′-diethyl* derivatives, as with all the carbocyanines, are twice as effective as the *2:2′-dimethyl* derivatives.

The symmetrical thiacarbocyanines with simple chains are prepared in the same way as the quinoline carbocyanines. For example: 2 mols of *2-methylbenzthiazole* ethiodide are condensed with 4 mols of ethyl orthoformate in dry pyridine: 8 g of the salt of the base, 9·2 cc ethyl orthoformate and 80 cc of pyridine. Recrystallize from alcohol.

The thiacarbocyanines are formed at the same time as the thiacyanines when a benzthiazole salt is condensed with a 2-methyl benzthiazole at a 100°C in pyridine. They are also formed when a 2-methyl benzthiazole alkiodide is heated with di-o-formylethylaminodiphenyl disulphide. $S_2(C_6H_4—$ $—N . C_2H_5—CHO)_2$ in pyridine solution. A thiacyanine is produced at the same time.

3:3′-diethylthiacarbocyanine. Two absorption bands with maxima at 559 and 525 mμ. Sensitizing action falls off gradually to 660 mμ with maxima at 582 and 528 mμ (Fig. 127).

3:3′-diallylthiacarbocyanine. Sensitization maxima at 600 and 545 mμ.

3:3′-diethyl-6:6′-dimethylthiacarbocyanine. Absorption maxima at 563 and 529 mμ. Sensitizing action similar to that of the simple diethyl derivative with maxima at 583 and 533 mμ.

3:3′-diethyl-6:6′-dimethoxythiacarbocyanine. Prepared from 6-methoxybenzthiazole. Its sensitizing action extends further to the red. Principle absorption at 628 mμ.

The *6:6′-diethoxy*, *5:6:5′:6′-tetramethoxy* or tetraethoxy,⁽⁷⁾ *7:7′-diethoxy* and *6:6′-ethyl-mercapto*⁽⁸⁾ derivatives have some interesting properties. The substitution of R—O— has a strong bathochromic effect, especially when two groups in —5:6— are present. The electronic interaction of these two alkoxy groups was the subject of a paper by Levkoev.⁽¹⁰⁾

The *dimethylamino* group is even more strongly bathochromic as it is a strong electron donor.⁽¹⁰⁾ It displaces the absorption maximum 55 mμ if in the 6:6′-position, 51 mμ in the 5:5′-position, but only 11 mμ in the 7:7′-position.

6:6′-diacylaminothiacarbocyanine: prepared by Levkoev, Cheifetz and Barvyn.⁽¹¹⁾

Alkylthiocarbamidothiacarbocyanines: prepared by Levkoev and Turitsyna.⁽¹²⁾

Chloro- and bromothiacarbocyanines. Described by König,⁽¹³⁾ their principal absorptions go from 562 to 575 mμ. The replacement of chlorine by fluorine does not change the spectrum (Kiprianov and Yagupolski).⁽¹⁴⁾

Thiazocarbocyanines. These are derivatives of 2-methyl benzthiazole, and are obtained by condensing the quaternary salt of the base with ethyl orthoformate in pyridine. The yield is less than 15%.

3:3′:4:4′-tetramethylthiazocarbocyanine. Principal absorption at 550 mμ. Almost uniform sensitization up to 680 mμ with a maximum at 590 mμ. The shift of 10 mμ towards the blue, compared with the thiacarbocyanine, is small compared with the considerable difference in their molecular weights. The sensitizing action of the diethyl derivative extends to 650 mμ with maxima at 590 and 535 mμ. It is even further towards the red with *3:3′-diethyl-4:4′-diphenylthiazocarbocyanine.*

The thiazocarbocyanines can be prepared with thiazoles having an *alkyl mercaptan* group in the 5-position, according to Wiesehahn's disclosures.(15) To prepare the base, ethylmercaptoacetone $C_2H_5—S—CH_2—CO—CH_3$, for example, is heated with bromine in chloroform. The yellow oil is condensed with thioacetamide using the general method.

Thiazolinocarbocyanines. These are sensitizers for the blue. 3:3′-diethylthiazolinocarbocyanine has its absorption maximum at 443 mμ and its sensitization maximum at 475 mμ.(16)

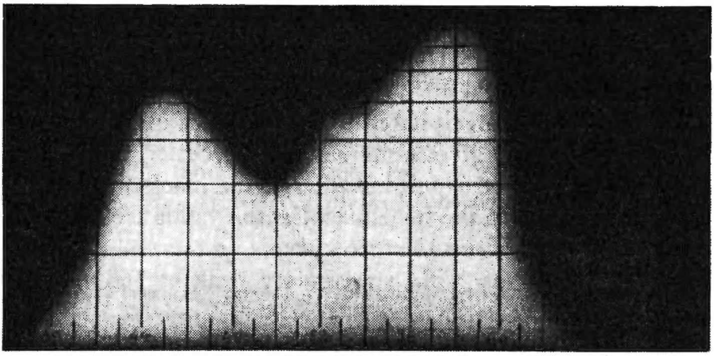
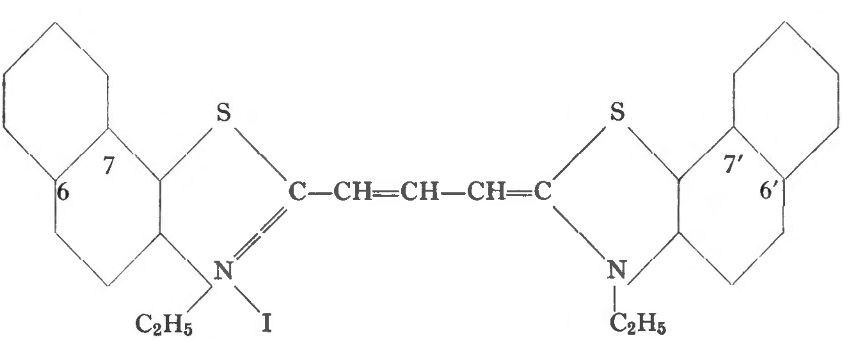


FIG. 127. Sensitization: 3: 3′-diethylthiacarbocyanine.

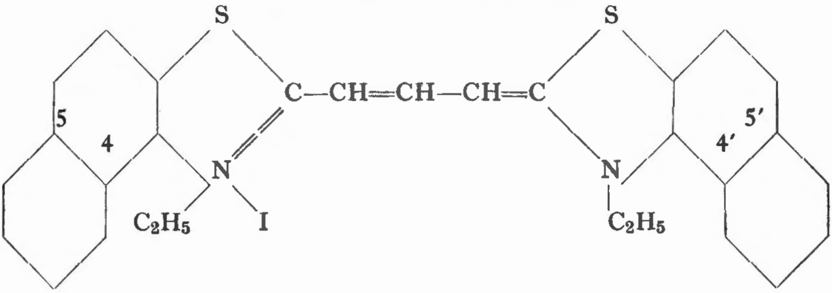
727. Benzothiacarbocyanines with a simple chain

The benzothiacarbocyanines contain two naphthothiazole nuclei.

Their absorption maxima are situated 35–40 mμ nearer the extreme red than the lighter derivatives. The sensitization maxima are shifted 50–60 mμ. The benzothiacarbocyanines are quite powerful red sensitizers. Contrary to the action with the thiacarbocyanines, chain substituents increase their efficiency but slightly.



3 : 3′-diethyl-6 : 6 : 6′ : 7′-dibenzothiacarbocyanines



3 : 3'-diethyl-4 : 5 : 4' : 5'-dibenzothiacarbocyanine

Preparation. Condensation of 2 mols of *2-methyl-α* or *β-naphthothiazole* p-toluene-sulphonate (para. 687) with 4 mols *ethyl orthoformate* in *pyridine* (para. 700), using the general method for preparing the carbocyanines (paras. 725–*B*). The dyes can be precipitated with potassium iodide, or better, with potassium bromide, which gives a more soluble product, but it is preferable to leave them as the p-toluene-sulphonates. As the reactivity of the naphthothiazole bases is lower than the benzthiazoles, the yields are somewhat lower.

3:3'-diethyl-4:5:4':5'-dibenzothiacarbocyanine (*p-toluene-sulphonate*). Principal absorption at 600 mμ with a secondary peak at 560 mμ. Sensitizing action up to 720 mμ with a maximum at 640 mμ. Preparation:

212 g of *2-methyl-β-naphthothiazole ethyl-p-toluene-sulphonate* (para. 687), 223 g distilled *ethyl orthoformate* and 1650 cc *pyridine* are heated in the oil bath in a flask fitted with a reflux condenser. After 1½ hours at 120°C and 4 hours at 130°C, the solution is cooled and left in ice for 12 hours. The product is filtered off and washed successively with 500 cc pyridine, 335 cc ethanol, 850 cc water, 250 cc ethanol and 700 cc ether. 74 g of dry dye is obtained. The mother liquors deposit crystals which when similarly washed produce a further 28 g of the product.(17)

3:3'-diethyl-6:7:6':7'-dibenzothiacarbocyanine. Prepared from 2-methyl-α-naphthothiazole. Sensitizes to 690 mμ with a maximum at 635 mμ and a depression at 510 mμ in the blue-green.

728. Simple selenacarbocyanines

The constitution of these cyanines is similar to that of the thiacarbocyanines except that the S atoms are replaced by Se atoms. They are obtained from the quaternary salts of *2-methylbenzselenazole* (para. 689).

3:3'-diethylselenacarbocyanine. 14·5 g of 2-methylbenzselenazole and 15 cc ethyl orthoformate are boiled in 150 cc pyridine for one hour.(18) The solution becomes purple and a crystalline deposit is formed. The product is poured into water and left for 12 hours. The precipitated selenacarbocyanine is recrystallized from 13 litres of methanol. M. Pt. 267°C. Yield, 8 g.

Absorption maxima at 542 and 450 mμ. Sensitizes to 645 mμ with a maximum at 570 mμ.

The *5:5'-diethoxy* derivative sensitizes further towards the red.

3:3′-diethyl-6:7:6′:7′-dibenzoselenacarbocyanine is effective up to 680 mμ with a maximum at 610 mμ.⁽²⁰⁾ Obtained from 2-methyl-α-naphthoselenazole.

The *selenazolinocarbocyanines* have similar properties to the thiazolinocarbocyanines and are prepared by condensing 2-methylselenazoline quaternary salts (para. 680) with ethyl orthoformate.⁽²⁰⁾

729. Simple oxacarbocyanines

3:3′-diethyloxacarbocyanine. 20 g (2 mol) 2-methylbenzoxazole ethiodide (para. 690) is boiled with 30 cc (4 mol) ethyl orthoformate in 200 cc dry pyridine for one hour. The solid which is deposited on cooling is crystallized from absolute alcohol (yield, 40%) in scarlet crystals, M. Pt. 277°C. Absorption at 485 and 460 mμ (Fig. 128). Sensitization maximum at 515 mμ (Fig. 70).

Substituted oxacarbocyanines. These are prepared from benzoxazole bases substituted in the 5- and 6- positions by the groups CH_3, C_2H_5, CH_3O, C_2H_5O, C_6H_5, $C_{10}H_7$, etc.⁽²¹⁾ *3:3′-diethyl-6:6′-diphenyloxacarbocyanine* is of this type.

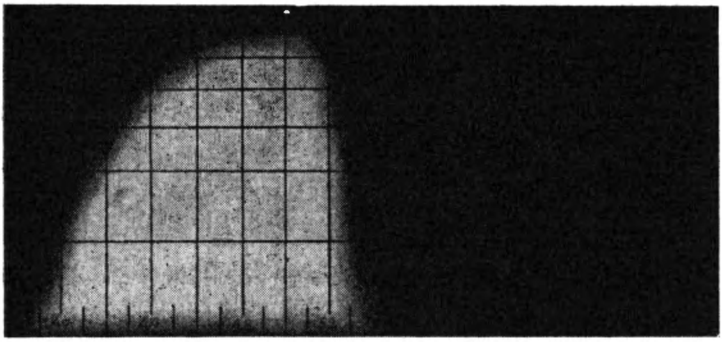


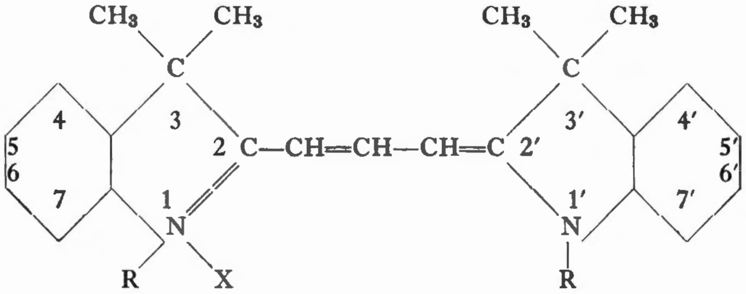
FIG. 128. Sensitization 3: 3′-diethyloxacarbocyanine.

3:3′-diethyl-6:6′-dimethylaminooxacyanine sensitizes to 650 mμ with a maximum at 590 mμ.

3:3′-diethyl-6:7:6′:7′-dibenzoxacarbocyanine. 2-methyl-α-naphthoxazol ethyl-p-toluene-sulphonate is condensed with ethyl orthoformate in dry pyridine. The dye is precipitated with an aqueous solution of ammonium bromide, and is recrystallized from alcohol. Sensitizes in the green up to 600 mμ with a maximum at 545 mμ. The *β-naphthoxazole* derivative has similar properties.

730. Indocarbocyanines

The *indocarbocyanines* are derived from 2:3:3-trimethylindoline. They are red dyes sensitizing in the yellow-green, and have the structure



The indocarbocyanines are more fast to light than the other cyanines. They are prepared by reacting ethyl orthoformate with the *2:3:3-trimethylindoline* alkiodides in pyridine. The indocarbocyanines give leuco bases on reduction in pyridine. Their absorption maxima are displaced 12 mμ towards the blue compared with the thiacarbocyanines. The indocarbocyanines appear to sensitize better by bathing than by incorporation in the emulsion.

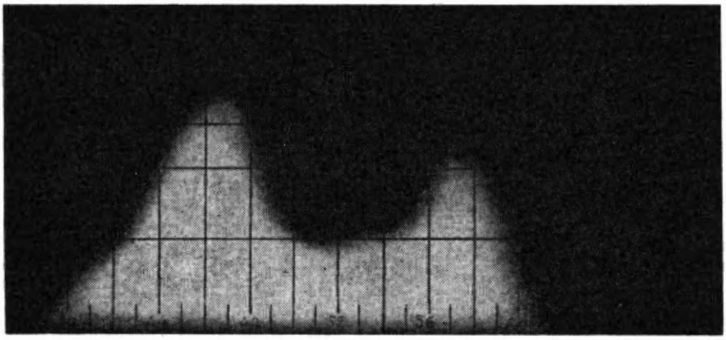


FIG. 129. Sensitization: 1: 1′-diethyl-3: 3: 3′: 3′-tetramethylindocarbocyanine.

1:3:1′:3′:3′-hexamethylindocarbocyanine(22) (indoline red, astrafloxine FF). Principal absorption at 546 mμ. Sensitization maxima at 580 and 530 mμ (by bathing).

Preparation: 8 g (2 mol) *2:3:3-trimethylindoline* methiodide and 12 cc (4 mol) ethyl orthoformate in 80 cc pyridine is refluxed for 1 hour. The product is poured into water, and is recrystallized from dilute alcohol acidified with hydriodic acid. M. Pt. 228°C. (Yield, 66%.) Acetic anhydride can be used in place of pyridine. (Yield, 65%.)

1:1′-diethyl-3:3:3′:3′-tetramethylindocarbocyanine. Sensitization maxima at 570 and 532 mμ (by bathing) (Fig. 71).

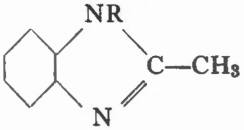
1:1′-diethyl-3:3:3′:3′-tetramethyl-5:5′-tetramethyldiaminoindocarbocyanine. Sensitizes in the red to 700 mμ.(24)

1:1′:3:3:3′:3′-hexamethyl-5:5′-dichloroindocarbocyanine. Prepared from 2:3:3-trimethyl-5-chloroindoline. Absorption maxima at 551, 517 and 489 mμ.

2:3-dihydro-β-quinindenecarbocyanine. Studied and prepared by Lal and Petrov.(24)

731. Iminazocarbocyanines

These dyes, also called imidocarbocyanines, are prepared by condensing ethyl orthoformate and the 2-methylbenziminazole(25)



quaternary salts, which are prepared by treating *o-phenylenediamine* hydrochloride with acetic acid then with diethyl sulphate in the presence of caustic soda using Phillips' technique.(26)

Riester(27) first obtained the iminazocarbocyanines using iodoform and sodium ethoxide.

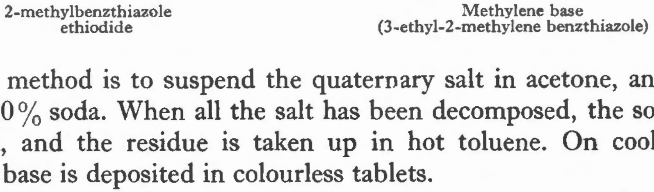
Kendall(28) has recently made a study of the iminazocarbocyanines.

732. Asymmetrical carbocyanines with unsubstituted chains

The carbocyanines with two different nuclei have absorption spectra intermediate between the spectra of the two corresponding symmetrical carbocyanines. When the nuclei are very different, benzoxazol and benzthiazole, for example, it becomes possible to obtain the maximum sensitivity at a new wavelength, which is not possible with the two symmetrical dyes taken separately.

There are three quick general methods for preparing the asymmetrical carbocyanines with unsubstituted chains.

A. The '*methylene base*' is formed by treating the quaternary salt (ethiodide for example) of a 2-methyl-heterocyclic base with 1–2% caustic soda in iced solution. The yellowish precipitate is dissolved in ether; the ether solution is dried over potassium carbonate, then concentrated until crystallization starts. The methylene base then crystallizes on cooling.



2-methylbenzthiazole ethiodide

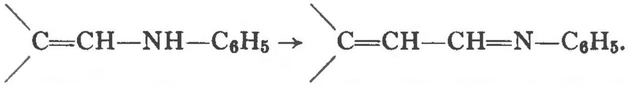
Methylene base (3-ethyl-2-methylene benzthiazole)

Another method is to suspend the quaternary salt in acetone, and to stir this with 50% soda. When all the salt has been decomposed, the solution is evaporated, and the residue is taken up in hot toluene. On cooling, the methylene base is deposited in colourless tablets.

The methylene base is heated with the quaternary salt of another heterocyclic base in the presence of formalin, for 20–30 mins. The carbocyanine is produced by condensation. It is recrystallized from methanol. To remove the periodide which is present as an impurity (if the ethiodide has been used) the methanol solution is treated with sulphur dioxide. Preparation example: 3·4 g of N-ethylquinaldine methylene base is heated for 20 mins. with 6·3 g p-toluquinaldine ethiodide and 1·5 cc 37% formalin in 80 cc alcohol. The purple solution deposits a mass of crystals on cooling, and these are dissolved in boiling methanol and treated with SO_2. Recrystallize from methanol. In this way *1:1′-diethyl-6-methylcarbocyanine* iodide is obtained. With benzthiazole bases, 2·5 cc of formalin is used for 5 g of base.

B. The quaternary salt of a heterocyclic base is heated to 100°C with *diphenylformamidine* (para. 725 *E*) $C_6H_5—N{=}CH—NH—C_6H_5$. This, as we have seen, gives a *β-anilidovinyl derivative* which will condense with a quaternary salt of another base, by heating for 30 mins. at 100°C with 4 mols of acetic anhydride and 1 mol of anhydrous sodium or potassium acetate, to give an asymmetrical carbocyanine with an unsubstituted chain. It is recrystallized from methanol.

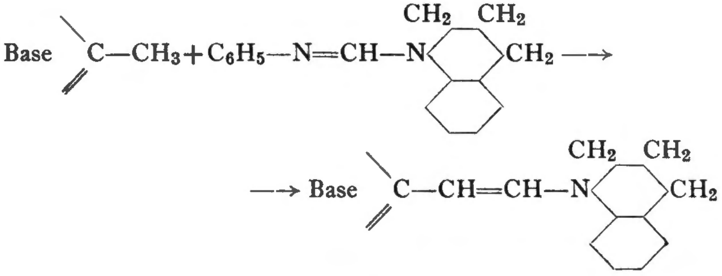
Another way of working is to treat the β-anilidovinyl derivative with sodium methoxide. This produces the change:



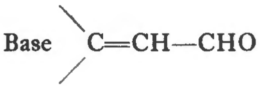
$$>C{=}CH—NH—C_6H_5 \rightarrow >C{=}CH—CH{=}N—C_6H_5.$$

This is then condensed with the quaternary salt of another base in pyridine in the presence of piperidine.

C. A quaternary salt of a 2-methyl-heterocyclic base is heated with a *quinoline amidine derivative* in acetic anhydride:



The product is then hydrolyzed to the *aldehyde* with soda in aqueous alcohol

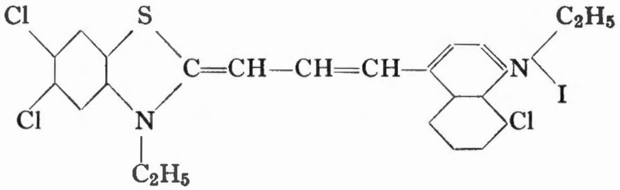


$$\text{Base}>C{=}CH—CHO$$

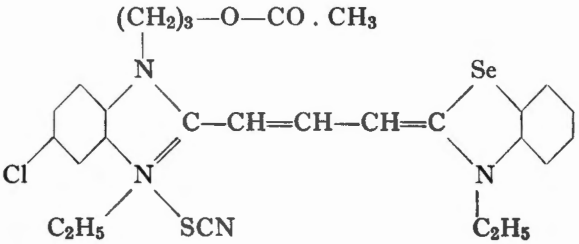
and this aldehyde is finally condensed with the *diethyl sulphate of another heterocyclic base* to give the diethyl sulphate of the asymmetrical dye. The ethiodide can be prepared by precipitating with potassium iodide.

1:1′-diethyl-6-methyl carbocyanine. Sensitizing action to 695 mμ with maxima at 550 and 640 mμ.

1:3′-diethyl-8-chloro-5′:6′-dimethyl-4-quinocarbocyanine. This dye, which has been used for the red sensitization of Agfacolor paper is obtained by method *C* from 2:5:6-trimethylbenzthiazole (ethiodide). The aldehyde is condensed with 8-chlorolepidine diethyl sulphate. Note the extended extreme red sensitivity due to the use of the 4- position of the quinoline nucleus, which lengthens the chain between the two nitrogen atoms.

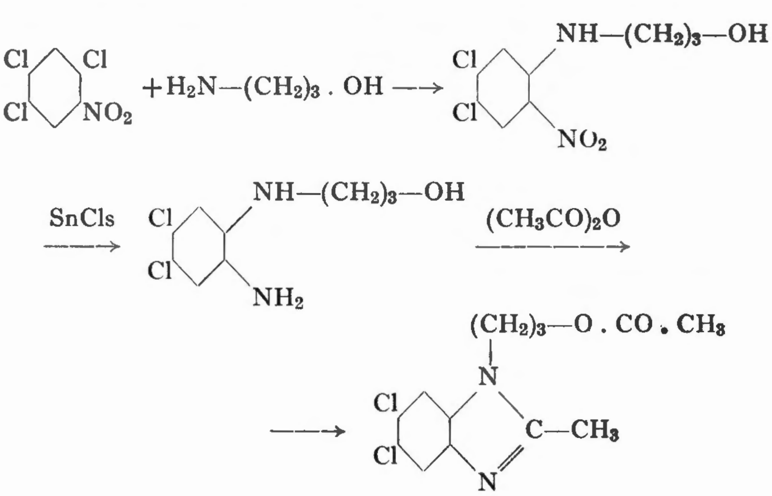


1:3′-diethyl-3-acetoxypropyl-5-6-dichloroimidazoselenacarbocyanine,

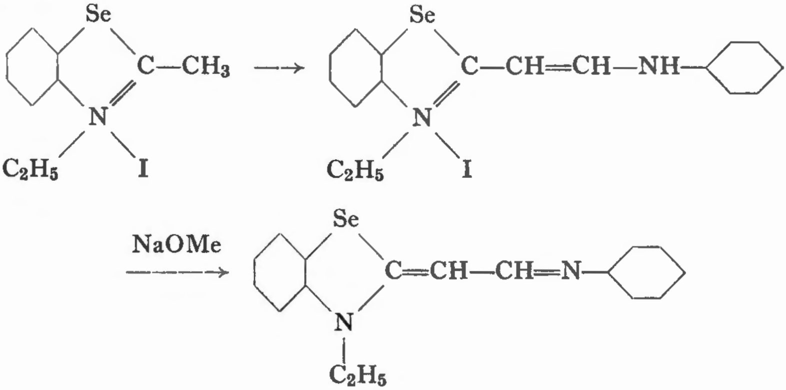


an asymmetrical carbocyanine similar to that used for the green sensitization of reversal Agfacolor. It can be prepared by a variation of method *B* given above.

To obtain the base *2-methyl-3-ω-acetoxypropyl-5:6-dichlorimidazole,* 2:4:5-trichloronitrobenzene is condensed with 3-aminopropanol. The resulting product is reduced with $SnCl_2$, and then treated with acetic anhydride:



This base is converted to the ethyl quaternary salt and is then condensed with the anilidovinyl derivative of 2-methylbenzselenazole, previously treated with sodium methoxide.



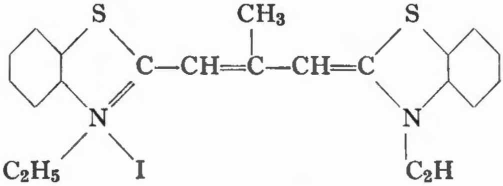
After condensing in pyridine in the presence of piperidine, the dye is converted to the thiocyanate with NH_4CNS.

Asymmetrical N-arylquinoline-indoline carbocyanines. Prepared by Pilyugin.(29)

Asymmetrical furyl-pyrryl and furyl-indoline carbocyanines. Prepared by Strell, Kloianoff and Brem-Rupp.(29b)

733. Chain substituted symmetrical carbocyanines

The symmetrical chain substituted carbocyanines, and particularly the *meso-methyl thia-, selena-, and oxacarbocyanines,*



Mesomethylthiacarbocyanine

are much more powerful sensitizers than the corresponding carbocyanines with no chain substituent. This increase in activity due to the presence of the methyl group in the trimethine chain is, however, less noticeable when the nuclei are from the naphtho-bases. It is even less in the case of quinoline carbocyanines. The mesomethyl thia-, selena-, and oxacarbocyanines with benzthiazole, thiazole, thiazoline, benzselenazole and benzoxazole nuclei are among the best known sensitizers. To extend the sensitivity towards the red, it is, however, necessary to introduce substituents into the nucleus—methyl, ethyl, methoxy, ethoxy or, best of all, dimethylamino groups—to avoid using the naphtho-azole bases.

As a general rule, a methyl substituent in the chain shifts the absorption maximum towards the *blue*, the amount of shift reaching 20 mμ. The oxacarbocyanines and thiazolinocarbocyanines are exceptions, the shift being 6 mμ towards the *red* with the former.

The meso substituent can be a heavier group than CH_3, but there is generally no advantage in using heavy substituents as they can reduce or suppress the sensitizing activity.

There are *two methods for preparing meso substituted symmetrical carbocyanines.*

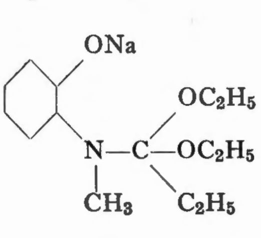
A. 2-methylbenzthiazole ethiodide, heated in pyridine, produces a small quantity of mesomethyl thiacarbocyanine. By replacing the ethiodide by the corresponding p-toluene-sulphonate, and working in pyridine containing piperidine or triethylamine, Brooker and White obtained a yield of 56 %.(30) The central substituted group $—C(CH_3)=$ of the trimethine chain is provided by one molecule of the base, which decomposes. No unsubstituted carbocyanine is produced, because the heterocyclic salts react as 'methylene' bases.

The method of Brooker and White is mainly effective with the thiacarbocyanines and the selenacarbocyanines. With the naphthothiazole and benzoxazole derivatives the yields are low.

B. We have seen (para. 725b) that ethyl orthoformate can provide the central member of the trimethine chain. By replacing the orthoformate by the orthoacetate $CH_3—C\equiv(OC_2H_5)_3$ (whose preparation is given in para. 701) the mesomethyl compound is produced due to the presence of the CH_3 group in the orthoacetate.

With ethyl or methyl orthopropionate, the orthovalerate, orthocaproate, orthophenylacetate, orthophenoxybutyrate, orthobenzoate, or orthotoluate, the carbocyanines are formed which have, respectively, the ethyl $C_2H_5—$, butyl $C_4H_9—$, amyl $C_5H_{11}—$, benzyl $C_6H_5 . CH_2—$, phenoxypropyl $C_6H_5—O—C_3H_7—$, phenyl $C_6H_5—$ and p-tolyl $CH_3—C_6H_4—$ substituents in the meso position.(31) Other types: see 31b.

The ortho esters can be replaced by the amide of an acetal acid such as



obtained by treating 2-alkylbenzoxazole dimethyl sulphate with sodium ethoxide. It is the alkyl group of the benzoxazole which becomes the meso substituent.(32)

Rosenhauer, Schmidt and Unger were able to introduce the phenyl radical into the chain by reacting *phenylchloroform* with 2 mols of *1-methyl-2-methylene-quinoline*(32b)

$$CH_3[Q]{=}CH_2 + ClC-Cl(C_6H_5)-Cl + CH_2{=}[Q]CH_3 \rightarrow$$

1-methyl-2-methylene-quinoline

Phenylchloroform

$$CH_3Cl[Q]-CH{=}C(C_6H_5)-CH{=}[Q]CH_3 + 2HCl$$

Carbocyanine

There is a similar reaction with the *methylene bases* of benzthiazole.

The absorption maxima of 3:3′-diethylthiacarbocyanine with various meso substituents are:

unsubstituted	methyl	ethyl	n-propyl	n-butyl	benzyl	phenyl
557	543	547	547	547	550	560 mμ

There is therefore a shift of the absorption maximum towards the blue, particularly with the methyl substituent. This shift is counteracted when the substituent is an aromatic radical.

With 3:3′-diethyl 4:5:4′:5′-dibenzothiacarbocyanine, 3:3′-diethyselenacarbocyanine and 3:3′-diethyloxacarbocyanine the absorption maxima are:

3:3′-carbocyanine	unsubstituted	methyl	ethyl	phenyl
Dibenzothiacarbocyanine	595	575	577	592 mμ
Selenacarbocyanine	567	552	557	574 mμ
Oxacarbocyanine	482	488	490	— mμ
Thiazolinocarbocyanine	443	—	460	— mμ

With the oxacarbocyanine and the thiazolinocarbocyanine a shift of the absorption maximum towards the red is noticed.

Condensation with the orthoesters is generally carried out in pyridine. It is sometimes advantageous to add triethylamine, for example in the preparation of meso substituted oxacarbocyanines. The quaternary salt can be an alkiodide if the ethyl orthoester is used, but with a methyl ester it is better to use a p-toluene-sulphonate of the base as the yields are very low with the alkiodides.(33) For 2 mols of base, 3 mols of the orthoester are needed, i.e an excess of 200%.

A yield of 50–60% is obtained when an ethyl-p-toluene-sulphonate of the base is condensed with ethyl orthoacetate in *n-propanol* in the presence of triethylamine.(34)

734. Meso-substituted symmetrical thiacarbocyanines

3:3′-diethyl-9-methyl thiacarbocyanine. This dye, which has been widely used for the manufacture of ortho-panchromatic emulsions, has two absorption maxima, at 543 and 510 mμ. It sensitizes strongly to 640 mμ with maxima at 590 and 540 mμ. It can be prepared by the general methods:

(*a*) 9·15 g (3 mol) 2-methylbenzthiazole ethiodide and 3 g (3 mol) anhydrous triethylamine in 30 cc pyridine is refluxed for 30 mins. on the oil bath at 160°C. It is stirred or shaken frequently to avoid the accumulation of a deposit at the bottom of the flask. After cooling, 200 cc ether is added to ensure complete precipitation of the dye, which is filtered, washed with hot water and acetone. Yield, 56% which is reduced to 51% after recrystallizing twice from methanol.(35) It is sufficient to grind the crude dye with boiling water, filter, and wash successively with 8 cc pyridine, 5 cc ethanol, 10 cc distilled water, 4 cc ethanol and 20 cc ether. M. Pt. 286–287°C.

(*b*) 2-methylbenzthiazole ethiodide is condensed with ethyl orthoacetate in pyridine(36) or better, in n-propanol.(34) Heat the ethyl-p-toluene sulphonate obtained from 15 g 2-methylbenzthiazole with 26 g ethyl orthoacetate and 12·5 g triethylamine in 60 cc n-propanol for 1 hour at the boil. The dye is precipitated with a hot aqueous solution of potassium bromide. It is washed with water and acetone and is recrystallized from 330 cc methanol (for 10·3 g crude dye).

3:3′:9-triethylthiacarbocyanine. 6·1 g 2-methylbenzthiazole ethiodide is refluxed for 45 mins. with 5·3 g ethyl orthopropionate in 25 cc pyridine. The dye is precipitated by adding ether. It is filtered, then suspended in acetone, cooled, filtered, washed with water, and recrystallized from methanol (75 cc per g). Yield, 52% of the crude product and 41% after purification, M. Pt. 236–237°C.

3:3′-diethyl-9-phenylthiacarbocyanine. 7 g of 2-methylbenzthiazole ethyl-p-toluene-sulphonate is refluxed for 45 mins. with 6·7 g triethyl orthobenzoate in 25 cc pyridine. The dye is precipitated by adding ether, and is redissolved in methanol and reprecipitated as bromide or iodide by adding potassium bromide or iodide in aqueous solution. It is washed with water and acetone and is finally recrystallized from methanol (210 cc per g). The iodide melts at 300–301°C.

3:3′-diethyl-9-methyl-6:7:6′:7′-dibenzothiacarbocyanine. Principal absorptions at 572 and 575 mμ. Sensitizes to 680 mμ with a maximum at 620 mμ. The dye is produced by refluxing 12 g (3 mol) of 2-methyl-α-naphthothiazole ethyl-p-toluene-sulphonate with 2 g (2 mol) triethylamine, in 20 cc pyridine for 15 mins. It is precipitated by adding 150 cc ether, dissolved in 30 cc methanol and re-precipitated with 5 g potassium iodide in 50 cc water. The crude product is washed with 75 cc water, treated with 75 cc acetone and recrystallized from methanol. Yield, 6·6%. M. Pt. 297°C.

The preparation method is to heat 8 g 2-methyl-α-naphthothiazole ethyl-p-toluene-sulphonate with 4·85 g ethyl orthoacetate and 50 cc pyridine for 1 hour. The solution is mixed with an aqueous solution of 5 g potassium iodide or bromide. The precipitated dye is washed with water, acetone (50 cc) and is recrystallized from methanol (215 cc) per g. Yield of crude product, 58% and 43% of pure. M. Pt. of bromide, 261°C.

3:3′-diethyl-9-methyl-4:5:4′:5′-dibenzothiacarbocyanine is a stronger sensitizer than the previous one, with maxima at 650 and 550 mμ. It is prepared in the same way using 2-methyl-β-naphthothiazole ethyl-p-toluene-sulphonate. The bromide is recrystallized from methanol (140 cc per g). Yields 36% and 27% before and after crystallization. Absorption maxima at 575 and 535 mμ. M. Pt., 240°C.

3:3′-diethyl-7-methylthiazolinocarbocyanine. Sensitizes silver chloride strongly in the blue. The mesoethyl compound behaves similarly, with a sensitizing maximum at 483 mμ and absorptions at 455 and 460 mμ. Preparation: reflux 102·8 g of 2-methylthiazoline ethiodide (para. 688), 129·6 g ethyl orthoacetate, 20 cc triethylamine and 350 cc pyridine (both anhydrous) for 4 hours. Concentrate under reduced pressure. Cool in iced water for several hours. Add ether until a tar is formed. Leave, decant, and dissolve the residue in chloroform. Wash this solution several times with water then dry it over anhydrous sodium sulphate. Distil the chloroform and dissolve the residue in acetone. Filter through paper, and leave to crystallize (initiate crystallization by rubbing the inside of the vessel). Filter and recrystallize in the minimum of acetone. Again filter, and wash with a little acetone then with ether. At least 40 g of dye is obtained (50 %). Again crystallize, this time from 80 cc boiling ethanol and wash the crystals obtained on cooling with alcohol and ether. 35 g of pure product is obtained (42 %). Some dye can be recovered from the combined concentrated mother liquors. The dye obtained is dissolved in boiling ethanol. Crystals are obtained on cooling.

For the mesoethyl derivative, Brooker(37) used 9 g 2-methylthiazoline ethyl-p-toluene-sulphonate, 8·1 g methyl orthopropionate and 10 cc pyridine. Heating time: 3 hours. The dye was precipitated with potassium iodide and recrystallized from methanol (10 cc per g). M. Pt., 182–184°C.

Meso-substituted thiacarbocyanines with acyl nuclear substituents. The substituents in the 5- or 6- positions have the structure R . COO—.(38)

735. Meso-substituted symmetrical selenacarbocyanines

The constitution, properties and preparative methods of the meso-substituted symmetrical selenacarbocyanines are similar to those of the thiacarbocyanines. The absorption and sensitization spectra are slightly shifted toward the red compared with those of the thiacarbocyanines (9–10 mμ).

3:3'-diethyl-9-methylselenacarbocyanine. Absorption maximum at 552 mμ. Strong sensitization to 650 mμ with maxima at 610 and 535 mμ. Preparation:(39) the ethyl p-toluene-sulphonate obtained from 3·9 g of 2-methylbenzselenazole (para. 689) and 4 g ethyl-p-toluene-sulphonate is refluxed for 20 mins. with 3·2 g ethyl orthoacetate and 20 cc pyridine. The dye is precipitated with ether, redissolved in methanol and converted to the iodide by adding excess potassium iodide solution. Recrystallize from methanol (550 cc per g). Yields of crude and pure product 36 and 23 %. M. Pt., 296°C.

Other method: reflux for 30 mins. 6 g 2-methylbenzselenazole ethiodide with 1·4 cc triethylamine and 10 cc anhydrous pyridine (B. Pt., 114°C). Cool and leave overnight. Wash the crystals successively with 5 cc pyridine, 5 cc alcohol, 20 cc water, 8 cc alcohol and 20 cc ether. 1·2 g of crude dye is obtained.

3:3':9-triethylselenacarbocyanine.(40) Heat 7·9 g of 2-methyl benzselenazole ethyl-p-toluene sulphonate and 5·3 g ethyl or methyl orthopropionate in 25 cc pyridine under reflux for 15 mins. The dye is precipitated with ether, taken up in alcohol, converted to the less soluble iodide with potassium iodide, then recrystallized from methanol (35 cc per g). Yields of crude and pure products, 20 and 16%. M. Pt., 146–148°C.

The *mesophenyl* derivative is similarly prepared using ethyl orthobenzoate.

Selenazolinocarbocyanines with *mesosubstituents* were prepared by White⁽⁴¹⁾ and are strong blue sensitizers for silver chloride emulsions.

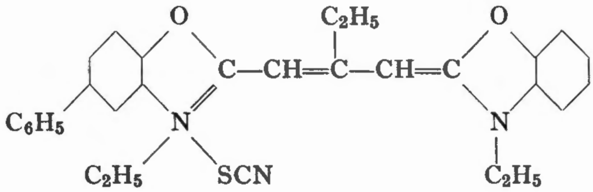
736. Meso-substituted symmetrical oxacarbocyanines

The meso-substituted symmetrical oxacarbocyanines are strong sensitizers for the blue-green when simple nuclei are used, and for the green when the benzoxazole nucleus has heavy substituents such as phenyl. These are very useful dyes.

3:3'-diethyl-9-methyloxacarbocyanine (iodide). Absorption maxima at 488 and 465 mμ. Maximum sensitization at 510 mμ. Preparation:⁽⁴²⁾ reflux 8·7 g (2 mol) 2-methylbenzoxazole ethiodide (para. 690), 9·7 g (4 mol) ethyl orthoacetate (para. 701), 1·5 g anhydrous triethylamine and 30 cc anhydrous pyridine for 15 mins. Cool and add ether to ensure complete precipitation of the dye. Filter, wash with water and acetone, and recrystallize from methanol (60 cc per g). M. Pt. 274°C. Yield, 12% crude and 10% recrystallized.⁽⁴³⁾ Another method is to heat 4·34 g (3 mol) of the ethiodide of the base with 1·52 g (3 mol) of triethylamine in 10 cc n-propanol for 30 mins. The dye is worked-up as above. Yields: 6 and 5%.

3:3':9-triethyloxacarbocyanine. Principal absorption at 490 mμ. Preparation: heat 2·9 g of 2-methylbenzoxazole ethiodide, 2·64 g ethyl orthopropionate in 15 cc pyridine under reflux for one hour. After cooling, add ether to assist precipitation of the dye. Filter, suspend in boiling acetone, again filter and wash with water. Recrystallize from methanol. M. Pt., 269–270°C. Yields: crude 13%, pure 8%.

3:3'-diethyl-9-methyl-5:5'-diphenyloxacarbocyanine. Green sensitizer. Used in negative, reversal and positive Agfacolor films as the thiocyanate.



2-methyl-5-phenyl-benzoxazole diethyl sulphate (para. 681, 690) is condensed with ethyl orthopropionate in pyridine, following the general method. The dye solution is finally poured into a solution of ammonium thiocyanate.

The *9-methyl* derivative of this dye has also been prepared by heating 8·4 g of 2-methyl-5-phenylbenzoxazole ethyl-p-toluene-sulphonate with 6·5 g ethyl orthoacetate and 1 cc triethylamine in 10 cc pyridine for 30 mins. On cooling the dye is precipitated with ether. A tar is formed which is separated by decanting before dissolving in the minimum of boiling methanol. A 10% solution of potassium thiocyanate equal to double the volume of the methanol is added. The new tar, which slowly solidifies, is ground with water, filtered and recrystallized from methanol. Low yield.

3:3′-dipropyl-9-ethyl-5:5′-diphenyloxacarbocyanine (nitrate). Green sensitizer which was used for Agfacolor paper. The n-propyl-benzene-sulphonate of the base is heated with ethyl orthopropionate in pyridine. The dye is converted to the nitrate by pouring the solution into a solution of potassium nitrate.

3:3′-diethyl-9-methyl-6:7:6′:7′-benzoxacarbocyanine. Green sensitizer with maximum at 550 mμ. It is prepared by heating 2·2 g of 2-methyl-α-naphthoxazole diethyl-sulphate (para. 691) with 3 cc ethyl orthoacetate in 10 cc pyridine for one to two hours. The dye is precipitated with ether, filtered, dissolved in alcohol, potassium bromide solution is added, and the dye is reprecipitated with ether and recrystallized from alcohol.(44)

The β-naphthoxazole derivative has been prepared by simply heating 23 g (1 mol) of the diethyl sulphate of the base with 23 g (2-mol) ethyl orthoacetate for two hours. The dye is precipitated with ether, filtered, washed with water, redissolved in 200 cc ethanol and reprecipitated by pouring this solution into 200 cc 10% potassium iodide. The blood-red precipitate (2·2 g) is ground with ether in a mortar, filtered, washed with ether and recrystallized from boiling isopropyl alcohol. Poor yield.

737. Symmetrical carbocyanines with special meso substituents

So far we have only envisaged the existence of carbocyanines with simple meso substituents. Actually, one or more of the carbon atoms of the trimethine chain can carry more or less complex groups. These substituents are not always beneficial from the point of view of normal sensitizing activity, but they can sometimes induce supersensitizing properties.

Alkoxy or alkylthio substituents, RO— and RS—.(45) These have a bathochromic effect, shifting the absorption maxima towards the red. The 9-methylthio-thiacarbocyanines have their absorption maxima at about 595 and 545 mμ. They are prepared by condensing a benzthiazole quaternary salt with the dialkylmercaptovinyl derivative. By the action of primary or secondary amines, the meso group —NHR is introduced which has a hypsochromic effect with a magnitude of 56–89 mμ, as nitrogen is an electron donor.

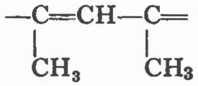
F. Schultz(45b) obtained them by condensing the ethyliminodithiocarbonic diethyl ester with the ethiodide of a 2-methylbenzthiazole in alcohol in the presence of acetic anhydride. NRR′ derivatives have been obtained by Kodak.(45c)

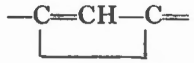
Alkylcarboxy or arylcarboxy substituents obtained by heating the ethiodide of a base with succinic anhydride

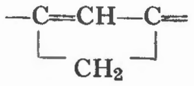
$$\lfloor \mathrm{CO{-}CH_2{-}CH_2{-}CO{-}O} \rfloor$$

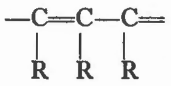
or phthalic anhydride (CO—C_6H_4—CO—)O in pyridine.(46) The sensitizing activity is lower than that of the mesomethyl derivative.

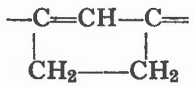
Thiophene derivative meso substituents.⁽⁴⁷⁾
Pyrimidazolone derivative meso substituents.⁽⁴⁸⁾
The following substituents have been obtained by Agfa:⁽⁴⁹⁾

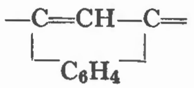

$-\underset{CH_3}{C}=CH-\underset{CH_3}{C}=$


$-\underbrace{C=CH-C}_{}=$


$-\underbrace{C=CH-C}_{CH_2}=$

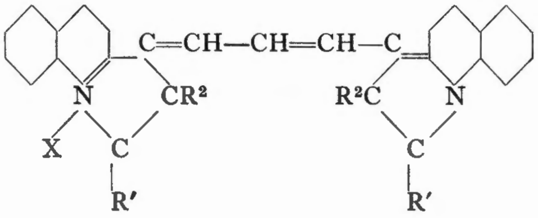

$-\underset{R}{C}=\underset{R}{C}-\underset{R}{C}=$


$-\underbrace{C=CH-C}_{CH_2-CH_2}=$


$-\underbrace{C=CH-C}_{C_6H_4}=$

For example, the *3:3′-diethyloxacarbocyanine* with a $-CH_2-CH_2-$ chain substituent sensitizes from 500—620 mμ with a maximum at 570 mμ. Cyclization of the trimethine chain has the effect of shifting the absorption maximum towards the red.

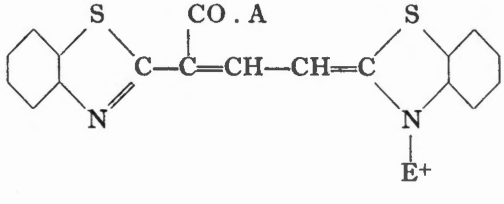
8- or 10-acylaminothiocarbocyanines: they are obtained from 2-aminobenzothiazol after the method of Kiprianof and others. (*Ukrain. Khim.*, 1955, 726). The blue-green dyes obtained from pyrrocoline derivatives⁽⁴⁹ᵇ⁾ can be considered as chain-substituted dicarbocyanines, for example.



Combination of mesomethyl dyes with aromatic aldehydes. Some of these compounds are sensitizers⁽⁴⁹ᶜ⁾ and 20 of them have been prepared.

737b. Carbocyanine bases

These cyanines have a cyclammonium nucleus in the basic state as shown below. They are substituted in the α-position by a group A—CO—



resulting from the decarboxylation of a carbethoxy, carbamido, carbanilido, carbhydrazide, or carbhydrazone group (paras. 742 and 743). They were disclosed as sensitizers by van Dormael and Nys.⁽⁴⁹ᵈ⁾ The substituent is not in the molecule plane.

738. Meso-substituted asymmetrical carbocyanines

The meso-substituted asymmetrical carbocyanines enable emulsions to be sensitized in spectral regions which are not readily achieved with symmetrical carbocyanines. The main function of the meso substituent in the trimethine chain is to enhance the sensitizing action. For example, such dyes are used in extreme speed orthochromatic emulsions whose region of sensitivity must not exceed 600 mμ; a symmetrical thiacarbocyanine would sensitize too far into the red, whilst the action of an oxacarbocyanine is too near the blue, but a meso-substituted oxathiacarbocyanine has the required strong action in the green and yellow. The absorption and sensitization maxima are intermediate between those of the corresponding symmetrical dyes. As examples, the following comparative characteristics of meso-substituted asymmetrical dyes are given:

1st nucleus	*2nd nucleus*	*Meso Substituent*	*Absorption Maximum mμ*	*Sensitization Maximum mμ*
Benzthiazole	Benzthiazole	C_2H_5	547	594
Benzoxazole	Benzoxazole	C_2H_5	490	512
Benzthiazole	Benzoxazole	C_2H_5	525	560
Benzthiazole	5-diethylamino benzthiazole	CH_3	585	620
Benzthiazole	β-naphthothiazole	CH_3	565	610

The three main methods for the preparation of meso-substituted asymmetrical carbocyanines are used:

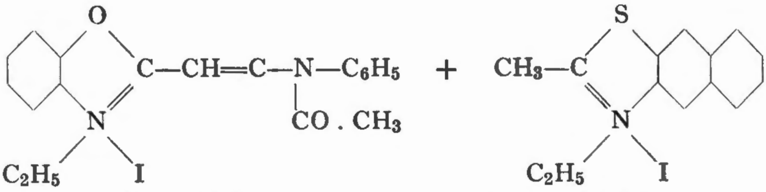
A. Condensation of a quaternary salt of a heterocyclic base with a reactive methyl group to give an *acetanilidomethylvinyl* compound, whose preparation has been described in para. 696. The reaction is similar to that of the simple *formamidine* derivatives in the case of asymmetrical carbocyanines with unsubstituted chains (para. 732b).

B. Formation of a nitrogenous heterocyclic compound having a *ketone* group in place of the usual CH_3 (called *acetylmethylene* derivative), then condensing the latter with a molecule of the quaternary salt of another heterocyclic base.

C. Formation of a nitrogenous heterocyclic derivative having a *thioketone* group in place of the reactive methyl, then condensing with another quaternary salt of a heterocyclic base. There are several variations to this method.

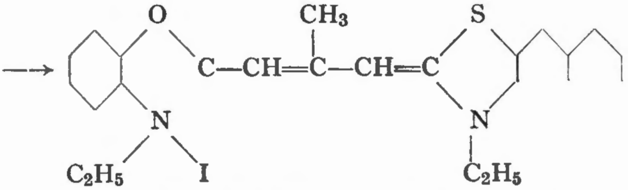
739. Preparation of meso-substituted asymmetrical carbocyanine using the amidines

Piggott and Rodd(50) showed that a nitrogenous heterocyclic base containing a reactive methyl group will condense with *diphenylformamidine* $C_6H_5—NH—CH=N—C_6H_5$ in the presence of *acetic anhydride* $(CH_3CO)_2O$ to give an *amino vinyl* compound [base]—$CH=CH-N(CO.CH_3)-C_6H_5$ which can condense with a molecule of a further heterocyclic base. If the central methine group of the formamidine is substituted, a meso-substituted asymmetrical carbocyanine is obtained. Thus *diphenylacetamidine* gives, with 2-methylbenzoxazole ethiodide, *2-ω-acetanilidomethylvinylbenzoxazole* ethiodide, whose preparation has been given (para. 696), which can be condensed with the ethiodide of a different base: by boiling 2 g 2-ω-acetanilidomethylvinylbenzoxazole ethiodide in 15 cc pyridine for 90 mins., with 2 g 2-methyl-ββ′-naphthothiazole ethiodide, a dye which sensitizes to the yellow is obtained by precipitation with ether and recrystallization from alcohol:(51)



2-ω-acetanilidomethylvinyl-benzoxazole (ethiodide)

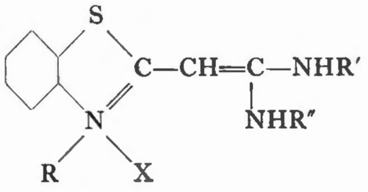
2-methyl-ββ′-naphto-thiazole (ethiodide)



3 : 3′-diethyl-9-methyl-oxa-5′ : 6′-benzthiacarbocyanine (iodide)

For the use of *diphenylethane amidine* in the preparation of meso-substituted carbocyanines see Hishiki.(52)

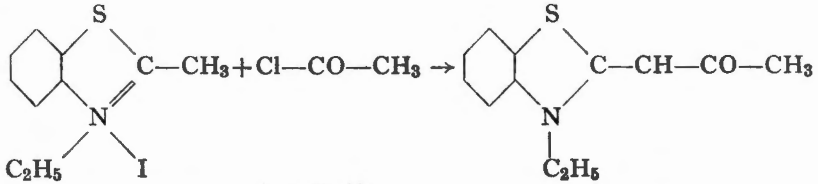
The use of condensation products of the following amide type:(53)



gives —NHR meso substituents.

740. Preparation of meso-substituted asymmetrical carbocyanines using ketone derivatives(54)

The quaternary salts of the nitrogenous heterocyclic bases with reactive methyl groups readily condense in pyridine with the *acid chlorides* to give *keto acylmethylene* compounds as in the following example:

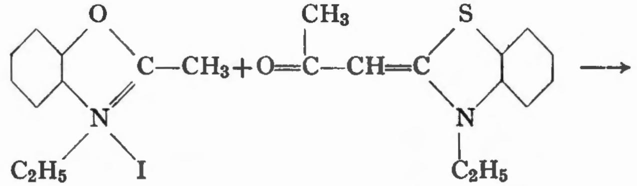


2-methylbenzthiazole ethiodide

Acetylchloride

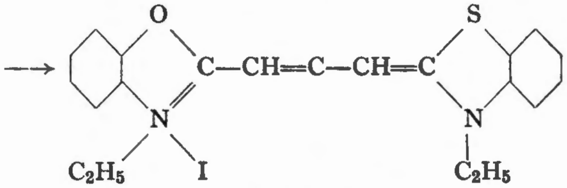
Acetylmethylene-3-ethylbenzthiazolidene

These keto derivatives readily unite with a molecule of the quaternary salt of another base in the presence of *acetic anhydride* to give a meso-substituted asymmetrical carbocyanine.



2-methylbenzoxazole ethiodide

Acetylmethylene-3-ethylbenzthiazolidene



3 : 3′-diethyl-9-methyl-oxa-thiacarbocyanine (iodide)

3-ethyl-2-acetylmethylenebenzthiazolidene. In a 1-litre 3-necked flask fitted with a mechanical stirrer, reflux condenser with a $CaCl_2$ tube and a dropping funnel, place 149 g 2-methylbenzthiazole ethiodide and 474 cc pure anhydrous pyridine. Cool to −10°C and add 48 g acetyl chloride, from the dropping funnel, over 15 mins. with continuous stirring, keeping the temperature at −10°C. Stir for 30 mins. at 0°C, then 15 mins. at 20°C and then heat for 25 mins. at 100°C. Remove most of the pyridine by distilling at 100°C at reduced pressure, and pour the residue into a 2-litre beaker containing 500 cc ice and water. A deep red tar is formed, which slowly solidifies. The residue in the flask is washed out with iced water. After leaving overnight in a bath of iced water, the product is filtered and washed with iced water. If there is still any residue in the distillation flask, it is dissolved in boiling alcohol, and precipitated by pouring into some of the aqueous filtrate. The total yield is 132 g of the damp keto derivative which is equal to 81 g of the dry product. It is recrystallized from 90–120° petroleum ether, then redissolved in acetone, and ether is added until a permanent turbidity is obtained. The ethyl-acetylmethylene-benzthiazolidene crystallizes rapidly. Yield, 63 g (60%).

3-ethyl-2-propionylmethylenebenzthiazolidene. The acetyl chloride in the above preparation is replaced by an equivalent amount of propionyl chloride. M. Pt. 151–155°C.

A method of synthesizing the acylmethylene derivatives developed by van Dormael and Ghys(55) is to react the *acylpyruvic esters* with the quaternary salts of nitrogenous heterocyclic bases having reactive alkyl mercapto groups.

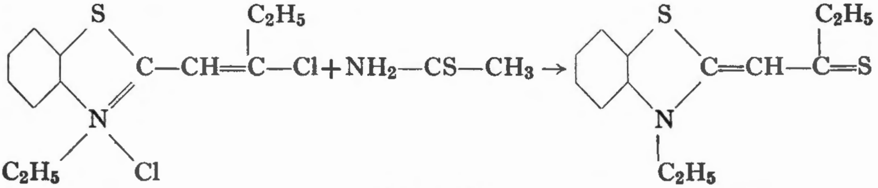
3:3′-diethyl-9-methyloxathiacarbocyanine. Reflux 28·9 g (1 mol) 2-methylbenzoxazole ethiodide and 22 g (1 mol) 3-ethyl-2-acetylmethylenebenzoxazolidene in 285 cc acetic anhydride for 10 mins. Cool in ice overnight. Filter the crystals and wash them successively with 140 cc acetic acid, 200 cc water, 150 cc alcohol and 250 cc ether. 7·8 g of crude dye (16%) is obtained.

The dye is a powerful green sensitizer.

A large number of other asymmetrical carbocyanines can be prepared in a similar way—selenathiacarbocyanines, oxabenzothiacarbocyanines, etc.

741. Preparation of meso-substituted asymmetrical carbocyanines using the thioketo derivatives

A. When *thioacetamide* is reacted with the *chlorovinyl* derivative of a nitrogenous heterocyclic base, a thioketo compound of similar structure to the acylmethylene compounds of the preceding paragraph is obtained.(56)



2-(chlorobutenyl)benz-thiazole ethiodide

Thioacetamide

2-Thiopropionylmethylene -3-ethylbenzthiazolidene

The quaternary salts of the thioacylmethylene compounds condense with the quaternary salts of the heterocyclic bases with reactive methyl groups, in absolute alcohol in the presence of triethylamine to give meso-substituted carbocyanines.

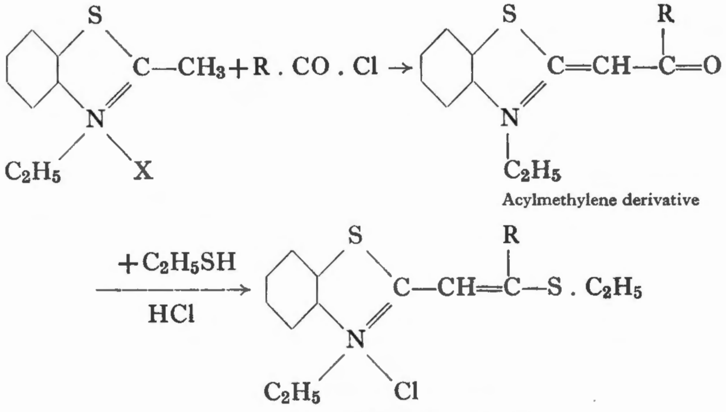
To obtain the *chlorovinyl derivative*, an *acylmethylene derivative* (prepared as indicated above) is heated with phosphorus oxychloride.

2-(2-chlorobutenyl)-benzthiazole (*ethyl chloride*). Dissolve 2·5 g (1 mol) 3-ethyl-2-acetylmethylenebenzthiazolidene in 15 cc benzene. Add 3 g (2 mol) phosphorus oxychloride with agitation. After leaving for 2 hours, dilute with 100 cc ether. The ether layer is separated, and the residue, which contains the product, is dissolved in absolute ethanol.

3-ethyl-2-thioacetylmethylenebenzthiazolidene. Add 3 g (2 mol) thioacetanilide to the above alcoholic solution and reflux for 20 mins. After cooling, pour into water. The product is filtered, washed with alcohol, and recrystallized from methanol.

3:3′-diethyl-9-methyl-5′-6′-benzooxathiacarbocyanine. Heat 4·6 g (1 mol) of the above thioacylmethylene compound with 4 g (1 mol) ethyl p-toluenesulphonate on the steam bath for one hour. The viscous mass is dissolved in 25 cc absolute alcohol. 6·5 g 2-methyl-β-naphthoxazole ethiodide and 2 g triethylamine are added and the mixture is refluxed for 15 mins. The dye is filtered off, and recrystallized from methanol. Sensitization maximum is about 630 mμ.

B. If a cyclammonium keto (or acylmethylene) derivative is treated with *ethyl mercaptan* C_2H_5SH in the presence of hydrochloric acid, a *mercapto derivative* or thioether of the cylammonium base is produced, whose reactivity is increased.

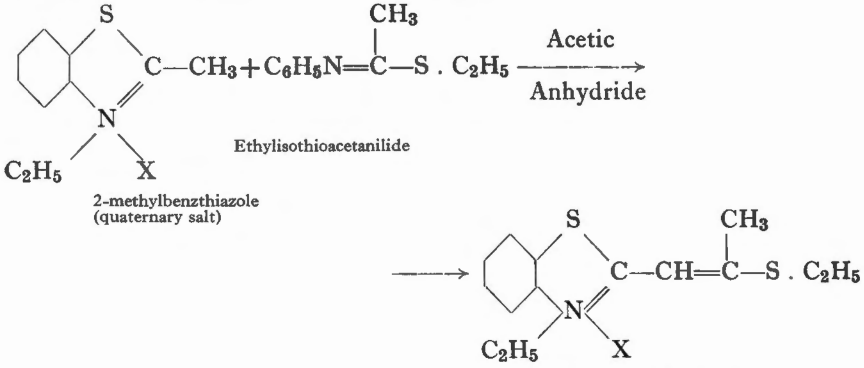


Acylmethylene derivative

Alkylmercapto derivative

The alkylmercapto derivatives condense with the quaternary salts of methyl heterocyclic bases to give meso substituted symmetrical or asymmetrical carbocyanines. In this way *3:3′-diethyl-6:6′-dinaphthyl-9-phenylthiacarbocyanine*(57) is obtained which has an absorption maximum at 574 mμ and sensitizes to 660 mμ with a maximum at 635 mμ and a gap in the green.

C. A heterocyclic base quaternary salt will react with ethyl-isothioacetanilide in the presence of acetic anhydride to produce a mercapto derivative identical with that obtained by method *B* above.(58)



Ethylisothioacetanilide

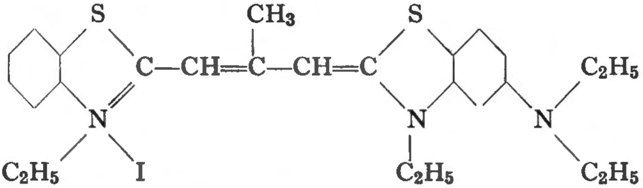
2-methylbenzthiazole (quaternary salt)

Ethylmercapto-acetylmethylene-benzthiazolidene (quaternary salt)

Heat 10 g methyl benzthiazole ethiodide and 7 g ethyl isothioacetanilide and 25 cc acetic anhydride for four hours. A brown viscous mass is produced which is extracted with ether. The residue is dissolved at 55°C in 12 cc alcohol. The mercapto derivative crystallizes on cooling.

The same method is used with the oxazole and selenazole bases.

The dyes are obtained by heating 2 g of the mercapto derivative with 3 g of the ethiodide of another heterocyclic base—2-methyl-5-diethyl aminobenzthiazole for example—10 cc pyridine and 2 cc piperidine for 2½ hours under reflux. By adding a solution of potassium iodide, the mesomethyl asymmetrical dye is precipitated. It is recrystallized from methanol. In the present example the dye is *3:3′-diethyl-9-methyl-5′-diethylaminothiacarbocyanine* whose sensitization and absorption maxima are at 620 and 585 mμ:



If the mercapto derivative alone is heated in pyridine containing piperidine, a symmetrical meso-substituted dye is formed, for example, 3:3′-diethyl-9-methylthiacarbocyanine.

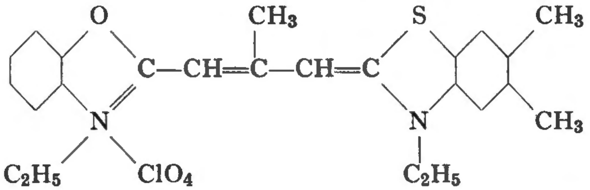
If the ethyl-isothioacetanilide is replaced by *ethyl-isothiopropianilide* a mesoethyl carbocyanine is obtained.

The dye can be precipitated with a 10% sodium perchlorate solution.

D. Another method using ethyl-isothioacetanilide has been disclosed. The anilide is heated with the diethylsulphate of the base to give a chain in which the mercapto group is eliminated and the anilide group retained:

$$[\text{Base}] \quad —CH{=}C(CH_3)—NH\,.\,C_6H_5.$$

This intermediate is then condensed with a molecule of the quaternary salt of another base in pyridine and isoquinoline to give the dye, which is precipitated with sodium perchlorate. The following green sensitizer which has been used in Agfacolor negative films is prepared in this way



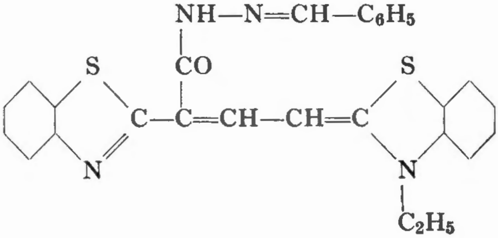
E. A *methylene base* (see para. 732a), treated with ethyl iodide and carbon disulphide is converted to a compound having an ethylmercapto meso-substituent (para. 755).

$$[\text{Base}]{=}\text{CH}_2 \longrightarrow [\text{Base}]{-}\text{CH}{=}\underset{\substack{|\\ \text{S}\,.\,\text{C}_2\text{H}_5}}{\text{C}}{-}\text{S}\,.\,\text{C}_2\text{H}_5$$

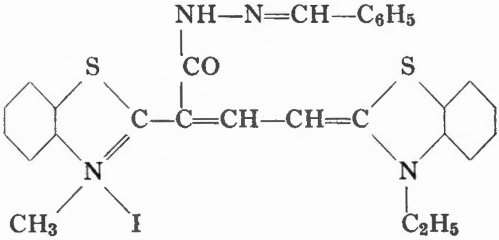
742. Carbocyanines with hydrazine chain substituents(59)

Ethyl-2-benzthiazolyl acetate [B]—CH_2—CO—O . C_2H_5 treated with hydrazine hydrate, forms benzthiazolyl acethydrazide [B]—CH_2—CO—NH—NH_2 which, with benzaldehyde C_6H_5CHO gives benzthiazolyl-hydrazone [B]—CH_2—CO—NH—N=CH—C_6H_5.

When a solution of 1·5 g of this hydrazone and 2·5 g of 2-β-anilidovinyl-benzthiazole ethiodide (see para. 696) in 70 cc alcohol, 0·75 cc triethylamine and 0·5 cc acetic anhydride is refluxed for 90 mins., and iced water is then added, a *dye-base* (formula (*a*) below) is formed. This can be crystallized from ether, and sensitizes chlorobromide emulsions to 605 mμ with a maximum at 560 mμ. If it is heated in a sealed tube with methyl iodide, it takes the structure (*b*) and sensitizes to 610 mμ with a maximum at 560 mμ. These two compounds show supersensitizing properties with carbocyanines and pseudocyanines.



(a)

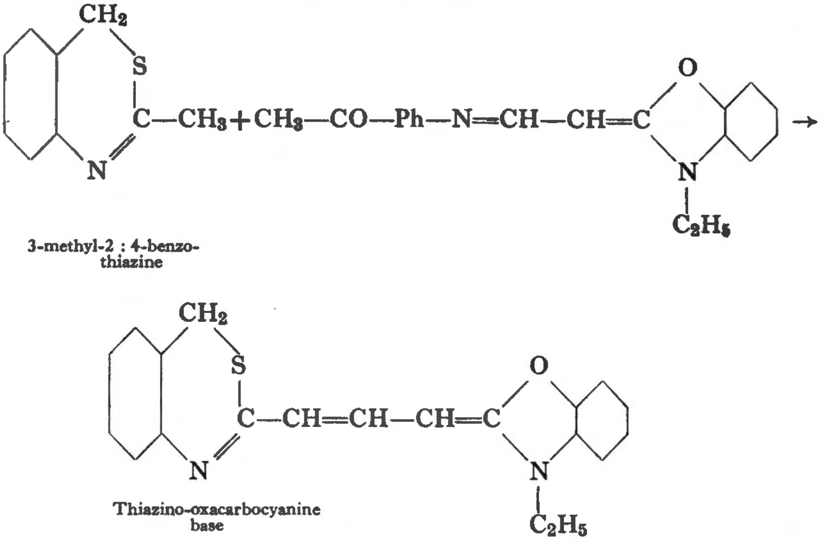


(b)

Cyanines and merocyanines, with hydrazine substituents, have also been obtained.

743. Carbocyanines derived from benzothiazines, perinaphthothiazines and thiodiazole

Beilenson and Hamer(60) obtained carbocyanines from *3-methyl-2:4-benzothiazine*. This is condensed with another thiazole, selenazole or oxazole base containing an aminovinyl substituent:



3-methyl-2 : 4-benzothiazine

Thiazino-oxacarbocyanine base

The resulting dye-base is a sensitizer, but is less powerful than the corresponding alkiodide. The sensitization maximum is displaced towards the blue compared with benzthiazole.

Among the other sulphur heterocyclic bases which can form cyanines, we would note *perinaphthothiazine*(61) and thiadiazole derivatives.(62)

Knott(63) has synthesized cyanines derived from *1:3-dithiocyclopentan-4-one*, *tetrahydroglyoxaline* and the 4- and 5- *thiazolidones*. The presence in the nuclei of a thio-ester bridge is considered favourable for the transmission of electrons between the auxochromic groups.

744. Oxadiazole carbocyanines

Asymmetrical carbocyanines containing a *5-phenyloxadiazole* nucleus are obtained by dissolving, for example, N-ethyl-2-methylthiazoline-ω-aldehyde in pyridine containing acetic acid, and adding with cooling and agitation, 2-methyl-5-phenyloxadiazole in small quantities. By adding methanol and a solution of sodium perchlorate and cooling, crystals are deposited. Absorption maximum at 455 mμ and sensitization maximum at 475 mμ.(64)

745. Acid cyanines

Acid cyanines have been suggested for the sensitization of photographic papers as they are more readily eliminated by washing. In practice this has been shown to be not completely correct. The acid cyanines are weaker sensitizers than the corresponding normal cyanines. They are produced by replacing the normally used alkyl halide with a halogenated fatty or aromatic acid derivative; for example, the heterocyclic base is condensed with β-chloropropionic acid, then converted to a carbocyanine.(65) In this case the acid radical is $—CH_2—CH_2—COOH$.

1. Hamer F. M.: *J.C.S.*, 1927, **130,** 2796.
2. Ogata T.: *Proc. Imp. Acad. Tokyo,* 1927, **3,** 334.
3. Calzavara E.: *IXth Cong. Int. Phot.*, Paris 1935.
4. Ogata T.: *Proc. Imp. Acad. Tokyo,* 1932, **119,** 22.
5. 6 : 7-methylenedioxide quinaldine is obtained from piperonal which is nitrated and condensed with acetone. The resulting lactylketone is then reduced with zinc and acetic acid.
6. Rosenhauer and Barlet: *Ber.*, 1929, **62,** 2724.
7. B.P. 418,749 (1934); Gevaert: F.P. 968,558 and Add. 59,382 (1949–1954).
8. G.P. 712,427.
9. Levkoev (and collaborators): *Zh. Obsh. Khimii,* 1954, 2034.
10. Levkoev and Portnaya: *Zh. Obsh. Khimii,* 1951, 2050.
11. Levkoev, Cheifetz and Barvyn: *Zh. Obsh. Khimii,* 1951, 1340.
12. Levkoev and Turitsyna: *Sci. et Ind. Phot.*, 1950, 327.
13. Koenig: *Ber.*, 1928, **61,** 2065.
14. Kiprianov and Yugupolski: *Zh. Obsh. Khimii,* 1952, 2209 and 2216.
15. Weisehahn G. A. and Gen. Aniline Corp.: F.P. 963,847.
16. Brooker L. G. S.: *J.A.C.S.*, 1936, 662; U.S.P. 1,942,854; B.P. 385,332.
17. See Brooker: U.S.P. 1,846,300 (1932) and 1,846,301 (1932); B.P. 359,463 and 400,951.
18. Clark L. M.: *J.C.S.*, 1928, **131,** 2313.
19. Brooker L. G. S.: B.P. 359,463 and 354,264 (1929).
20. White: U.S.P. 1,990,682; F.P. 742,962 (1933).
21. G.P. 709,873.
22. Hamer F. M.: *J.C.S.*, 1927, **130,** 2796.
23. F.P. 739,813 (1932).
24. Lal and Petrov: *J.C.S.*, 1948, 1895.
25. Van Dormael A.: *Sci. et Ind. Phot.*, 1949, 451.
26. Phillips: *J.C.S.*, 1928, 2393.
27. Riester: G.P. 733,026 (1937).
28. Kendall J. D.: *27th Cong. Int. Chem. Ind.*, Brussels 1954, No. 244.
29. Pilyugin: *Dokl. Ak. Nauk. S.S.S.R.*, 1952, 736.

29b. *Ber.*, 1954, 1019–1032.

30. Brooker and White: *J.A.C.S.*, 1935, **57,** 547.
31. Brooker L. G. S.: U.S.P. 1,846,302–3–4 (1932); F.P. 729,097–8–9 (1932).

31b. I.G.F.: F.P. 889,933.

32. Agfa: F.P. 774,410.

32b. *Ber.*, 1926, **59,** 2356.

33. Brooker and White: *J.A.C.S.*, 1935, 2480–2488.
34. Wuhrman: *Sci. et Ind. Phot.*, 1950, 441.
35. Brooker and White: *J.A.C.S.*, 1935, **57,** 549.
36. Hamer F. M.: *J.C.S.*, 1928, **131,** 3160.
37. Brooker L. G. S.: *J.A.C.S.*, 1936, **58,** 662.
38. Kodak: F.P. 1,086,275 (1954), U.S. priority, 1951.
39. White: U.S.P. 1,990,681 and B.P. 390,406 (1933); Brooker and White: *J.A.C.S.*, 1935, **57,** 574.
40. Brooker and White: *J.A.C.S.*, 1935, **57,** 2480.
41. White: U.S.P. 1,990,682 and F.P. 742,962 (1933).
42. U.S.P. 1,990,507 and F.P. 769,755 (1934).
43. Brooker and White: *J.A.C.S.*, 1935, **57,** 551.
44. Agfa: F.P. 767,694.
45. Ilford: B.P. 549,202; Gevaert: Belg., P. 443,674 and F.P. 912,715; Sveschnikov, Portnaya, Levkoev and Lifschitz: *Dokl. Ak. Nauk. S.S.S.R.*, 1952, 733.

45b. Schultz: F.P. 803,088.

45c. Kodak: F.P. 1,112,837 (1955), U.S. prior., 4/10/52.

46. Kodak: F.P. 864,570.
47. Agfa: F.P. 767,694.
48. Van Dormael.
49. F.P. 889,933; Preparation: G.P. Application 153,532, IVd/22e.
49b. Kodak: F.P. 1,034,559 (1949–1953), U.S. priority 1948.
49c. Nitzche, Busch, Witzel and Gansau: *Chem. Ber.*, 1952, 487.
49d. Van Dormael A. and Nys J.: *Bull. Soc. Chim. Belge*, 1948, **57**, 547–554.
50. B.P. 344,409 and 454,808.
51. Agfa: F.P. 768,047.
52. Hishiki Y.: *Rev. Sci. Res. Inst. Tokyo*, 1952, 250.
53. F.P. 1,078,791 (1954), Ger. priority 1952.
54. Keyes and Kodak: F.P. 808,598 (1936), U.S. priority 1935.
55. Van Dormael A. and Ghys T.: *Bull. Soc. Chim. Belge.*, 1948, 24–31.
56. Keyes and Kodak: F.P. 892,216 (1944), Brit. priority 1939.
57. Gevaert: B.P. 675,656 (1948).
58. Agfa: F.P. 749,334 (1933).
59. Gevaert: F.P. 970,548 (1950).
60. *J.C.S.*, 1942, 98.
61. Hamer F. M. and Rathbone J. H.: *J.C.S.*, 1943, 2187.
62. Du Pont: B.P. 513,471.
63. Knott E. B.: *J.C.S.*, 1955, 949–954.
64. Agfa: F.P. 869,728 and 869,764.
65. Agfa: F.P. 851,348 (1939); Gevaert: F.P. 895,151 (1944).

Chapter XXXIX

HEMICYANINES

PINAFLAVOLS

746. Constitution of the pinaflavols

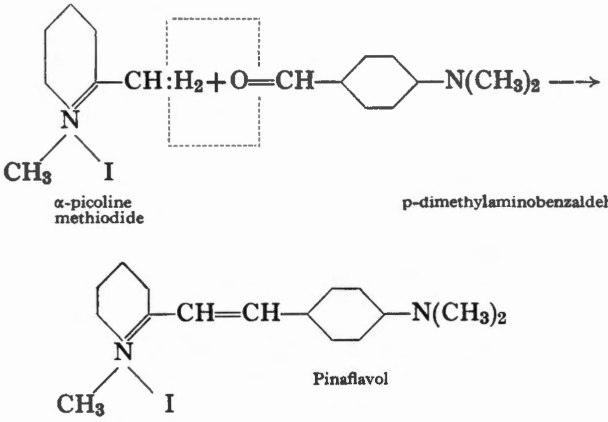
The pinaflavols or *styrylcyanines* contain a nitrogenous nucleus and a benzene nucleus (generally dimethylaniline $C_6H_5N(CH_3)_2$, linked by one or more vinyl groups —CH=CH—

$$\left[\begin{array}{c}\text{Heterocyclic nucleus with}\\ \text{pentavalent nitrogen}\end{array}\right]—(CH{=}CH)_n—C_6H_4—NR_2$$

In the simplest members n = 1.

The benzene nucleus can be considered as a derivative of *styrene* $CH_2{=}CH—C_6H_5$ having the very active auxochrome group in the para position.

The pinaflavols, discovered by Koenig, are formed by condensing a quaternary salt of a *nitrogenous heterocyclic base* (pyridine, quinoline, benzthiozole, etc.) containing a *reactive methyl group* with *p-dimethylaminobenzaldehyde* (para. 703) in the presence of alkali or piperidine in alcoholic solution:



α-picoline methiodide

p-dimethylaminobenzaldehyde

Pinaflavol

The activity of the methyl group of the nitrogenous base increases when the latter is quaternized (alkiodide) in the same way as in cyanine preparation.

The *pinaflavols* have interesting sensitizing properties. Their absorption bands are simple and broad whereas those of the cyanines are double and sharp.

747. Preparation of the pinaflavols

1-methyl-2-p-dimethylaminostyryl pyridine (true *Pinaflavol*) is the simplest of the series. It was prepared by Mills and Pope in the following way:⁽¹⁾

20 g α-picoline methiodide is dissolved in 270 cc of alcohol together with

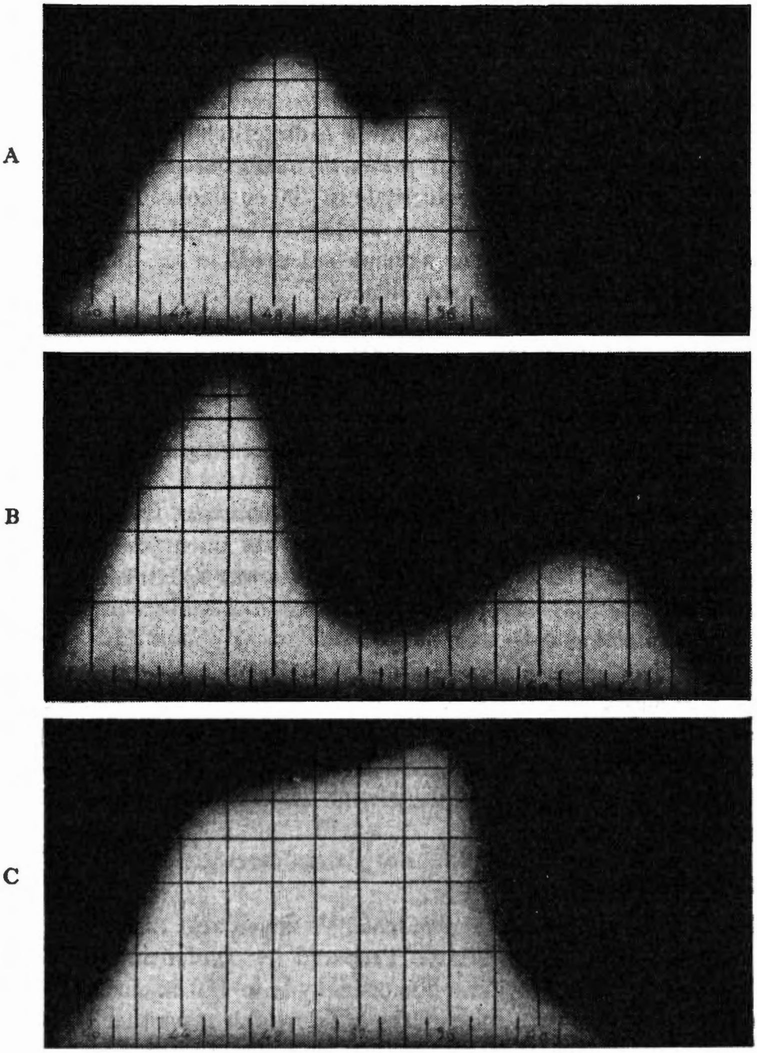


FIG. 130. Sensitization by hemicyanines.

(A) Pinaflavol;
(B) 1-methyl-5:6-benzo-2-p-dimethylaminostyryl quinoline;
(C) 3:5-dimethyl-4-phenyl-2-p-dimethylaminostyryl benzthiazole.

12·7 g p-dimethylaminobenzaldehyde and 3·5 cc piperidine, and the mixture is refluxed for 5 hours. The orange-red solution is cooled, when a solid is deposited. This is recrystallized from methanol as bright red prisms. M. Pt. 275°C.

Absorption is in the blue and green with a badly defined maximum at 475 mμ. Sensitizes to 570 mμ, decreasing to 620 mμ. Maximum at 550 mμ (Fig. 130). The diethyl derivative sensitizes to 650 mμ with a maximum at 560 mμ.

The *α-picoline* used in this preparation is obtained by transformation of pyridine methiodide at 300°C using Ladenburg's method.(2) Heated with methyl iodide, it gives α-picoline methiodide which crystallizes in yellow needles. M. Pt. 224°C.

1-ethyl-6-dimethylamino-2-p-dimethylamino styryl quinoline (Lumière's *Pantochrome*) is a quinoline pinaflavol with a 6-dimethylamino substituent, it is prepared by refluxing 34·2 g of *p-dimethylaminoquinaldine ethiodide* with 14·9 g of p-dimethylaminobenzaldehyde in 200 cc alcohol with 4·2 g piperidine. After boiling for 3 hours and cooling, a solid is deposited which is filtered off, washed with a little alcohol and dried in air. It is successively recrystallized from acetic acid and alcohol.(3)

Absorption: 2 bands, one from 490 to 580 mμ, the other from 660 mμ to the end of the spectrum; the first belongs to the styryl cyanine, the second to another cyanine. The sensitization is relatively uniform from 520 to 630 mμ, and then drops gradually to 700 mμ.

Similar compounds without the heterocyclic amino substituent are weak sensitizers.

1-methyl-5:6-benzo-2-p-dimethylaminostyryl quinoline. This compound is obtained from α-naphthoquinaldine and has its maximum absorption at 525 mμ. It sensitizes to 690 mμ with a maximum at 620 mμ (Fig. 130).

With *2-methylacenaphthopyridine* a heavier dye, effective to 710 mμ is formed, but its action is weaker.

The *lepidines* condense with p-dimethylamino-benzaldehyde to give the 4-styryl quinolines which are weak sensitizers. *2:4-dimethylquinoline* combines with 2 molecules of p-dimethylaminobenzaldehyde to produce a double styrylcyanine.(4) Its sensitizing action is very weak (to 700 mμ). We would finally note the existence of o-dimethylamino-styryl derivatives which are not sensitizers.

748. Thiazole styryl cyanines

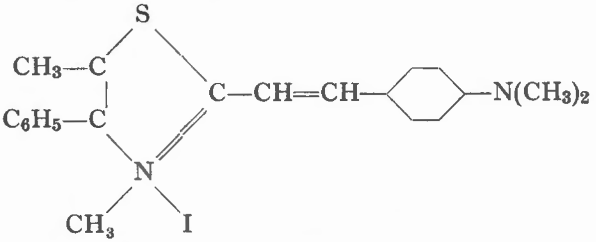
3-methyl-2-p-dimethylaminostyrylthiazole.(5) Sensitizes to 580 mμ in the green with a maximum at 530 mμ. Prepared by condensing 8 g 2-methylthiazole with 5 g p-dimethylaminobenzaldehyde in 120 cc alcohol and 1·2 cc piperidine. After 4 hours' boiling, the solid which separates on cooling is washed with water and ether, and then recrystallized from methanol.

The 3-ethyl derivative is similarly obtained. It sensitizes in the green.(6)

3:4-dimethyl-2-p-dimethylaminostyrylthiazole is prepared from 2:4-dimethylthiazole and sensitizes to 595 mμ with a maximum at 550 mμ.

3-methyl-4-phenyl-2-p-dimethylaminostyrylthiazole sensitizes to 620 mμ with a maximum at 550 mμ. The starting base is 4-phenyl-2-methylthiazole (para. 676 and 688).

3:5-dimethyl-4-phenyl-2-p-dimethylaminostyrylthiazole is prepared by heating 15·6 g 2:5-dimethyl-4-phenylthiazole methiodide with 7·1 g p-dimethylaminobenzaldehyde and 1·7 cc pyridine in 150 cc alcohol, for one hour. The base is obtained by gently heating an equimolecular mixture of ω-bromopropiophenone and thioacetamide.(7) Sensitizes to 640 mμ, almost uniform to 580 mμ with a maximum at 555 mμ (Fig. 130).



3:5-dimethyl-4-phenyl-2-p-dimethyl aminostyrylthiazole

3-methyl-4-β-naphthyl-2-p-dimethylaminostyrylthiazole. The sensitizing action of this dye extends to 630 mμ, with a maximum at 580 mμ. It is prepared from 2-methyl-4-β-naphthylthiazole, which is obtained from bromo-β-naphthylmethylketone and thioacetamide.(8)

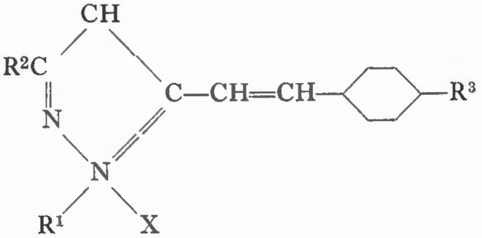
3-methyl-2-p-dimethylaminostyrylbenzthiazole. This is the first member of the *benzthiazole* styryl cyanines. It is prepared by the general method and sensitizes to 670 mμ with a maximum at 570 mμ. The absorption maximum is at about 525 mμ.

3-ethyl-4:5-benzo-2-p-dimethylaminostyrylbenzthiazole is a derivative of 2-methyl-β-naphthothiazole. Sensitizes more in the red to 690 mμ with a maximum at 615 mμ. The 6:7-benzoderivative (from methyl-α-naphthothiazole) is a weak sensitizer.

The styrylcyanines from *benzoxazole* and *indoline* are dyes which have mediocre sensitizing properties.

We would finally note the existence of styryl derivatives of benziminazole such as 1:3-dimethyl-p-dimethylaminostyrylbenziminazole which sensitizes to 580 mμ with a maximum at 520 mμ.

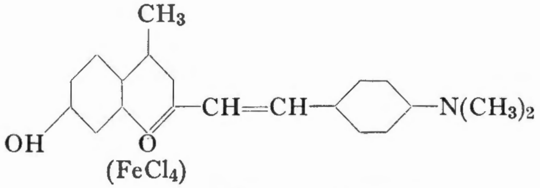
Yellow or orange sensitizers having the following structure have been disclosed by C.I.B.A.(9)



Finally, *chain-substituted hemicyanines* can be prepared, according to Picus and Spoerri,(10) by condensing a quaternary salt of a heterocyclic base having a reactive methyl group with a *monoketone* such as p-dimethylaminobenzalacetone.

749. Styryl derivatives of oxygen heterocyclic nuclei

Of the large number of styryl compounds of this type, only 4-methyl-7-hydroxy-2-p-dimethyl-aminobenzopyrylium (ferric chloride)(11) has any photographic activity. Its action extends to 640 mμ.

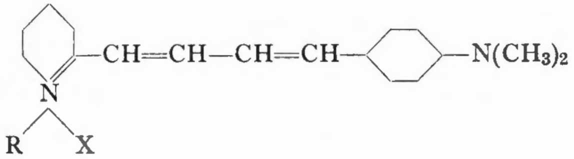


4-methyl-7-hydroxy-2-p-dimethylamino benzopyrylium

Another compound, derived from *xanthene*, *3:6-dihydroxy-9-dimethylaminostyrylxanthylium*, shows a slight increase in sensitivity.(12)

750. Styrylvinyl cyanines

These are analogous to the pinaflavols in whose formula n = 2, that is, they have the chain —CH=CH—CH=CH— instead of —CH=CH—



Pyridine styrylvinylcyanine

The *styrylcyanines* are produced when *dimethylaminocinnamaldehyde*(13) $(CH_3)_2N—C_6H_4—CH=CH—CHO$ is condensed with a *nitrogenous heterocyclic base*, picoline, quinaldine or benzthiazole ethiodides for example. Equimolecular quantities of the two constituents are heated for several hours in alcohol in the presence of a small amount of pyridine or piperidine. The reaction can also be carried out in acetic anhydride.

These sensitizers are weak. The best is the pyridine derivative which acts up to 640 mμ with a maximum at 560 mμ.

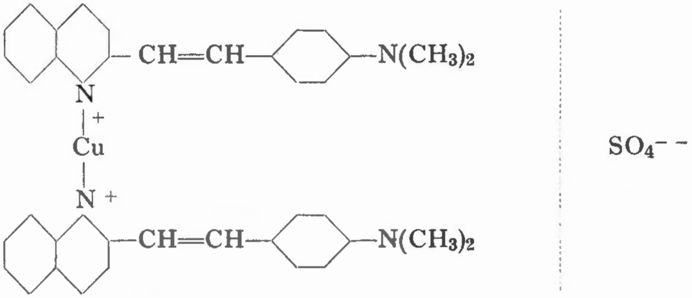
König, Schrameck and Rosch synthesized polyvinyl aldehydes with very long chains—*trivinylene-p-dimethylaminobenzaldehyde* $(CH_3)_2N\ .\ C_6H_4—$ $—CH=CH—CH=CH—CH=CH—CHO$ and *pentavinylene-p-dimethylaminobenzaldehyde* $(CH_3)_2N—C_6H_4—CH=CH—CH=CH—CH=CH—$ CHO.

In this case the displacement of the absorption maximum towards the red as the chain increases is very clear. If the aldehyde chain is shown by —(CH=CH—)$_n$—CHO it is seen that

n	Absorption maximum	Displacement
0	340 mμ	—
1	390 ,,	50 mμ
3	440 ,,	50 ,,
5	470 ,,	30 ,,

751. Double hemicyanines

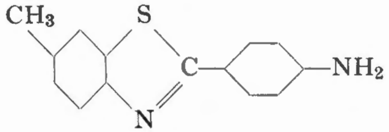
Jennen(14) obtained double hemicyanines by introducing a metallic atom as a link between two heterocyclic nuclei, for example:



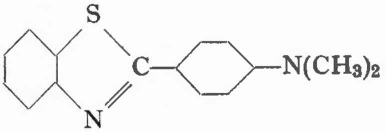
This pink dye is obtained by heating 1·3 g of 2-p-dimethylaminostyrylquinoline in 200 cc methanol with 5 cc 2N . $CuSO_4$ on the waterbath for 30 mins. The precipitate which forms on cooling in ice is filtered and recrystallized from methanol. $CuSO_4$ can be replaced by $AgNO_3$.

751b. Thioflavines

If, in the general hemicyanine formula, the chain is absent (n = 0), dyes are obtained in which the heterocyclic and benzene nuclei are directly joined via the α-position to the nitrogen. The thioflavines can be considered as hemicyanines of this type, whose nuclei are a benzthiazole nucleus and an amine such as dimethylaniline. Two thioflavine molecules can be linked by an azo group —N=N— to give another series of more complex dyes of which *thiazole yellow* is the best known. The starting point of these dyes is *dehydrothio-p-toluidine*.



Dehydro-p-toluidine



Thioflavine T

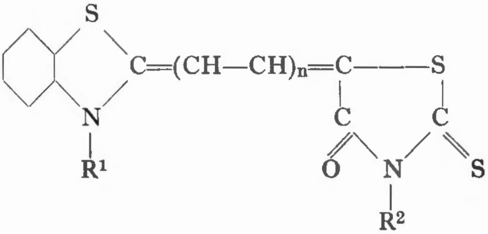
The thioflavine dyes have been disclosed for increasing the general sensitivity of under-ripened emulsions. They have a certain sensitizing action in the blue-green. Kögel disclosed them as non-fogging ripening accelerators.

MEROCYANINES

752. Structure of the merocyanines

Ketomethylene heterocyclic compounds (see paras. 697–699) such as *rhodanine*, *thiohydantoin*, *pyrazolone* and *oxazoledione* contain a reactive methylene group $>CH_2$ adjacent to a keto group $>C{=}O$. They readily condense with quaternary salts of heterocyclic bases having a reactive group or chain to give the merocyanines.

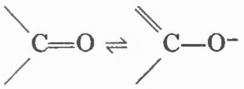
The merocyanines, therefore, have a heterocyclic nucleus with trivalent nitrogen and a ketomethylene nucleus linked directly or via a chain with an even number of carbon atoms $(=CH-CH)_n=$



Example of a merocyanine (n—0, 1, 2, 3, ...)
Benzthiazole nucleus + rhodanine nucleus.

In the styrylcyanines, the chain is $(-CH=CH)_n-$, whilst in the ordinary cyanines it has an odd number of carbon atoms: $-CH(=CH-CH)_n=$.

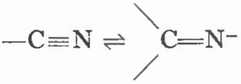
As we have already seen (para. 671) the merocyanines are internally ionized dyes. The second charge carrier is the group $>CO$:



$$>C{=}O \rightleftharpoons >C{-}O^-$$

It is this CO group which activates the CH_2 group, and non-cyclic compounds can be used for this, such as malonic ester $R-O-CO-CH_2-CO-O-R$.

The properties of the keto group are also found in the nitrile group, whose derivatives also produce merocyanines



$$-C{\equiv}N \rightleftharpoons >C{=}N^-$$

The merocyanines were prepared and disclosed as photographic sensitizers independently by Kendall and Brooker. In general, the simple ones are mediocre sensitizers, but they have considerable interest as they can be condensed with a second molecule of the heterocyclic base to give complex merocyanines which have remarkable red sensitizing properties.

The most widely used ketomethylene nuclei are *rhodanine*, *thiohydantoin*⁽¹⁵⁾ and *pyrazolone*, but in the same way the following can be used: *isomers* of *rhodanine*;⁽¹⁶⁾ thiohydantoin (paras. 697 and 698); and in general the various thiazole (or oxazole) ketones—the *thiazole-5-ones*⁽¹⁷⁾ substituted in the 2-position with alkyl or alkoxy radicals (which are obtained by cyclizing thiocarboxyglycine esters) or amino or alkylamino radicals; *2-thioselenazolidone-4-* and *2-selenoselenazolidone-4* (obtained by reacting selenoglycolic acid with ethyl isothiocyanate or isoselenocyanate).⁽¹⁷ᵇ⁾

Other merocyanines have been prepared using nuclei of *barbituric acid*, *3:5-dioxopyrazolidine*,⁽¹⁸⁾ *indandione-1-3*.⁽¹⁹⁾ The latter are notable for the extent of the displacement of the electron from the nitrogen atom through the methylene chain.

The solubilities of the dyes can be increased by the inclusion of a *carboxylic* or *sulphonic* group in the ketomethylene nucleus. The *diacetylamino derivatives* have been recommended as being at the same time the most soluble and the most effective.⁽²⁰⁾

The heterocyclic nucleus is usually benzthiazole, benzselenazole, benzoxazole or other base of the same type. The nucleus can contain a chlorophenyl group.⁽²¹⁾

For pyrimidazole merocyanines, see footnote ⁽²²⁾.

753. Merocyanines with no methine chain

Merocyanines in which the cyclammonium and ketomethylene nuclei are linked directly, can be prepared in three simple ways.

A. Condensation of two molecules of the alkiodide of the heterocyclic base (without a reactive methyl group) with one molecule of the ketomethylene compound in the presence of two molecules caustic potash in absolute ethanol.

B. Condensation of the ethiodide of 2-iodoquinoline (para. 694) or 2-iodobenzthiazole with a ketomethylene compound in the presence of triethylamine in absolute alcohol.

C. Condensation of one molecule of the 2-alkyl mercaptan of the cyclammonium base (paras. 693–695) with one molecule of the ketomethylene compound in the presence of one molecule of triethylamine in absolute alcohol. Examples:

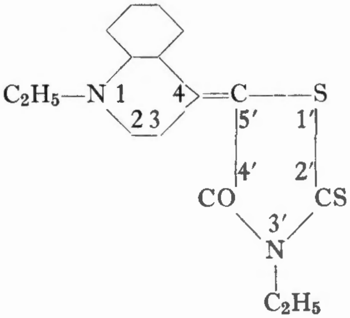
1:3′-diethyl-4-quino-5′-rhodanine. Reflux 5·7 g *quinoline ethiodide* (para. 675), 1·61 g *3-ethyl rhodanine* (para. 699) and 1·64 g caustic potash in 50 cc absolute alcohol for 10 mins. Recrystallize from acetic acid (45 cc per g). Yield, 60% of crude dye and 47% after recrystallizing. Sensitizes to 605 mμ with maximum at 530 mμ (formula (*a*)).⁽²³⁾

1-ethyl-3′-phenyl-2-quino-5′-rhodanine. Reflux 8·2 g *2-iodoquinoline ethio-*

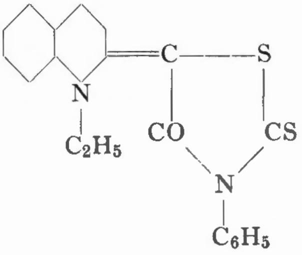
dide (para. 694) with 4·2 g *3-phenyl rhodanine* and 4·25 g triethylamine in 30 cc absolute alcohol for 15 mins. The dye which separates is filtered and recrystallized from acetic acid or methanol (formula (*b*)). Mediocre sensitizer to 580 mμ. The rhodanine can be replaced by 3·4 g barbituric acid (formula (*c*)).

3-ethyl-1′:3′-diphenyl-2-benzthiazolidene-5-(2)thiohydantoin.(23) Reflux 1·1 g *2-methylmercaptobenzthiazole ethiodide* with 0·9 g *1:3-diphenyl-2-thiohydantoin* (para. 698) and 0·35 g triethylamine in 15 cc absolute alcohol for 15 mins. The dye which separates on cooling (yield, 77 %) is recrystallized from acetic acid (35 cc per g). Final yield, 40 % (formula (*d*)).

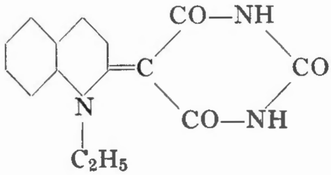
3-methyl-2-benzthiazolidene-indene.(24) Obtained as in the previous example using *2-methyl-mercaptobenzthiazole methyl-p-toluene-sulphonate* and *indene* (formula (*e*)).



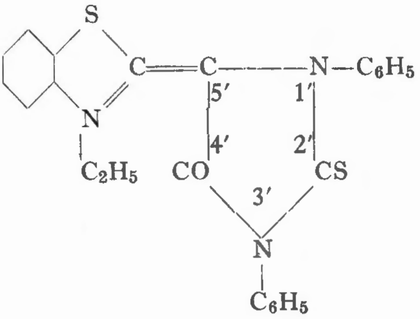
(*a*)



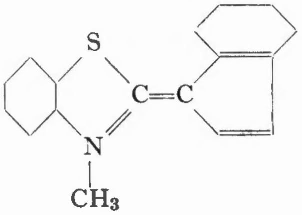
(*b*)



(*c*)



(*d*



(*e*)

753b. Neutrocyanines

They are merocyanine *bases*, produced when a methylmercaptobenzthiazol (for example) not quaternized, reacts with a rhodanine. The thiazole ring has a —NH— group. Slightly soluble, this compound sensitizes chlorobromide emulsions to blue 480 mμ. Other neutrocyanines can have a methine chain⁽²⁴ᵇ⁾ and bridged chain substituents.⁽²⁴ᶜ⁾

754. Dimethine merocyanines: synthesis with diphenylformamidine

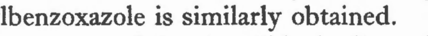
The dimethine merocyanines have a $=CH—CH=$ chain in which one link is provided by the reactive methyl group of a cyclammonium base and the other by an external agent such as *diphenylformamidine* $C_6H_5—N{=}CH——NH—C_6H_5$.

The use of diphenylformamidine for the synthesis of the polymethine chains of the carbocyanines is well known: we have already seen this in paras. 696, 725, 732 and 739. It has been applied to all other sensitizing dyes.(25) The quaternary salt of a nitrogenous heterocyclic base with a reactive methyl group will condense readily with diphenylformamidine to give a *β-anilidovinyl* compound.

$$RN^+[\text{Base}]—CH{=}CH—NH—C_6H_5 \mathrel{\vdots} X^-$$

The β-anilidovinyl compound will in turn condense with a ketomethylene compound in *acetic anhydride* in the presence of *triethylamine* to give a dimethine merocyanine with a shift in the double bond

$$—CH{=}CH— \rightarrow {=}CH—CH{=} \rightarrow$$



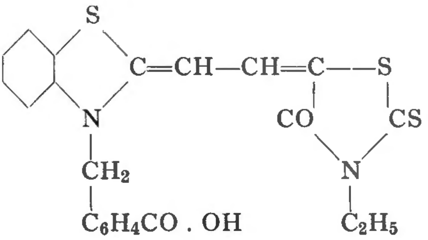
$$\rightarrow RN\,[\text{Base}]{=}CH—CH{=}\underset{|}{C}—\underset{|}{C}{=}O$$

Examples:(26) 12 g 2-methylbenzthiazole-p-carboxybenzylbromide (or the equivalent weight of another quaternary salt) is heated to 135°C for 20 mins. with 10 g diphenylformamidine. The cooled mass is washed with ether and recrystallized from alcohol. It is the salt of *β-anilidovinylbenzthiazole*. The salt of β-anilidovinylbenzoxazole is similarly obtained.

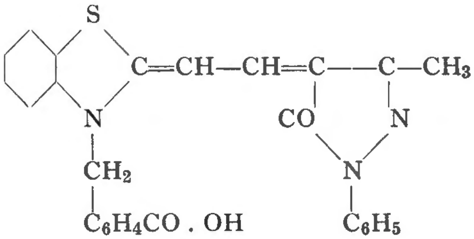
To prepare a merocyanine, 2·4 g β-anilidovinylbenzthiazole (p-carboxybenzylbromide in this example) is heated in 15 cc pyridine and 5 cc acetic anhydride with 1·2 g *3-ethylrhodanine*. The dye is precipitated by adding iced water, and is recrystallized from alcohol. Absorption maximum at 534 mμ, sensitization maximum at 605 mμ (formula (*a*)).

With 1·7g of 1-phenyl-3-methyl-pyrazol-5-one and 15 cc pyridine a dye of formula (*b*) is obtained, whose absorption maximum is at 495 mμ, and sensitizing limit at 580 mμ. It has been disclosed as a supersensitizer.

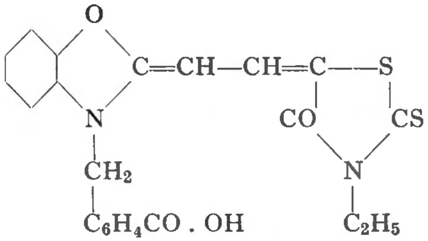
The condensation product of 2·25 g *β-anilidovinylbenzoxazole* p-carboxybenzylbromide with 0·8 g 3-ethylrhodanine heated for 30 mins. in 15 cc acetic anhydride and 1·1 cc triethylamine is a dye which after recrystallizing from alcohol has an absorption maximum at 494 mμ and a sensitizing maximum at 570 mμ (formula (*c*)).



(*a*)



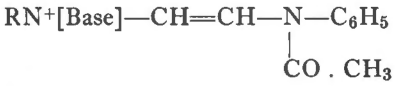
(*b*)



(*c*)

Dimethine merocyanines

If the quaternary salt of the base and the diphenylformamidine are reacted in *acetic anhydride*, the product, as we have already seen (para. 696) is a quaternary salt of the *2-ω-acetanilidovinyl* base



$$RN^{+}[\text{Base}]\text{—CH=CH—}\underset{\displaystyle \text{CO . CH}_3}{\text{N}}\text{—C}_6\text{H}_5$$

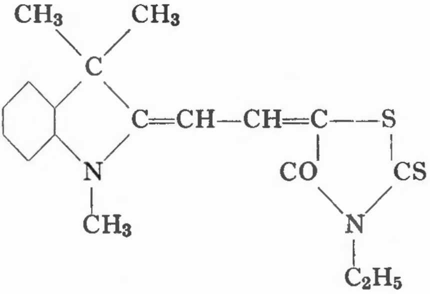
The acetanilidovinyl derivatives are very reactive and they condense readily with ketomethylene compounds to give merocyanines. This condensation takes place in pyridine⁽27⁾ or absolute ethanol or methanol in the presence of triethylamine⁽28,29⁾ or in acetic anhydride in the presence of sodium acetate.⁽28⁾

Merocyanines with an anil chain substituent have been obtained.⁽30⁾

A. Condensation in pyridine

Benzthiazole-ethylrhodanine dimethine merocyanine: Reflux 0·5 g 3-ethylrhodanine and 1·4 g 2-ω-acetanilidovinyl benzthiazole ethiodide (para. 696) in 15 cc pure anhydrous pyridine for 15 mins. Cool and leave in a cold place for 36 hours. Filter and wash the crystals successively with 5 cc pyridine, 5 cc ethanol, 40 cc water, 10 cc ethanol and 20 cc ether. 0·56 g (52%) of dye is obtained.

Trimethylindoline-ethylrhodanine dimethine merocyanine. Reflux 0·55 g 3-ethylrhodanine and 1·56 g 2-ω-acetanilidovinyl-1:3:3-trimethylindoline in 17·5 g pure anhydrous pyridine for 15 mins. Precipitate the dye with 100 cc water. Filter and wash with water, alcohol and ether. Yield, 0·57 g (49%).



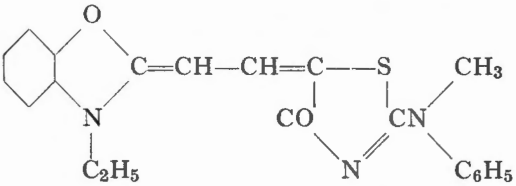
Trimethylindoline-ethylrhodanine dimethine merocyanine.

B. Condensation in absolute alcohol in the presence of triethylamine.

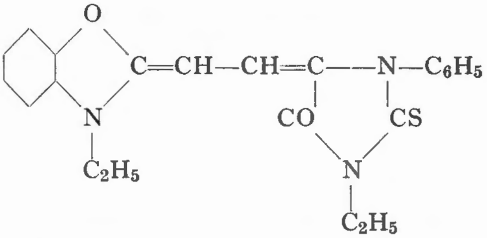
Benzoxazole-methylphenylisothiohydantoin dimethine merocyanine. 4·34 g *2-ω-acetanilidovinylbenzoxazole* ethiodide and 7·06 g *methylphenylisothiohydantoin* (para. 698) are refluxed for 10 mins. in 25 cc absolute ethanol and 1·5 cc triethylamine (1 mol). After recrystallizing from methanol the yield drops from 20% to 16%. Sensitizes silver chloride to 550 mμ with a maximum at 500 mμ.

Benzoxazole-3-ethyl-1-phenyl-2-thiohydantoin dimethine merocyanine (or 3:3′-diethyl-1′-phenyl-benzoxazolidene (ethylidene-2′-thiohydantoin). Reflux 2·2 g *3-ethyl-1-phenyl-2-thiohydantoin* para. 698), 4·3 g *2-ω-acetanilidovinylbenzoxazole* ethiodide and 1·06 g triethylamine in 35 cc absolute alcohol for 15 mins. Recrystallize from acetic acid (25 cc per g). Strong sensitizer for silver chloride to 580 mμ with maximum at 530 mμ.

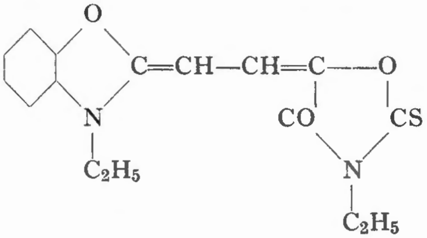
Benzoxazole-3-ethyl-2-thio-2:4-(3:5)-oxazoledione dimethine merocyanine. Reflux 0·7 g *3-ethyl-2-thio-2:4-(3:5)-oxazoledione* (para. 692), 2·2 g *2-ω-acetanilidovinylbenzoxazole* ethiodide and 1·06 g triethylamine in 20 cc absolute ethanol for 15 mins. Yield, 56%, which drops to 25% after twice recrystallizing from acetic acid (50 cc per g). Sensitizes silver chloride strongly to 590 mμ with a maximum at 530 mμ.



Benzoxazole-methylphenylisothiohydantoin merocyanine.



Benzoxazole-ethylphenylthiohydantoin merocyanine.



Benzoxazole-oxazoledione merocyanine

C. Condensation in acetic anhydride.

Benzoxazole-hydantoin dimethine merocyanine. Reflux 1 g *hydantoin*, 4·3 g *2-ω-acetanilidovinyl benzoxazole ethiodide* and 0·9 g sodium acetate in 50 cc acetic anhydride for 5 mins. Poor yield of 22% which drops to 4% after recrystallizing 4 times from methanol. Sensitizing maximum at 460 mμ.

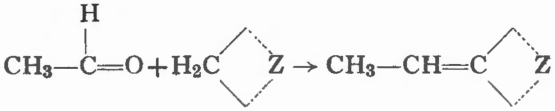
Notes.

In all the above preparations, the ethiodide of the base can be replaced by the *ethyl-p-toluene-sulphonate.*

Alternatively, the previous combination with the formamidine can be carried out with the ketomethylene compound: for example, 3·9 g diphenylformamidine is refluxed with 2·66 g rhodanine in 25 cc acetic anhydride for 20 mins. Condensation with a quaternary salt of a reactive methyl cyclammonium base is then carried out (see also (30b)).

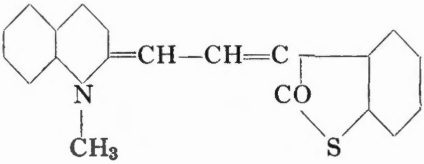
755. Dimethine merocyanines: syntheses via aldehydes, ketones and orthoesters

A. A ketomethylene compound like rhodanine will condense with *aldehydes* or *ketones* to give ethylidene chain ketomethylene compounds. According to an Ilford patent,(30c) the chain is introduced normally into the 5-position; for example, with acetaldehyde we have:



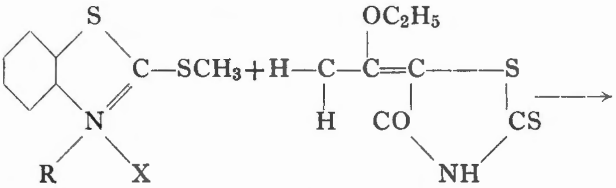
The ketomethylene compound, with an ethylidene chain thus formed, will condense with the *methylmercapto* cyclammonium quaternary salts in *pyridine* at the boil, to give dimethine merocyanines.

Using a similar reaction, Glauert and Mann(30d) synthesized merocyanines from *thioindoxyl-3-aldehyde* by heating with the ethiodide of a 2-methyl cylammonium base in the presence of piperidine in alcohol. Good sensitizers in the 550–700 mμ range were obtained depending on the base used: pyridine, quinoline, indoline, benzthiazole, etc., for example:



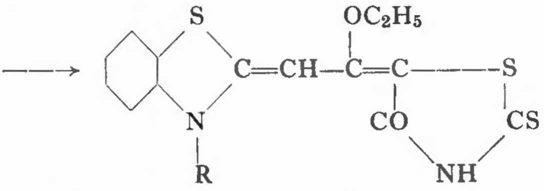
Knott has disclosed, however,(31) that rhodanines condensed with acetaldehyde, crotonaldehyde, pyruvic acid, etc., are more prone to produce the *4-alkylidene* derivatives.

B. The same writer(32) has shown that by the action of an *orthoester* such as ethyl orthoacetate, on a ketomethylene compound, a *5-alkoxyethylidene* derivative is obtained. Thus with rhodanine, 5-ethoxyethylidene rhodanine is produced, and this will condense with the 2-methylmercapto derivative of the quaternary salt of a heterocyclic base such as benzthiazole. The merocyanine produced has an ethoxy substituted chain.



2-methylmercapto-benzthiazole quaternary salt)

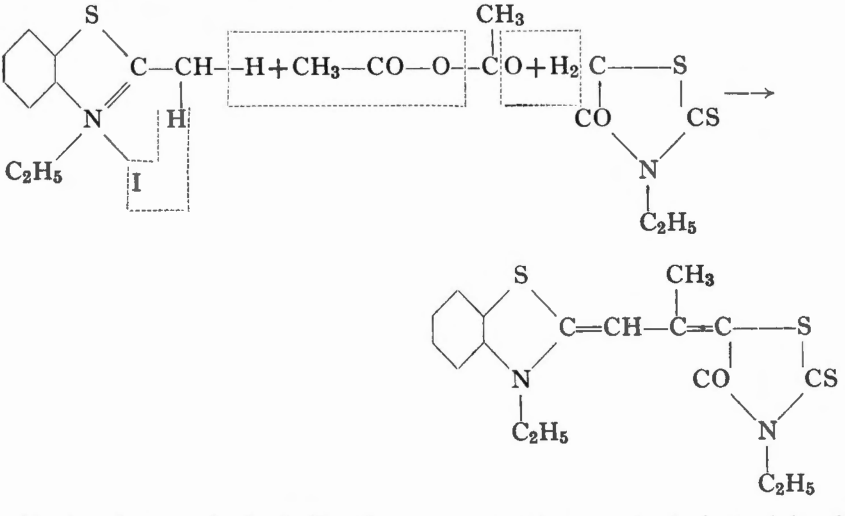
5-ethoxyethylidene rhodanine



Benzoxazole-rhodanine dimethine merocyanine with ethoxy substituent

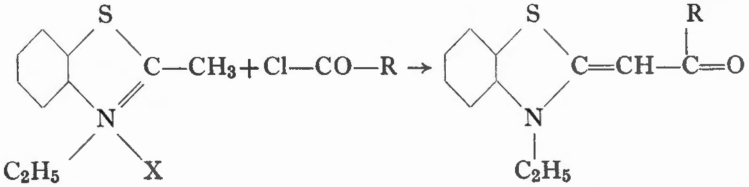
5-alkoxyethylidene rhodanine, treated with ammonia or an amine results in a *5-aminoethylidene rhodanine* which can also be used for the preparation of merocyanines.

C. According to another Ilford patent,⁽³³⁾ an alkyl substituted dimethine cyanine can be prepared by heating the methyl-p-toluene-sulphonate of a heterocyclic nitrogenous base with a cyclic ketomethylene compound in *acetic anhydride*. For example: 7·5 g 2-methylbenzthiazole is heated for 2½ hours at 140–150°C with 9·4 g methyl-p-toluene-sulphonate, and the resulting quaternary salt is refluxed for 25 mins. with 8 g 3-ethylrhodanine and 8 cc acetic anhydride in 45 cc pyridine. The solution is then poured into 20 cc ethanol and the precipitated dye is washed on the filter with alcohol. M. Pt. 234°C. Sensitization to 630 mμ with a maximum at 560 mμ. With benzoxazole the reaction mixture is poured into 100 cc water, when an oil separates. This is treated with methanol to precipitate the dye, which is washed with alcohol and ether before recrystallizing.



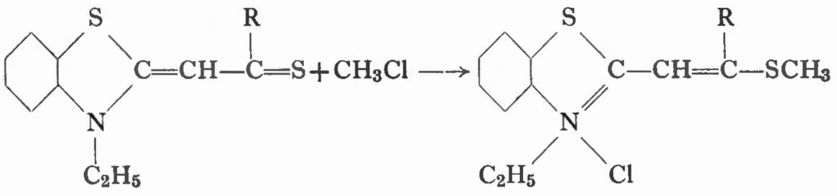
D. Another method of dimethine merocyanine synthesis is to join the chain to the cyclammonium nucleus before condensing with the ketomethylene compound.

We have already seen, in connection with the asymmetrical chain substituted carbocyanines (para. 740) that by reacting an acid chloride with a μ-methyl cyclammonium salt, an ω-ketone is formed.



2-acylmethylene-3-ethyl benzthiazolidene.

An ω-ketone, treated with ***phosphorus pentasulphide*** P_2S_5, is converted to a thioketone, which will react with ***methyl chloride*** CH_3Cl to give the corresponding alkyl mercapto derivative, with a displacement of the double bonds:

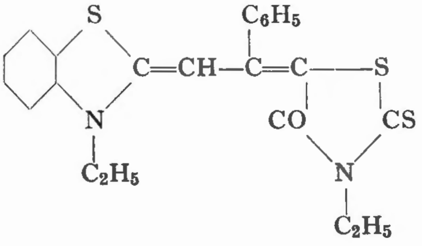


Thioketone

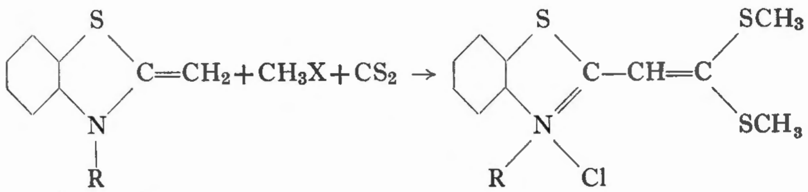
Methylmercapto derivative

The same compound is produced when the heterocyclic ω-ketone is reacted with methylmercaptan (see para. 741b).

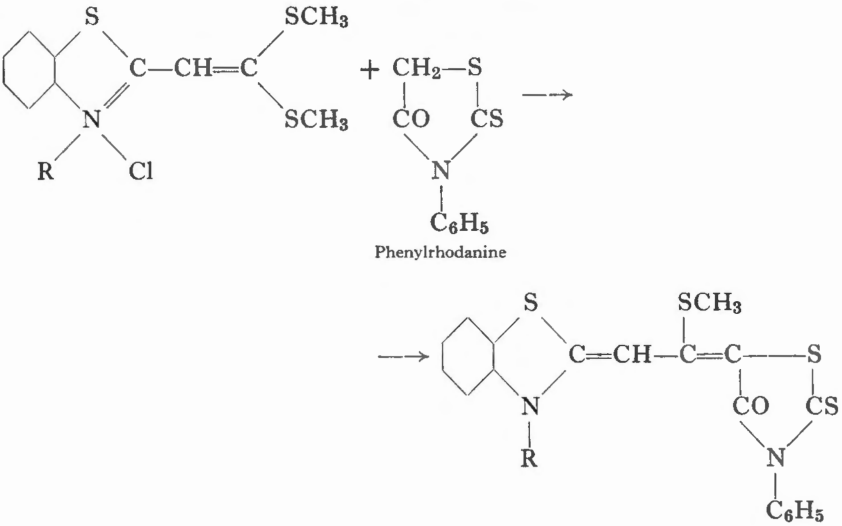
We know that an alkylmercapto derivative reacts readily with compounds containing a reactive methyl or methylene group, as in the cyclic ketomethylene compounds. This method can be used to synthesize ***merocyanines with a substituted dimethine chain.*** For example, starting with benzthiazole, benzoyl chloride $C_6H_5CO . Cl$ and ethylrhodanine, a phenyl substituted merocyanine is obtained which is used in the preparation of complex merocyanines.



If a ***methylene base*** (para. 732) is used instead of a 2-methyl base, and treated with ***methyl chloride*** and ***carbon disulphide***, a ***dimethylmercapto*** compound is formed in which both —SCH_3 groups are reactive, and which can therefore be condensed twice with nuclei containing reactive methyl or methylene groups.



Benzthiazole methylene base



Benzthiazole-phenylrhodanine merocyanine with methylmercapto substituted chain

756. Sensitizing action of some dimethine merocyanines

Cyclammonium base	*Ketomethylene compound*	*Sensitizing limit* (mμ)	*Sensitizing maximum* (mμ)
Thiazoline Me.	3-ethyl-2:4(3:5)—oxazoledione	545	495
	3-ethyl-1-phenyl-2-thiohydantoin	560	505
Benzoxazole Et.	rhodanine	630	545–565
	3-ethylrhodanine	635	560
	3-isopropylrhodanine	640	520–570
	3-allylrhodanine	640	535
	3-β-hydroxyethylrhodanine	640	520–545
	2-thiohydantoin	540	515
	3-ethyl-1-phenyl-2-thiohydantoin	580	530
	1-acetyl-2-thiohydantoin	605	545
	3-phenyl-2-thiohydantoin	570	520
	methylphenylisothiohydantoin	550	500
	diphenylisothiohydantoin	555	495
	3-ethyl-2-thio-2:4(3:5)-oxazoledione	590	530
	1-phenyl-3-methylpyrazolone	590	450–530

Cyclammonium base	*Ketomethylene compound*	*Sensitizing limit* (mμ)	*Sensitizing maximum* (mμ)
Benzthiazole Et.	rhodanine	650	585
	3-isopropylrhodanine	655	590
	1-phenyl-2-thiohydantoin	620	570
	1:3-diphenyl-2-thiohydantoin	650	570
	ethylphenylisothiohydantoin	600	520
	2-thio-2:4(3:5)-oxazoledione	570	520
	1-phenyl-3-methyl-pyrazolone	580	540
	thioindoxylic acid	660	540–600
β-naphthothiazole Et.	3-ethylrhodanine	680	562–615
	2-diphenylamino-4(5)-thiazolone	620	565
Indoline Me.	rhodanine	620	560
	3:5-dihydroxythiazole	540	515
Quinaldine	3-ethylrhodanine	700	635
6-ethoxyquinaldine	3-ethylrhodanine	700	530–640

757. Polymethine merocyanines

As with the carbocyanine, lengthening the methine chain of the merocyanines considerably extends the sensitizing spectrum. Tetra and hexamethine merocyanines have been prepared, especially from 3-ethylrhodanine.⁽³⁴⁾

As we shall see in the section on dicarbocyanines, *propiolaldehyde* (propargylaldehyde) heated with aniline hydrochloride gives β-anilinoacrolein anil

$$\underset{\text{propiolaldehyde}}{CH{\equiv}C{-}CHO} + \underset{\text{aniline (hydrochloride)}}{2C_6H_5{-}NH_2 \,.\, HCl} \longrightarrow$$
$$\longrightarrow \underset{\beta\text{-anilinoacrolein anil}}{C_6H_5NH{-}CH{=}CH{-}CH{=}N \,.\, C_6H_5}$$

This anil is the next higher homologue of diphenylformamidine which is frequently used for the formation of methine chains. It is easy to see that by combining β-anilinoacrolein anil with a 2-methyl cylammonium quaternary salt a nucleus with a polymethine chain is obtained, which can be condensed with a ketomethylene compound in the known way. Example: *2-ω-acetanilido-Δ1·3-butadienylbenzoxazole ethiodide.*⁽³⁵⁾ Reflux 8·7 g (1 mol) 2-methylbenzoxazole ethiodide with 7·5 g (1 mol) β-anilinoacrolein anil hydrochloride in 60 cc acetic anhydride. After cooling, stir with 50 cc ether and leave at 0°C overnight. The ether is decanted and the viscous mass is mixed with 20 cc acetone. The product which crystallizes is filtered and washed with acetone. Yield, 10 g (73 %).

The acetanilidobutadienyl derivatives of *benzthiazole*, *benzselenazole* and *naphthothiazole* are similarly obtained. The amounts used, for example, are 3·5 g 2-methylbenzselenazole ethiodide and 2·5 g anil in 20 cc acetic anhydride or 7 g 2-methyl-β-naphthoxazole and 5 g of anil in 45 cc acetic anhydride.

Benzoxazole-ethylrhodanine tetramethine merocyanine (3-ethyl-5-(3-ethyl-2-benzoxazoylidene-butenylidene)-rhodanine). Reflux 1·15 g 2-ω-acetanilidobutadienylbenzoxazole ethiodide with 0·4 g 3-ethyl rhodanine and 0·25 g (1 mol) triethylamine in absolute ethanol for 10 mins. The crude dye (55 %) is recrystallized from acetone (800 cc per g). Net yield 22 %. Sensitizes to 715 mμ with a maximum at 655 mμ.

*Benzoxazole-diphenylamino-*5(5)*-thiazolone tetramethine merocyanine*. Sensitizes to 655 mμ with a maximum at 600 mμ.

Benzthiazole-phenyl-2-thiohydantoin tetramethine merocyanine. Heat 0·5 g 3-phenyl-2-thiohydantoin with 1·2 g 2-ω-acetanilidobutadienylbenzthiazole ethiodide and 0·25 g triethylamine in 10 cc absolute alcohol for 10 mins. The dye is washed with warm ethanol, then dissolved in pyridine and reprecipitated with methanol. Sensitizing action to 700 mμ with maximum at 670 mμ.

With *benzthiazole* and *3-ethyl-2-thio-2:4*(*3:5*)*-oxazolone* the action extends to 730 mμ with a maximum at 660 mμ.

Benzselenazole-diphenyl-2-thiohydantoin tetramethine merocyanine. Action from 630 to 760 mμ with maximum at 720 mμ and minimum at 570 mμ. With 2-diphenylamino-4(5)-thiazolone the sensitization extends to 800 mμ with a maximum at 720 mμ and a gap in the green. The same thiazolone, combined with *β-naphthothiazole* produces a merocyanine which sensitizes to 800 mμ with a maximum at 740 mμ.

β-ethoxyacrolein acetal $C_2H_5O—CH{=}CH—CH{=}(OC_2H_5)_2$ a homologue of ethyl orthoformate condenses, according to Sprague,⁽³⁶⁾ with a 2-methyl cyclammonium salt giving an intermediate which in turn can be condensed with a ketomethylene compound.

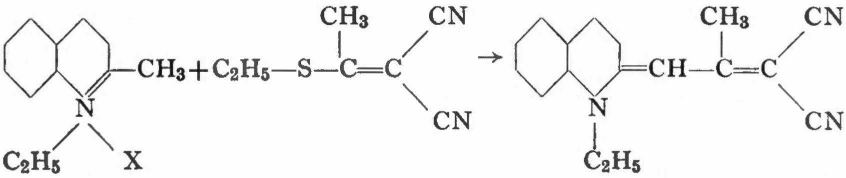
Merocyanines with more than 4 methine groups are obtained by replacing the β-anilido acrolein anil with one of the long-chain compounds considered in connection with the tri-, tetra-, and pentacarbocyanines (next chapter).

758. Merocyanines with nitrile groups

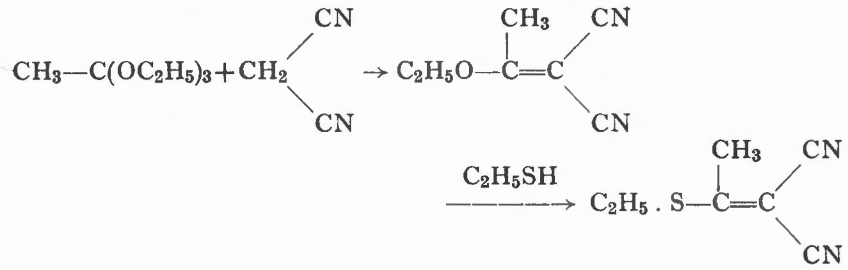
By condensing a cyclammonium salt containing reactive methyl group with a compound containing one or more nitrile groups, a merocyanine is produced in which the second element is non-cyclic, the charge carrier being $—C{\equiv}N \leftrightharpoons {=}C{=}N^{(-)}$.

Thus the ethiodide of a μ-ω-acetanilidovinylbenzoxazole, benzthiazole, naphthothiazole or quinoline, will react with *benzoylacetonitrile* or *cyanacetanilide* in the presence of triethylamine in absolute alcohol.⁽³⁷⁾ The dyes obtained sensitize from the blue-green to red depending on the individual compounds. For example, dimethine merocyanines from benzoxazole and cyanacetanilide sensitizes silver chloride to 530 mμ with a maximum at 480 mμ.

Another interesting dye is the following, which sensitizes to 590 mμ with a maximum at 565 mμ

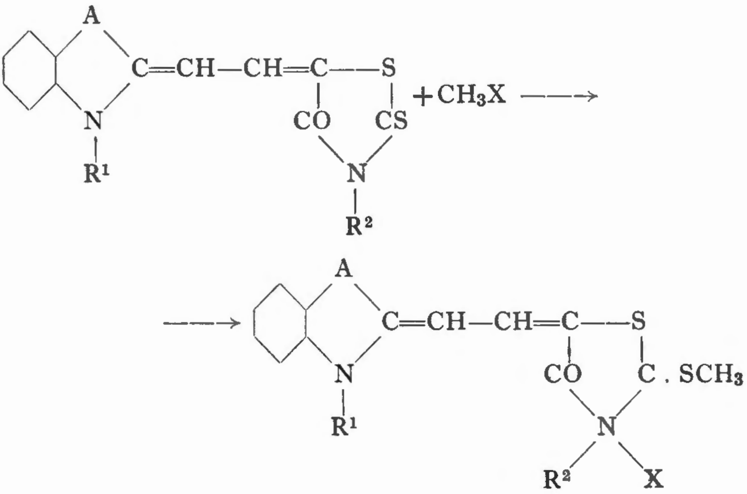


The nitrile intermediate is obtained in the following way from ethyl orthoacetate⁽³⁸⁾

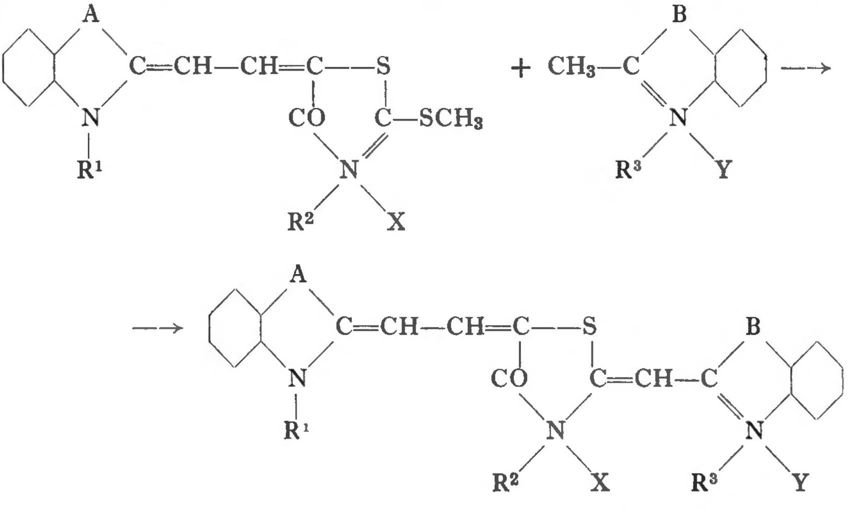


759. Complex merocyanines

When a *methyl halide* or *methyl sulphate* is reacted with a simple rhodanine merocyanine, the acid radical quaternizes the rhodanine nitrogen atom whilst the methyl group forms a methylmercapto group with the neighbouring sulphur



The —SCH₃ group is very reactive. It can therefore be condensed readily with other compounds which have a reactive methyl or methylene group, especially with the quaternary salt of another μ-methyl cyclammonium base. A complex asymmetrical merocyanine is obtained in which the second unit is a cyanine or a carbocyanine, according to the length of the methine chain.



Complex merocyanine

The complex merocyanines are powerful sensitizers. They are of great value for the *red* sensitization of emulsions for colour processes as they have a *gap in the green*. They are much deeper than the simple merocyanines used as intermediates: they are blue whilst the latter are magenta. Obviously, their absorption spectra depend on the nuclei used, the length of the two methine chains and the presence of substituents. With thiazoline or benzoxazole as the two extreme nuclei, the absorption maximum is still situated in the blue or the green, particularly if the chains are short. Examples:

5-methylbenzoxazole=allylrhodanine=CH-5-methylbenzoxazole. Max. Abs. 475 mμ.

Benzthiazole=ethylrhodanine=CH-α-naphthothiazole. Max. Abs. 562 mμ.

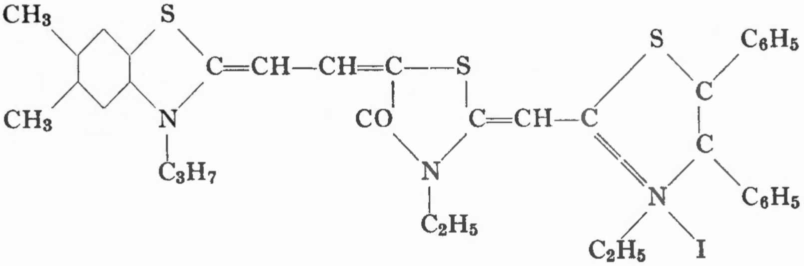
The complex merocyanines are prepared by heating the *dimethylsulphate of the simple merocyanine* with the *alkiodide of a μ-methyl heterocyclic base* in *n-propanol*-in the presence of *triethylamine*, or in *pyridine* or *isoquinoline*. The heating time varies from 30 to 120 mins. To obtain the iodide of the dye, it is precipitated with potassium iodide.

Ethylbenzthiazole-ethylrhodanine-ethylbenzthiazole dimethine complex cyanine. Heat 0·4 g of the dimethine merocyanine from 3-ethylbenzthiazole-3-ethylrhodanine with 0·29 g dimethyl sulphate on the oil bath at 130°C for 2 hours. Grind the resulting solid with 20 cc ether.

Put the quaternized merocyanine (0·56 g) into a 20 cc flask and add 0·35 g

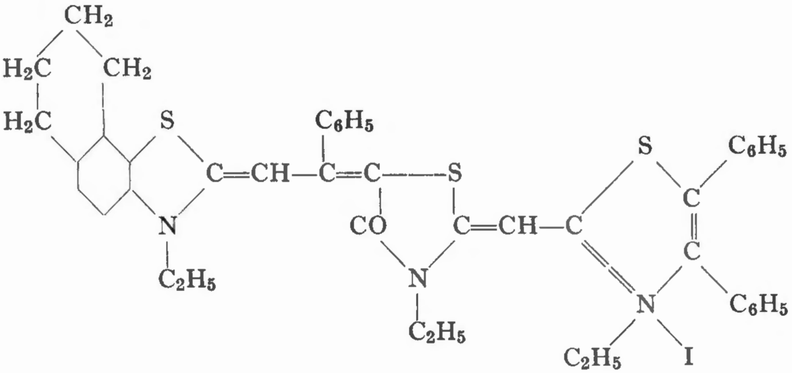
3-methylbenzthiazole ethiodide and 3 cc pure anhydrous pyridine. Heat for 30 mins. at 90°C. Cool, filter, and wash successively with 2 cc pyridine, 2 cc ethanol, 25 cc distilled water, 4 cc ethanol and 20 cc ether. 0·45 g dye is obtained (yield, 63%). Absorption maximum 609 mμ, sensitizing maximum 632 mμ.

3-propyl-5-ethoxy-6-methylbenzthiazole-3-ethyl rhodanine-4:5-diphenyl-3-ethylthiazole complex dimethine merocyanine. Absorption maximum at 609 mμ. Sensitizes from 550 to 680 mμ with a maximum at 640 mμ. Has been used for Agfacolor reversal films.



React 5-ethoxy-2:6-dimethyl benzthiazole (n-propyl iodide) with diphenylformamidine in acetic anhydride (see para. 696) and condense the resulting product with 3-ethylrhodanine (para. 754a) in pyridine. The resulting merocyanine is quaternized with dimethyl sulphate and then combined, in pyridine, with 2-methyl-4:5-diphenylthiazole.

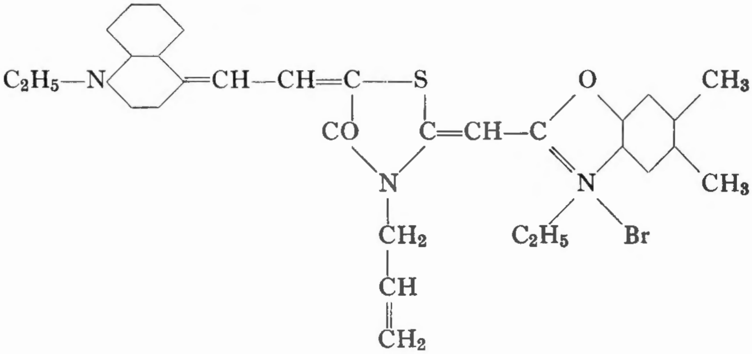
3-ethyl-tetrahydro-α-naphthothiazole-meso-phenyl-ethylrhodanine-3-ethyl-4:5-diphenylthiazole complex dimethine merocyanine. This red sensitizer has been used for Agfacolor negative film.



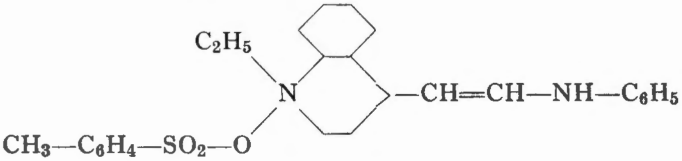
The ethyl benzene-sulphonate of the 2-methyl naphthothiazole base is treated with benzoyl chloride in pyridine (para. 755). The resulting ketone [Base]=CH—CO—C_6H_5, treated with P_2S_5 is converted to the thioketone [Base]=CH—CS—C_6H_5 which, with dimethyl sulphate, gives a thioether. [Base ethylsulphate]—CH=C(C_6H_5)—SCH_3, which is condensed with

3-ethyl rhodanine in n-propanol in the presence of triethylamine. This merocyanine is quaternized with methyl sulphate and then condensed in pyridine with 2-methyl-4:5-diphenylthiazole ethyl sulphate.

4-quinoline-3-allylrhodanine-3-ethyl-5:6-dimethylbenzoxazole complex dimethine merocyanine. Absorption maximum at 657 mμ, sensitizes from 625 to 755 mμ with a maximum at 705 mμ. This dye has been used for Agfacolor paper.

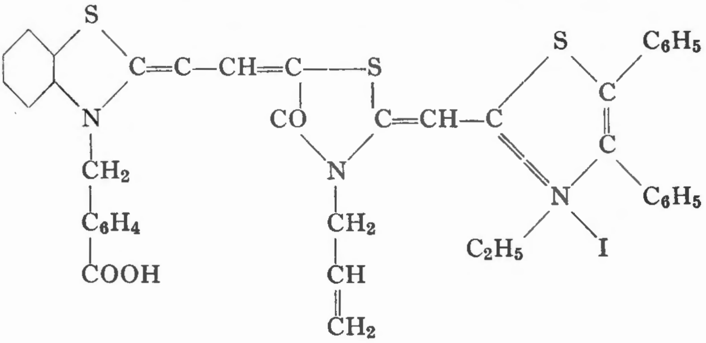


Lepidine ethyl-p-toluene-sulphonate is heated with diphenylformamidine and acetic anhydride to give



which is heated with 3-allylrhodanine in pyridine. The merocyanine is extracted with propanol, converted to the dimethyl sulphate and condensed with 2:5:6-trimethyl benzoxazole diethyl sulphate. The dye is precipitated with a solution of potassium bromide. M. Pt. 262°C.

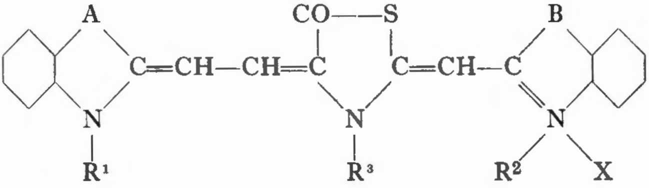
3-(p-carboxybenzyl)benzthiazole-allyl rhodanine-3-ethyl-4:5-diphenylthiazole complex dimethine merocyanine.(39) Absorption maximum at 590 mμ, sensitizes to 685 mμ with a maximum at 645 mμ.



1·4 g of 3-allyl-5-(acetanilidomethylene) rhodanine is refluxed for 30 mins. with 1·6 g 2-methyl-benzthiazole p-carboxybenzyl-bromide in the presence of 0·6 cc triethylamine in 20 cc alcohol. A mixture of 1·1 g of this merocyanine, washed with alcohol, 0·85 g 2-methyl-4:5-diphenylthiazole and 10 g methyl-p-toluene-sulphonate is then melted at 150°C for 1 hour. Then 15 cc pyridine and 0·5 cc triethylamine are added and the mixture is refluxed for 15 mins. The dye is precipitated with ether, taken up in alcohol and reprecipitated with a 20% solution of potassium iodide.

The same merocyanine, with a phenyl substitutent has an absorption maximum at about 611 mμ and a sensitizing maximum at about 645 mμ.

Complex merocyanines with a 5-thiazolidone nucleus.(40)



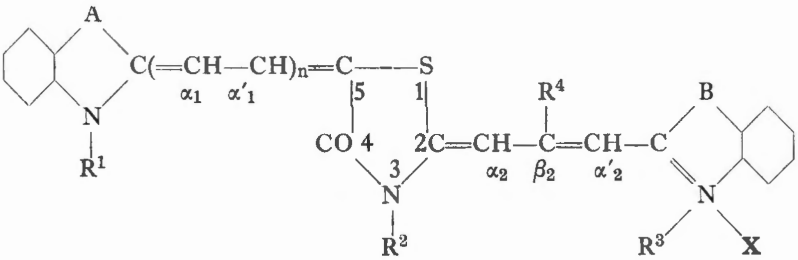
A and B represent O, S, $C(CH_3)_2$, etc.

760. Sensitizing action of some complex merocyanines(41)

Abs. Maxima mμ		Sensitization Max. mμ	Sensitization Range mμ
605	4:5 diMebenzthiazole=CH—CH—ethylrhodanine= =CH—4:5 diPh. thiazole	635	545–675
595	Benzselenazole=CH—CH=ethylrhodanine= =CH—4:5 diPh. thiazole	620	540–660
605	Benzthiazole=CH—CH=ethylrhodanine= =CH—5-MeObenzselenazole	640	555–675
620	4:5 diPh. thiazole=CH—CH=allylrhodanine= =CH—4-Ph-5-Methiazole	650	555–675
585	Tri-Me-indoline=CH—CH=ethylrhodanine= =CH—α-naphthothiazole	615	540–640
595	5-MeO-tri Me indoline=CH—CH=rhodanine= =CH—α-naphthothiazole	635	550–670
630	Quinoline(2)=CH—CH=allylrhodanine= =CH—5:6-diMe benzthiazole	660	595–670
635	Quinoline(2)=CH—CH=allylrhodanine= CH—6-acylaminobenzthiazole	660	595–675
650	Quinoline(4)=CH—CH=allylrhodanine= =CH—benzoxazole	700	620–730
670	4:5 di Me benzthiazole$(=CH—CH)_2$= =allylrhodanine=CH—benzoxazole	715	640–740
700	Benzthiazole$(=CH—CH)_2$=allylrhodanine= =CH—benzthiazole	725	650–760

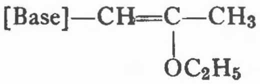
761. Complex merocyanines with trimethine second chain: rhodacarbocyanines

These compounds have the rhodanine merocyanine and the carbocyanine structures.



The introduction of a trimethine chain into the molecule of the complex merocyanine has the effect of shifting the absorption and sensitization maxima towards the red.

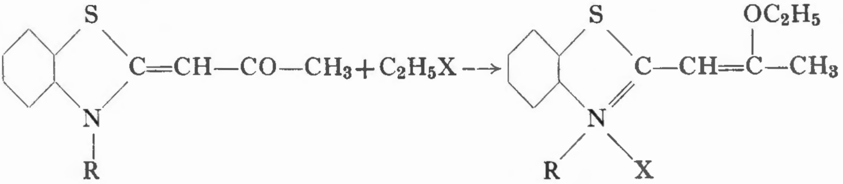
These complex merocyanines are synthesized by condensing a quaternized rhodanine merocyanine, having therefore an *alkylmercapto group* —SCH_3, with the quaternary salt of a cyclammonium base having an *ω-keto chain* with a terminal reactive methyl group. It is always necessary to acetylate the CO group to ensure a double bond by using one of the oxygen valencies to attach the alkyl group via an ether group:⁽⁴²⁾



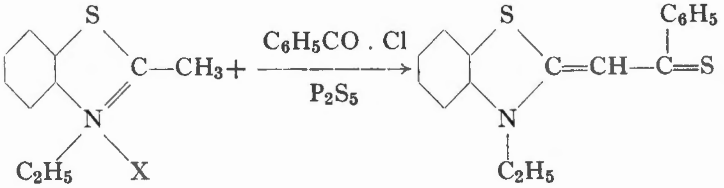
$$[\text{Base}]\text{—CH=}\underset{\displaystyle OC_2H_5}{\text{C}}\text{—}CH_3$$

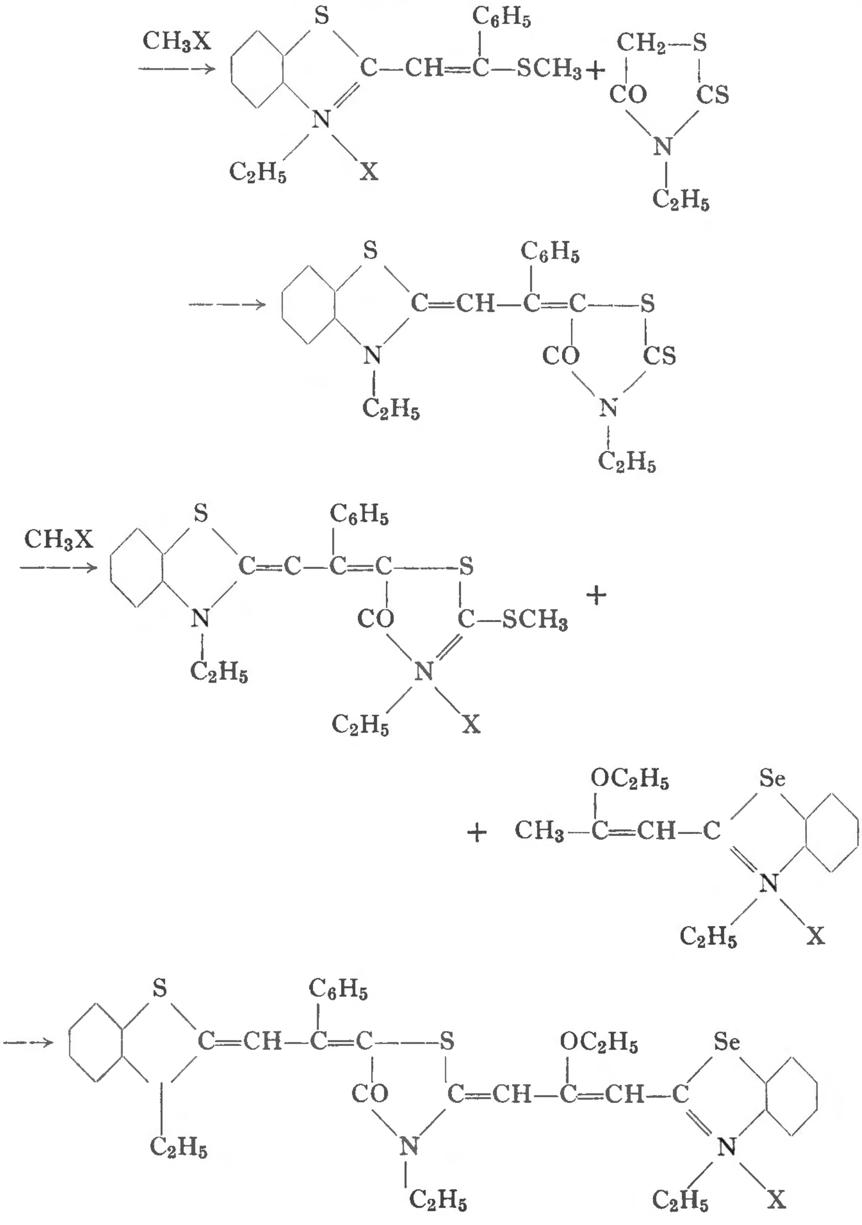
This alkoxy group becomes a substituent in the trimethine chain.

We have already seen that an ω-ketone is produced by the action of an *acid chloride* on the salt of a cyclammonium base (para. 740). The ω-ketone, treated with ethyl halide or sulphate is converted to the corresponding acetal:



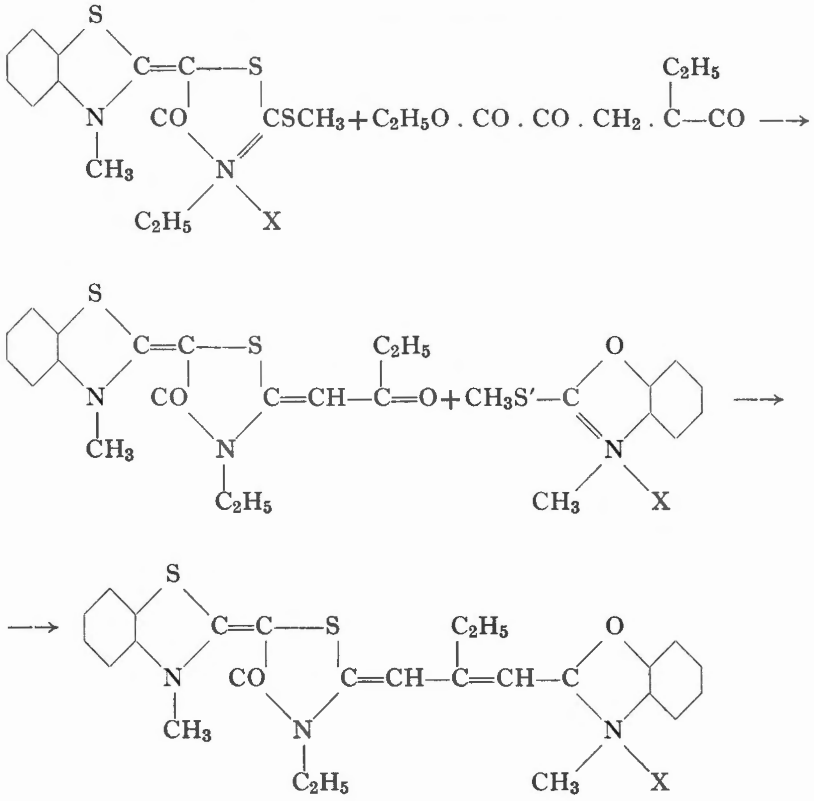
The synthesis of a merocyanine with a trimethine chain is summarized in the following example:⁽⁴³⁾





The dye has an absorption maximum at about 661 mμ, and sensitizes to 730 mμ with a maximum at about 700 mμ and *a complete gap in the yellow-green* to 595 mμ.

Another method of synthesis is to condense a keto-chain substituted merocyanine with a quaternary salt of the methylmercapto derivative of the cyclammonium base.(44)



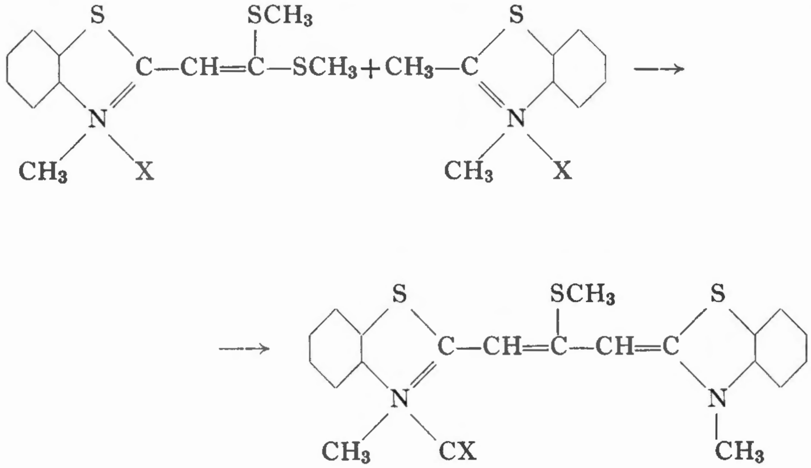
By replacing ethyl propionylpyruvate with benzoylacetic ester C_6H_5—CO—CH_2—CO—OC_2H_5, a merocyanine with the reactive chain $\rangle C{=}CH{-}C(C_6H_5){=}O$ is obtained, which gives a merocyanine with a mesophenyl substituent in the trimethine chain (sensitization from 600 to 720 mμ).

762. Tetranuclear complex rhodanine merocyanines

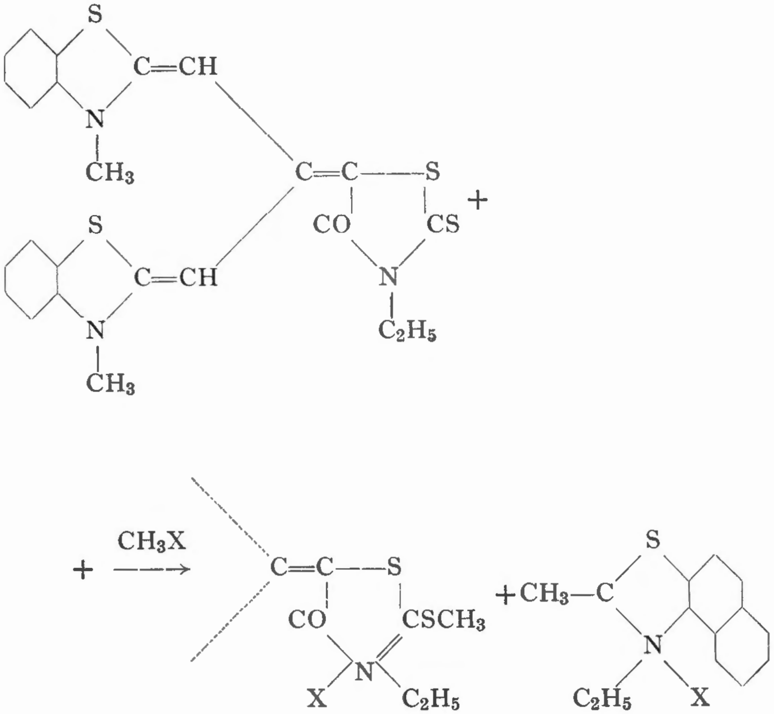
A complex merocyanine can have a cyclammonium substituent on the dimethine chain, which makes the ketomethylene nucleus part of a conjugated system with both nitrogenous heterocyclic nuclei. The complete compound is a tetranuclear complex merocyanine.

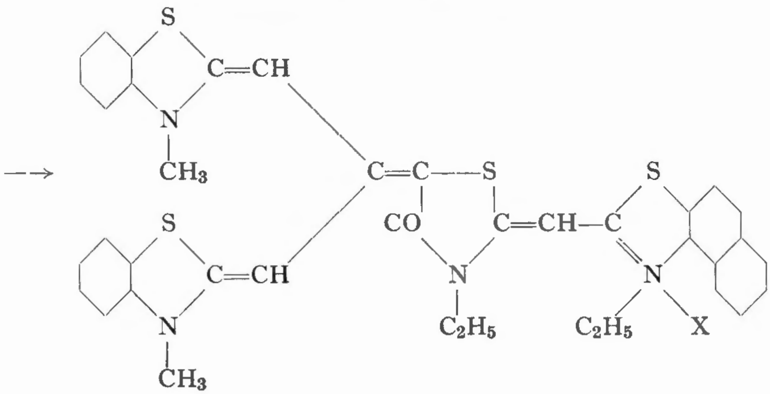
A method of syntheses for this type of compound has been disclosed by Gevaert:(45)

The quaternary salt of a cyclammonium base with an alkylmercapto chain (para. 755E) is first condensed with the quaternary salt of another 2-methyl base. This gives a carbocyanine with a meso alkyl mercapto substituent:



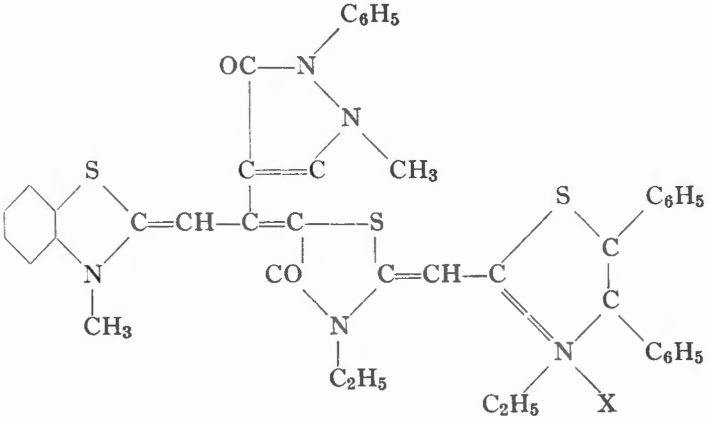
The —SCH_3 group of this carbocyanine is very reactive and combines readily with ethylrhodanine to give a trinuclear merocyanine which, when quaternized with dimethyl sulphate, can condense with a molecule of another cyclammonium base:





This dye has an absorption maximum at about 627 mμ and sensitizes to 690 mμ with a maximum at 660 mμ.

A second type of tetranuclear merocyanine has been prepared⁽⁴⁶⁾ by introducing an *antipyryle* nucleus as a substituent. The procedure is similar to the preceding one: a base with an alkylmercapto chain is reacted with phenylmethylpyrazolone. The resulting merocyanine, which still has a free SCH_3 group is first quaternized with a methyl salt, then condensed with a molecule of ethylrhodanine. This gives a merocyanine with an antipyryle substituent. The $>C{=}S$ group of the rhodanine is then converted to $>C{-}S{-}CH_3$ with a methyl salt, and the trinuclear compound is condensed with a quaternized 2-methyl base. The tetranuclear dye finally obtained has, for the structure given below, a maximum absorption at about 613 mμ and sensitizes to 700 mμ with a complete gap in the green.

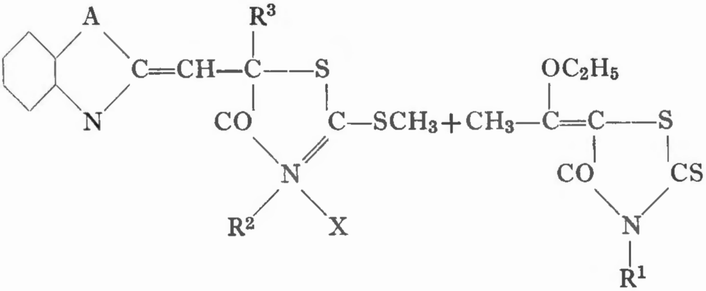


By condensing the initial pyrazolone-merocyanine with a cyclammonium salt, a carbocyanine is obtained⁽⁴⁷⁾ which sensitizes in the red with a gap in the green, but is inferior to the ordinary carbocyanines, with a tendency to second order sensitizing.

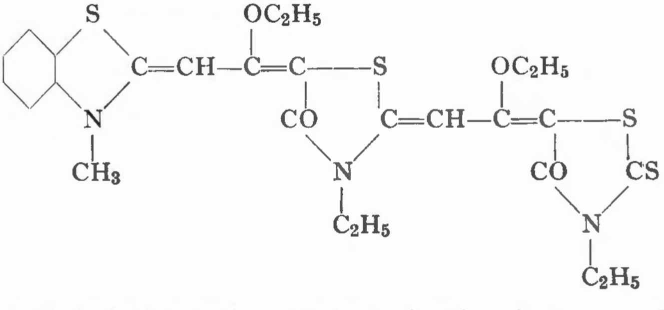
The meso substituent can be a 2:3-dihydropyrimidazolone nucleus, obtained by the action of chloracetic acid on α-aminopyridine.⁽⁴⁸⁾

763. Double merocyanines

A rhodanine merocyanine whose rhodanine nucleus has been quaternized with a methyl salt, and which therefore has a reactive —SCH_3 group, can condense with either a 2-methyl quaternary salt to give a complex merocyanine, or with a ketomethylene compound with a *ketonic chain having an alkoxy substituent*⁽⁴⁹⁾ (para. 761). In the second case a double merocyanine is formed (having two resonance systems)



The following dimerocyanine with two meso ethoxy groups has an absorption maximum at 636 mμ and sensitizes to 730 mμ in the extreme red with a maximum at about 675 mμ.



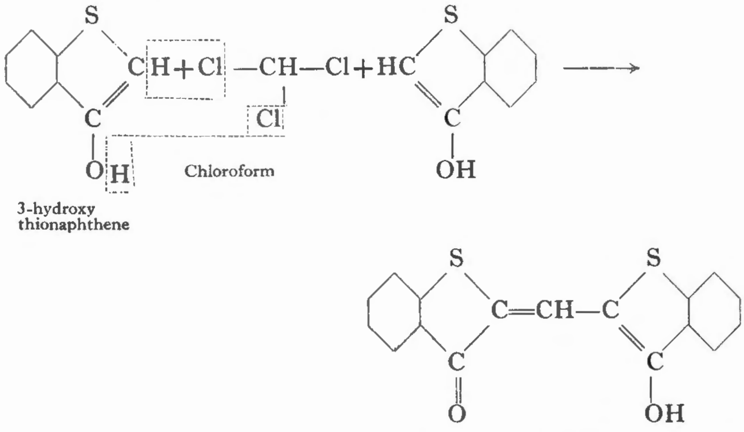
The central rhodanine nucleus can be replaced by its isomer—5-thiazolidone having the methylene group in the 4-position.⁽⁴⁰⁾

OXANOLS

764. Constitution and preparation of oxanols

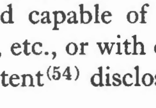
The oxanols (or oxanines) are acid dyes containing a methine chain linking two ketomethylene nuclei (see para. 671). They are mediocre sensitizers due to their lack of planarity which prevents their adsorption in a closely packed layer.

Two molecules of hydroxythionaphthene will condense under the influence of chloroform or ethyl orthoformate in the presence of sodium alkoxide to give an oxanol dye as follows:(50)

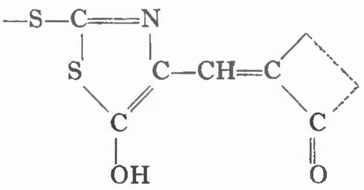


3-hydroxy-3′-oxy-2 : 2′-methenyldithionaphthene

To obtain a trimethine chain corresponding to a carbocyanine, the condensing agent must be β-ethoxyacrolein acetal used in the preparation of dicarbocyanines. Similarly, condensation of a hydroxythionaphthene with glutaconic dialdehyde dianil produces a pentamethine-dithionaphthene which corresponds to a dicarbocyanine.

A second preparative method is to condense the hydroxythio or selenonaphthene base with one molecule of *3-hydroxy-2-formylthio* or *selenonaphthene* in the presence of sodium alkoxide or in the presence of hydrochloric acid in acetic acid solution.(51) The formyl derivative has the CHO group attached to the active carbon of the thionaphthene:  $C{-}CHO$.

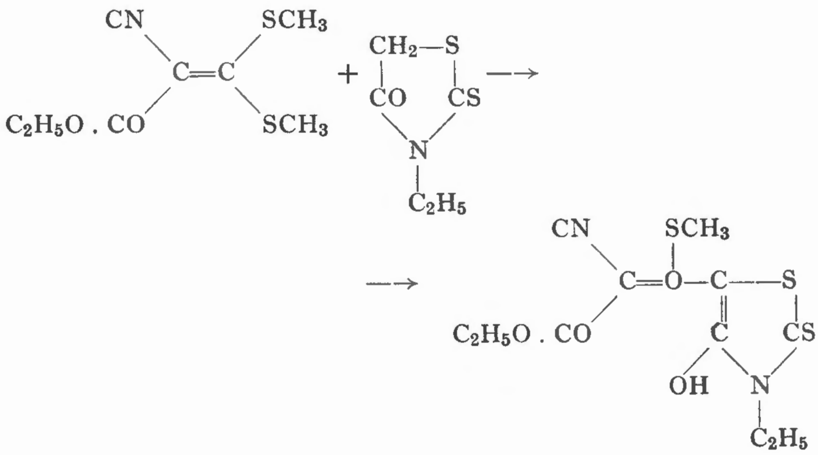
Many other oxanols have been obtained with various known heterocyclic ketomethylene compounds. Knott(52) used *thiazole-5-ones* and *phenoxazol-5-one*. Zenno(53) condensed *1:2-diaryl-3:5-dioxypyrazolidines* with ethyl orthoformate in the presence of a compound capable of supplying hydrogen: acetamide, ethyl malonate, acetophenone, etc., or with diphenylformamidine, whilst by using hydrazines, a Kodak patent(54) disclosed oxanols with the structure:



The oxanols are mainly effective with silver chloride. Those from thionaphthene have their absorption maxima at about 590 mμ.

765. Oxanols with a single cyclic nucleus

Kendall and Edwards⁽⁵⁵⁾ condensed β-cyano-β-carbethoxyketone dimercaptal with ethyl rhodanine. The oxanol dye produced has a free meso —SCH_3 substituent. It sensitizes silver chloride with a maximum at 510 mμ.



DYES RELATED TO THE CYANINES

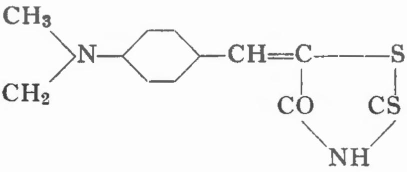
766. Ketomethylene hemicyanines

The ketomethylene compounds, whose methylene group is very reactive, will condense readily with *p-dimethylaminobenzaldehyde.* The resulting hemicyanines differ from the styryl dyes as they have an *odd* number of methine groups; they are similar to the oxanol dyes.

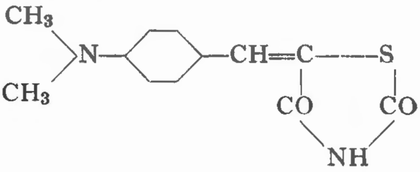
The first ketomethylene hemicyanines were obtained by Kendall in 1933.⁽⁵⁶⁾ They were weak sensitizers. To prepare them, *p-dimethylaminobenzaldehyde* is condensed with *rhodanine* (A) (sensitizing maximum at 565 mμ), *3:5-dihydroxythiazole* (B) (sensitizing maximum at 450 mμ, extending to 580 mμ), *ethyloxindole* (C) (sensitization to 540 mμ, with a maximum at 490 mμ), etc.

With *p-dimethylaminocinnamic aldehyde* and *rhodanine* (D) the sensitizing action extends to 640 mμ with a maximum at 580 mμ. The same condensation carried out with *dimethylglutaconic-dialdehyde-dianil chloride* gives the dye (E) which sensitizes to 645 mμ with a maximum at 615 mμ.

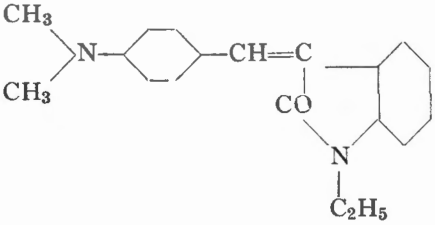
Preparation examples. 3·12 g of dimethylglutaconic-dialdehyde-dianil chloride is boiled with 3·66 g rhodanine in 100 cc dry alcohol until dissolved. 0·46 g sodium dissolved in 20 cc dry alcohol is added and boiling is continued for 30 mins. The purple crystals deposited on cooling are washed with ether and recrystallized from methanol. The same method is used with 1·96 g of aldehyde, 0·72 g thiohydantoin, 60 cc alcohol and 0·15 g sodium in 10 cc absolute alcohol.



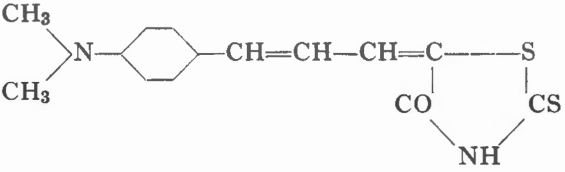
(A)



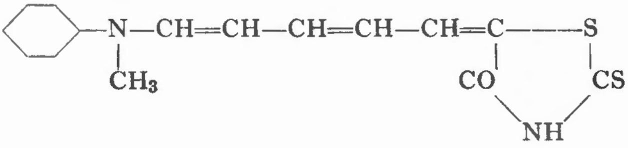
(B)



(C)



(D)



(E)

By treating *methylpyrazolones* (para. 697) with the aromatic aldehydes in the presence of sodium, ketomethylene hemicyanines are formed which sensitize *nuclear emulsions*, particularly to cosmic radiation.(57)

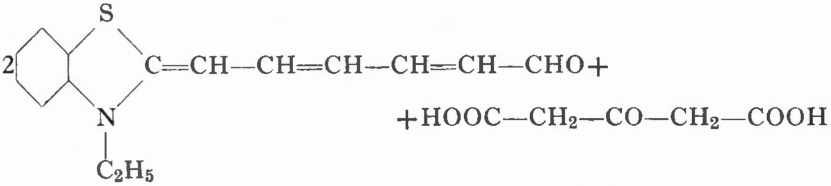
767. Acetone dicarboxylic ester derivatives

By condensing *acetonedicarboxylic acid* with 2 molecules of a *heterocyclic-ω-aldehyde* in the presence of acetic anhydride and pyridine, Riester(58) obtained a series of dyes notable for their two trivalent nitrogen heterocyclic nuclei linked by a long chain whose central link is a carbonyl group —CO— with the general structure

$$=CH-(CH=CH)_n-CO-(CH=CH)_n-CH=$$

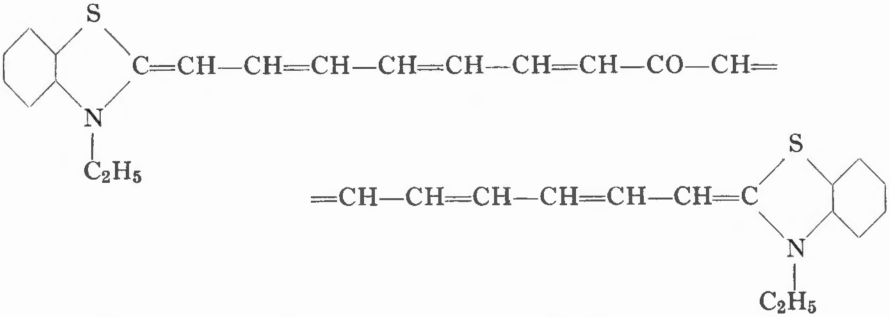
Depending on the length of the chain, the absorption is in the green, the red or the infra red.

The heterocyclic aldehyde can, for example, be *N-ethyl-thiazolidene aldehyde* or *N-ethylbenzthiazolidene-2-hexatrienal*. In the latter case we have:



N-ethylbenzthiazolinehexatrienal

Acetone dicarboxylic acid

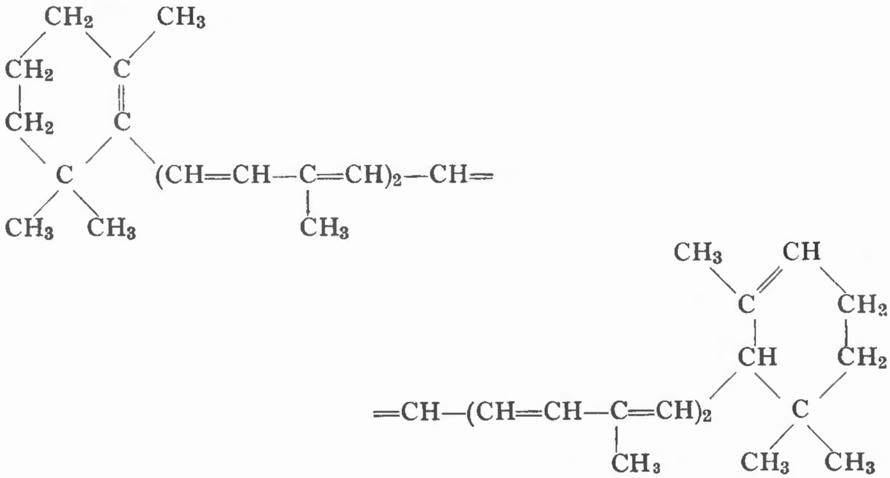


The chain length of this dye is greater than that of the pentacarbocyanines.

A Bayer patent claims the condensation of ketones in acid medium which gives yellow or orange dyes.(58b)

768. Carotenes

The *carotenes* are constituents of the natural pigments of vegetation. They have a constitution somewhat similar to that of the carbocyanines, for some of them are made up of benzene nuclei joined by a very long chain of vinyl groups. Thus α-carotene has the formula



α-carotene

The photographic action of the carotenoids such as α- and *β-carotene*, *crocetine*, *bixine*, *lycopene*, etc., was discovered by Calzavara.⁽⁵⁹⁾

They panchromatize silver chloride, although their absorption maxima are in the blue. They have no action on silver bromide.

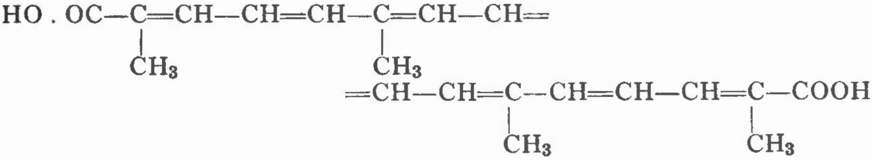
Sensitizing solutions have the following composition:

Solution of carotenes in pyridine 1:1000	2·8 cc
Acetone	104 cc
Water	223 cc

The carotene solution can be replaced by the same quantity of crocetine solution prepared as follows:

Safran crocetine	0·1 g
Triethanolamine 20%	2 cc
Water	25 cc
Alcohol 96%	50 cc
Water to	100 cc

Crocetine has the formula

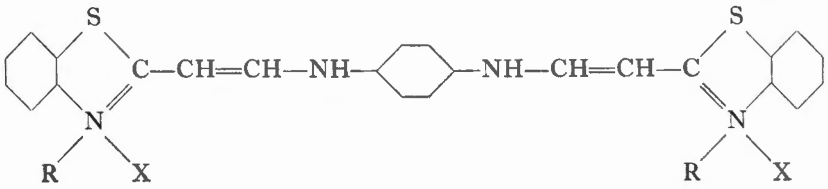


$$HO\,.\,OC-\underset{CH_3}{\underset{|}{C}}=CH-CH=CH-\underset{CH_3}{\underset{|}{C}}=CH-CH=$$
$$=CH-CH=\underset{CH_3}{\underset{|}{C}}-CH=CH-CH=\underset{CH_3}{\underset{|}{C}}-COOH$$

Gelatin contains compounds with polyene chains and this explains the natural extended colour sensitivity obtained with some silver chloride emulsions.

769. Diaminohemicyanines

Together with the acetone dicarboxylic acid derivatives, which are *double* semicarbocyanines with trivalent nitrogen, we can consider the double semicyanines with pentavalent nitrogen, derivatives of the *aromatic diamines.*⁽⁶⁰⁾ These dyes, which sensitize chloride emulsions, are prepared by condensing two molecules of a *heterocyclic ω-aldehyde* or anilidovinyl derivative with one molecule of an *aromatic diamine* such as p-phenylenediamine. For example, with the benzthiazole aldehydes, dyes of the following type are obtained:

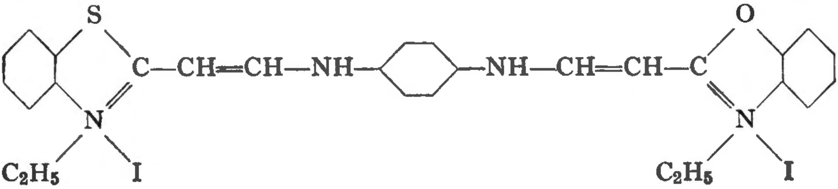


Some of these compounds have one or more carboxylic —COOH or sulphonic —SO_3H acid groups attached to the central nucleus.(61) They are then only weak dyes.

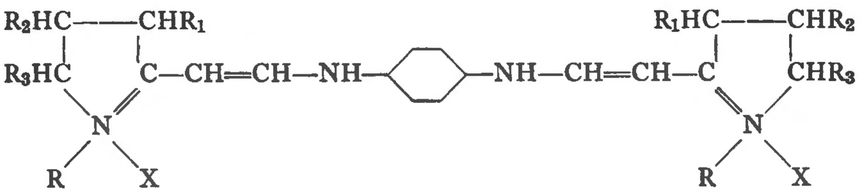
The diaminohemicyanines are good sensitizers. Their maximum effect is between 470 and 560 mμ depending on the weight and nature of the nuclei.

p-phenylene-bis-vinylbenzoxazole ethiodide. Obtained by Ilford by condensing β-anilidovinyl-benzoxazole ethiodide (para. 739) with p-phenylenediamine, and by Gevaert(62) by reacting 2-methylbenzoxazole ethiodide and p-phenylenediamine in the presence of ethyl orthoformate.

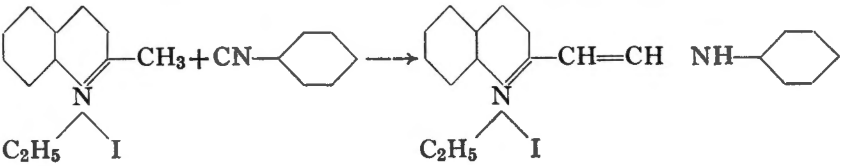
p-phenylenediamine-bis-vinylbenzthiazole-benzoxazole ethiodide. Reflux 11 g β-anilidovinyl-benzthiazole and 8 g p-phenylenediamine for 30 mins. in 100 cc alcohol.(63) The monoaminohemicyanine is obtained on cooling. It is recrystallized from alcohol. (M. Pt. 231°C.) [Base Et. I]—CH=CH—NH—$C_6H_4NH_2$. 5 g of this simple hemicyanine is then condensed with 5 g β-anildovinylbenzoxazole ethiodide in 100 cc alcohol by refluxing for 30 mins. The dye which is obtained on cooling is recrystallized from alcohol. M. Pt. 294–295°C. It sensitizes silver chloride strongly to 540 mμ. It has the formula:



By the same method, diaminohemicyanines with a central benzidine —NH—C_6H_4—C_6H_4—NH— group or even —C_6H_4—NH—CO—NH—C_6H_4— can be prepared. Another series of yellow or orange dyes has the structure(64)



We would finally note that Zenno(65) obtained aminovinyl compounds by treating ethiodide of a base with *phenylisonitrile* for 30 mins. at 160°C.



770. Azacyanines

The methine —CH= groups of cyanines can be replaced by nitrogen atoms —N=.

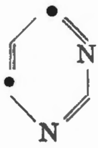
By heating *2-aminoquinoline* with *2-chloroquinoline* a 2:2′-diquinolylamine is produced, which when acetylated and converted to the dimethyl sulphate gives 1-methyldihydroquinolenyl-2-quinolyl-2′-imine after treating with dilute sulphuric acid. When treated with methyl iodide, the latter gives an orange-yellow dye which has three absorption bands—at 424, 404, and 285 mμ. It has the structure of a pseudocyanine in which the —CH= linkage is replaced by —N=. This quinoline azacyanine has no effect on photographic emulsions, but the thiazole derivatives sensitize silver chloride.

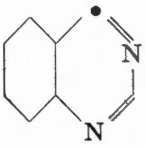
Another group of sensitizing azacyanines comprises compounds with tri- and pentavalent nitrogen heterocyclic nuclei linked by the chain —N==CH—N=. These dyes were obtained by Kendall.

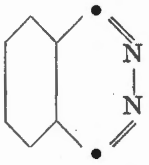
As we shall see in a following chapter, the chains —CH=N—CH= and —CH=N—N= produce, on the contrary, cyanines with *desensitizing* properties.

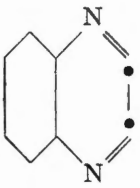
771. Diazine dyes

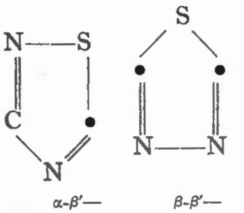
Kendall has prepared dyes from *diazine* nuclei, that is, containing two nitrogen atoms arranged as follows


Pyrimidine


Quinazoline


Phthalazine


Quinoxaline


α-β′— β-β′—

Thiodiazoles

in which the reactive positions are those indicated.

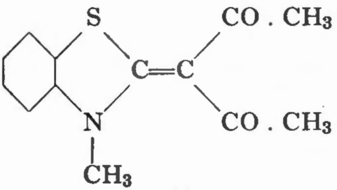
Only the *pyrimidines* and *quinazolines* yield acceptable sensitizers; the former can be symmetrical or asymmetrical, and the latter, only asymmetrical. The dyes produced from *phthalazines*, *quinoxalines* and *thiodiazoles* are inferior and have desensitizing properties.

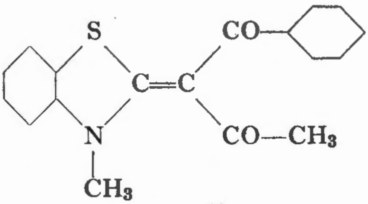
Naphthenone sensitizers—See Ogata, Zenno and Nishida.(65b)

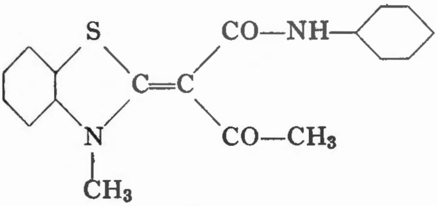
772. Anilinovinyl and keto derivatives of cyclammonium bases

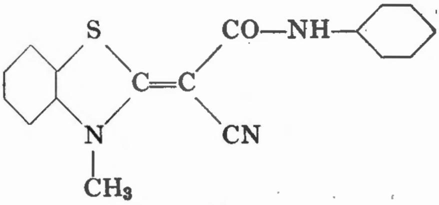
Anilinovinyl derivatives of nitrogenous heterocyclic bases (see para. 739) having para substituents in the aniline nucleus—especially Cl, OCH_3, SCH_3, $N(C_2H_5)_2$ or C_6H_5, appear to have interesting sensitizing and supersensitizing properties.(66) They are obtained by condensing the cyclammonium base salt with a substituted formamidine or aniline in the presence of ethyl orthoformate, or by reacting a substituted aniline with a cyclammonium salt which already has an acetanilinovinyl chain.

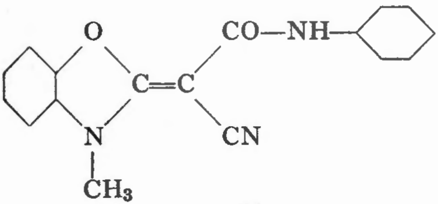
A Gevaert patent(67) discloses the supersentization of emulsions with ketomethylene derivatives of cyclammonium bases, whose formulae are given below. However, according to the writer's tests, these compounds do not seem to be supersensitizers, but only chemical sensitizers which increase the sensitivity of the large grains of an emulsion even in the absence of any colour sensitizer.

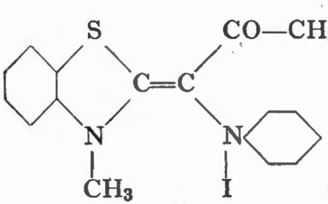

(a)

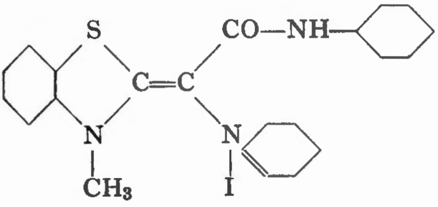

(b)

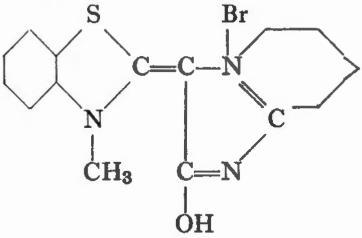

(c)


(d)


(e)


(f)


(g)


(h)

Preparation example: formula (f). First prepare N-acetonylpyridinium chloride $(C_5H_5N)^+\!-\!CH_2COCH_3 \,.\, Cl^-$ by carefully heating 2·14 g pure pyridine with 2·1 g monochloracetone for a few minutes. The mixture solidifies: grind up with 15 cc ether and wash with a further 30 cc ether and filter. 2·9 g of product is obtained. (Yield, 68%.)

Put 3·7 g 2-methylmercaptobenzthiazole dimethyl-sulphate (para. 693), 1·9 g acetonylpyridinium chloride, 13 cc absolute ethanol and 1·65 cc anhydrous triethylamine in a 50 cc flask fitted with a reflux condenser. Reflux for 10 mins. (oil bath at 105°C). Cool in ice, and pour the solution, with stirring, into 86 cc of 10% potassium iodide solution (aqueous) cooled in an ice bath. An orange product slowly crystallizes. Leave overnight in ice, filter, and wash successively with 50 cc water, 20 cc ethanol and 25 cc ether. Yield 2·15 g (43%). Recrystallize (according to the writer) from 83 cc pure boiling *acetic acid* containing 4·1 cc *distilled water* (very exactly). On cooling, light yellow crystals are obtained which are filtered, washed with 8 cc water, 5 cc alcohol then 10 cc ether. Yield, 15%, 0·77 g. Recrystallization from alcohol indicated in the patent does not result in ready crystallization. Observed melting point 152°C instead of the 97° given. *This compound increases the general sensitivity of a high-speed emulsion by 50%, using 30 mg per litre.*

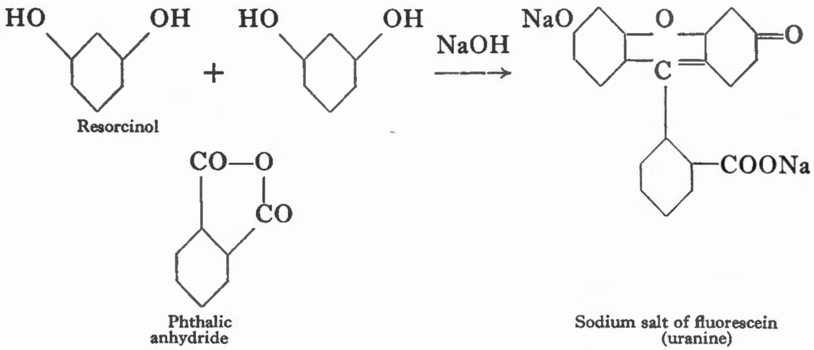
The compounds (a), (b), (c), (d), (e), (g) and (h) are similarly obtained using respectively the following compounds: *acetylacetonebenzoylacetone, acetoacetanilide, cyanacetanilide, pyridinium chloracetanilide, 2:3-dihydropyrimidazolone-2-hydrobromide.*

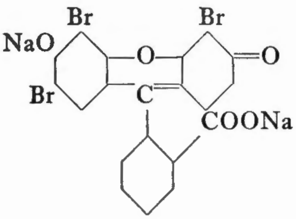
DYES NOT RELATED TO THE CYANINES

773. Phthaleins

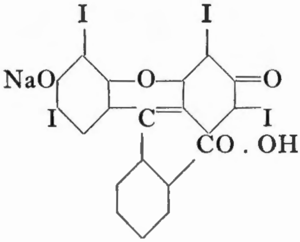
The *phthaleins* are related to triphenylmethane. They are dyes obtained by condensing phthalic anhydride with a phenol. If the phenol is replaced by resorcinol, *fluorescein* and its derivatives are obtained.

Brominated fluorescein is *eosin*, the iodo compound is *erythrosin* and with both chlorine and iodine substituents, *rose Bengal.*(68)

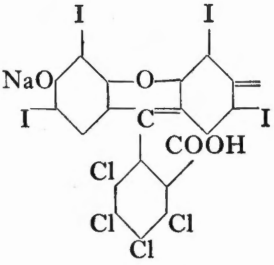




Eosin



Erythrosin



Rose Bengal

By replacing the phthalic acid with tartaric, succinic or saccharic acids the *tartreins*, *succineins*, and *saccharins*, analogous to the phthaleins, are obtained.

The fluoresceins have *sensitizing properties*, but only erythrosin is still used (Fig. 131).

Dye	*Absorption* mμ	*Sensitization* (mμ) *Limit*	*Max.*	*Depression*
Eosin	516 & 483	565	550	525
Erythrosin	526 & 490	585	565	520
Rose Bengal (tetrachlorinated)	550 & 512	600	575	535

Erythrosin is prepared by treating a solution of *fluorescein* in caustic soda with a solution of iodine in boiling soda.(69)

It is also obtained by treating an alkaline solution of fluorescein with alkaline ammonium persulphate or by electrolysis in the presence of iodine.

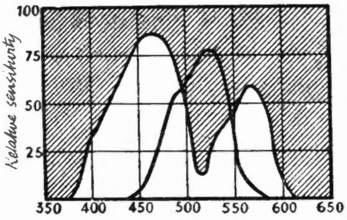


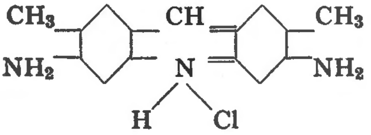
FIG. 131. Erythrosin: sensitization curve compared with absorption curve (indicated in the centre).

The crude erythrosin must be purified by working with dilute sulphuric acid and warm alcohol, then by dissolving in dilute soda and precipitation with acid. To remove the di-iodo compound, the dye is converted to the diacetate with acetic anhydride, and this is then decomposed with ammonia in acetone. Finally, the sodium salt is prepared. Amount used: 20 mg per litre of emulsion.

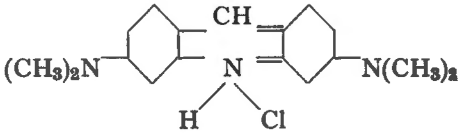
Hishiki obtained sensitizers by combining erythrosin with cyanines by heating in methanol.(69b)

774. Acridine dyes

Acridine yellow (*diaminodimethylacridine hydrochloride*) and *acridine orange* (*tetramethyldiaminoacridine hydrochloride*) are weak sensitizers;(70) the former sensitizes chloride emulsions in the blue, and the latter, bromide emulsions in the blue-green (500–540 mμ).



Acridine yellow



Acridine orange

Acridine yellow is obtained by reacting formalin with m-toluylenediamine; the resulting tetraminoditolylmethane is converted to diaminodimethyldihydroacridine by elimination of NH_3, and is then oxidized with ferric chloride.(71)

Acridine orange is obtained from *m-aminodimethylaniline*(72) which is condensed with formalin to give tetramethyl-tetraaminodiphenylmethane. The latter is converted to the dye by elimination of ammonia and oxidation.

775. Other dyes

The following dyes have a slight sensitizing action:

1. *Diphenylmethane dyes: Auramine O* (tetramethyldiaminodiphenylketoneimine hydrochloride). Used alone, it sensitizes silver chloride to blue but has no effect on silver bromide. According to Renwick and Bloch, when added to cyanine sensitized emulsions in very small quantities, it increases the colour sensitivity in areas where it is normally inactive. Furthermore, it reduces the fogging tendency of the isocyanines. Used at high concentrations, auramine is a desensitizer.

2. *Triphenylmethane dyes: Methyl violet* (pentamethyl-triaminotriphenyl carbinol chloride). Sensitizing tendency in the yellow-orange. *Crystal violet, ethyl violet* and *formyl violet* behave similarly.

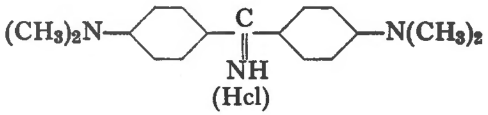
Coralline yellow, once used by Vögel, is the sodium salt of aurine, a phenolic triphenylmethane derivative. Its aqueous solutions are red.

3. *Azo dyes. Glycine red* (sodium salt of diphenyl-bis-azo-α-naphthylglycine-α-naphthylamine-sulphonic acid) and *glycine corinth* (sodium salt of diphenyl-bis-azo-α-naphthylglycine) and *Congo red* (sodium salt of diphenyl-bis-azo-di-α-naphthylamine-4-sulphonic acid).

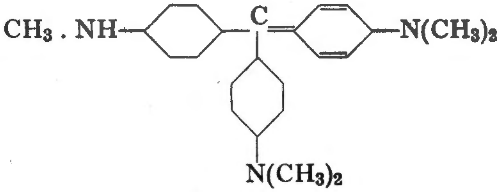
Slight action in the green.

4. *Anthraquinone dyes: Alizarin blue bisulphite* has been used for the infrared. It is the sodium bisulphite of 1:2-dihydroxyanthraquinone-β-quinoline.

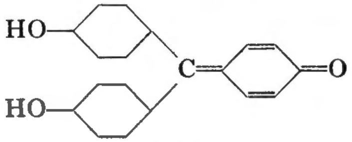
5. *Nigrosine*. Black dye of indefinite constitution related to the indulines. The sulphonated compound is water-soluble. Nigrosine also has been used for infra-red sensitizing.



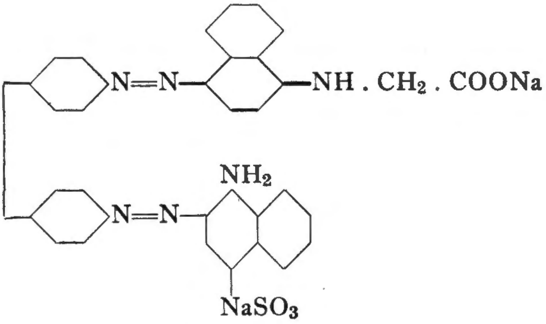
Auramine O



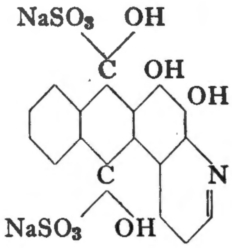
Methyl violet



Aurine



Glycin Red



Alizarin blue bisulphite

---

1. *J.C.S.*, 1922, **121,** 946.
2. *Ber.*, **17,** 772.
3. Barbier: *Bull. Soc. Chim. Franc.*, 1920, **27,** 427; Lumière A. & L. and Barbier: *Bull. Soc. Franc. Phot.*, 1920.
4. Bloch O. and Hamer F. M.: *Phot. Jour.*, 1930, **70,** 374.
5. Smith J. L. B.: *J.C.S.*, 1923, **123,** 2288.
6. B.P. 386,903 (1933).
7. Limpricht and Schwanert: *Ann. d. Chemie*, 1870, **155,** 68; Hubacher: *Ann. d. Chemie*, 1890, **259,** 244.
8. Smith J. L. B.: *J.C.S.*, 1923, **123,** 2288.
9. C.I.B.A.: F.P. 1,039,657 (1953), Swiss prior. 1950.
10. Picus N. and Spoerri P. E.: *J.A.C.S.*, 1948, 3073.

11. Heilbron, Walter and Buck: *J.C.S.*, 1925, **127**, 690.
12. Atkinson and Heilbron: *J.C.S.*, 1926, 670.
13. This aldehyde is prepared by König's method, by treating p-dimethylaminobenzaldehyde dissolved in sulphuric acid with paraldehyde, cold.
14. Jennen J. J. (and Gevaert): F.P. 965,301 (1947–1950).
15. Jeffreys R. A.: *J.C.S.*, 1954, 2221–2230.
16. Nys J.: *27th Cong. Int. Chimie*, Brussels, Aug. 1951, p. 2185.
17. Aubert P., Knott E. B. and Williams L. A.: *J.C.S.*, 1951, 2185.
17b. Agfa: F.P. 886,809.
18. Zenno H.: *Jl. Soc. Sc. Phot. Japan* (in Japanese), 1953, 99.
19. Zhiryakov V. G. and Levkoev I. I.: *Zh. Obsh. Khimii*, 1954, 710–717.
20. Sytnik and coll.: *Zh. Obsh. Khimii*, 1951, 705–711.
21. F.P. 1,089,944 (1954), U.S. prior. 1952.
22. Van Dormael A.: *Bull. Soc. Chim. Belge.*, 1949, 167–182.
23. F.P. Add. 48,226 and F.P. 793,722 (1935–1937).
24. F.P. 864,265 (1939–1941).
24b. Götze, Riester and Ritelen: *Mitt. Forshungslabo. Agfa*, 1955, 56–75.
24c. Agfa: F.P. 1,112,494 (1955), Ger. prior. 6/10/53.
25. Huning S.: *Liebigs Ann.*, 1951, 99–112.
26. Gevaert: F.P. 994,762 (1949–1951).
27. Kendall J. D.: B.P. 428,359.
28. Kodak: F.P. Add. 48,226 (1935–1937).
29. Gaspar B.: F.P. 865,129.
30. Hamer F. M.: *J.C.S.*, 1951, 296.
30b. Van Dormael, Nys and de Leuw: *Bull. Sci. Chim. Belge.*, 1948, 355 and 363.
30c. F.P. 865,131 (1941), Br. Prior. 1939.
30d. Glauert and Mann: *J.C.S.*, 1952, 2135–2144.
31. Knott E. B.: *J.C.S.*, 1954, 1490–1501.
32. Knott E. B.: *J.C.S.*, 1954, 1482–1490.
33. F.P. 829,059.
34. Deichmeister, Levkoev and Lifschitz: *Zh. Obsh. Khimii*, 1953, 1529–1535.
35. Kodak: F.P. 793,722 add. 48,226, p. 18, (1937), U.S. prior. 1935.
36. Kodak: F.P. 907,639 (1940–1943).
37. F.P. 793,722.
38. Van Dormael: *Chim. et Ind.*, July 1954, 73; Gevaert: F.P. 1,099,380 (1955), Belg. Prior. 6/5/53.
39. Gevaert: F.P. 994,762 (1949–1951).
40. Kodak: F.P. 1,086,259 (1954), U.S. prior. 1951.
41. Agfa: F.P. 873,338 (1942).
42. Gevaert: B.P. 632,638, Ger. Prior. 1943.
43. Gevaert: B.P. 646,137 (1947); Van Dormael: *Chimie et Ind.*, July 1954.
44. Gevaert: F.P. 969,827 (1948–50); Van Dormael and Ghys: *Bull. Soc. Chim. Belge.*, 1948, 364.
45. Gevaert: Belg. P. 521,309 (1953); Van Dormael: *Chim. et Ind.*, July 1954.
46. Gevaert: Belg., P. 502,683; Van Dormael and Nys: *Bull. Soc. Chim. Belge.*, 1953, 199.
47. Ilford: B.P. 544,645.
48. Van Dormael A.: *Bull. Soc. Chim. Belge.*, 1949, 167.
49. Gevaert: Belg., P. 508,678 (1952); F.P. 1,070,065 (1954).
50. F.P. 749,239 (1933).
51. B.P. 416,664 and 418,561 (1934).
52. Knott E. B.: *J.C.S.*, 1952, 2399.
53. Zenno H.: *Jour. Soc. Sci. Phot. Japan* Sept., 1954, 1 (in Japanese).
54. Kodak: F.P. 1,078,930 (1954), U.S. priority 1954.
55. Kendall J. D. and Edwards H. D.: B.P. 610,596 (1946).

56. Kendall J. D.: B.P. 428,222 and 428,359.
57. Wizinger R. and Grob-Albrecht V.: *Zeits. Naturforsch.*, 1951, 242.
58. F.P. 834,718 (1938).
58b. F.P. 1,111,518 (1955), Ger. Prior. 5/8/52.
59. *Sci. et Ind. Phot.*, 1936, 329; 1937, 83.
60. F.P. 811,990 (1936) method of preparation.
61. F.P. 865,618.
62. Van Dormael A. and de Cat A.: *Bull. Soc. Chimie Belge.*, 1949, 487 and also Gevaert: F.P. 966,841.
63. Van Dormael (Gevaert): F.P. 963,261, 1947–49.
64. Farbwerke Hoechst: F.P. 1,054,094 (1953), Ger. prior. 1950.
65. Zenno H.: *Jl. Soc. Sci. Phot. Japan*, March 1952, 96–101.
65b. Ogata, Zenno and Nishida: *Reports Sci. Res. Inst. Tokyo*, **28,** 256–263.
66. Van Dormael A., Jacken J. and Nys J.: *Bull. Soc. Chimie Belge.*, 1949, 477.
67. Gevaert: F.P. 965,555 (1950), Belg., prior. 1947.
68. There are two types of rose Bengal—the dichloro and tetrachloro.
69. Gomberg and Tabern: *Jl. Ind. Eng. Chem.*, 1922, **14,** 115 and Mulhausen: *Dinglers Polytechn.*, 1886, **263,** 106; 1887, **266,** 283; 1892, **283,** 234.
69b. Hishika: *Reports Sci. Res. Inst. Tokyo*, 1953, 72–79.
70. *Chrysaniline* and its nitrate; *phosphine* also belong to the acridine group.
71. F.P. 201,798 and 380,487.
72. F.B. 205,459 and *Jl. Soc. Chem. Ind.*, 1892, **11,** 30.

Chapter XL

INFRA-RED SENSITIZATION

THE POLYCARBOCYANINES

776. The infra-red spectrum

The infra-red spectrum begins at the end of the visible spectrum at about 760 mμ, and extends far along the scale to the long wavelengths. However, only the near infra-red region is of direct photographic interest.

Infra-red sources are the *sun*, the *arc lamp* using carbons impregnated with certain metallic salts, and particularly the incandescent *electric lamp*. The emission maximum of a 500 W projector lamp is at 900 mμ. That of an overrun 'photoflood' is between 800 and 850 mμ, whilst that of a clear flash-bulb is at 900 mμ.

In 1815, Fraunhöfer gave the symbol A to the first line in the visible spectrum, situated at 759 mμ in the extreme red. In 1840 Mathiessen, Gladstone and Brewster succeeded in extending the limit of visibility to 820 mμ by placing a cobalt glass, a deep red glass or a solution of iodine in carbon disulphide, in front of the eye; other workers later thought they could go still further.

To explore the infra-red spectrum more precisely, sensitive detection apparatus was needed; among the non-selective instruments used were: the *bolometer* (alteration of resistance of an electric conductor);(1) the *thermopile*; the *radiomicrometer* (moving coil galvanometer in conjunction with a thermocouple); the *radiometer* (blackened vanes turning in an evacuated bulb). The photoelectric cell and the *sensitized photographic plate* are selective detectors. The infra-red sensitive photoelectric cells are made from a crystal of natural molybdenite MoS_2 connected in series with a battery and a galvanometer. The radiation alters the resistance of the crystal depending on the intensity, the wavelength, the temperature, etc. (sensitivity maxima at 700, 800, 1020 and 1800 mμ; some samples are sensitive between 2000 and 4000 mμ).

777. Recording methods

Several diverse methods have been proposed for recording infra-red on ordinary photographic plates.

Phosphorescent method: projection of radiation on to a phosphorescent screen previously exposed to ultra-violet rays; after excitation with U.V. rays the luminescence is allowed to fade, and then the screen is placed in contact with a photographic emulsion. When exposed to infra-red radiation, the screen emits visible radiations which are recorded on the plate. In this way the line at 1529 mμ can be clearly recorded with an exposure of 30 seconds.

The phosphorescent screens which are actually used are of Ca and Sr *sulphides* (sensitivity up to 1700 mμ with a maximum at 1000 mμ), or *zinc sulphide* activated by lead sulphate and traces of Cu and Mn (sensitivity from 1250 to 1600 mμ) or Cu and Co.

The activators play an important role for the phosphorescent emission depends on them. With mixed calcium and strontium sulphides, the activator can be samarium and europium, or samarium and cerium when the emission is orange-red. Using zinc sulphide and manganese, the emission maximum is at 590 mμ.

The U.V. excitation can be carried out using an Osram lamp(2) enclosed in black Wood's glass (emission max. 360 mμ), and the I.R. radiation is obtained with a 60 W lamp together with a Schott U.G.U. 2·5 mm filter which passes only the wavelengths above 900 mμ.

Evaporation method: The evaporation of a very thin layer of a slightly volatile substance, exposed under reduced pressure, records to 10 μ.(3) The image is formed by interference effects of thin films of varying thickness. Suza and Yosihara use smokes.(4)

Reversal effect. The reversal effect produced by infra-red radiation on a photographic layer which has already been exposed to short wavelength radiation was disclosed long ago by Herschell and Draper. Waterhouse used wet collodion plates stained with certain dyes (see para. 214). Millochau made similar experiments using plates treated with *malachite green* (up to 930 mμ). Other dyes giving comparable results are *iodine green*, *brilliant green* and *safranine*.

For example, a plate treated with a 4:100,000 aqueous-alcoholic solution of iodine green, then exposed at 10–40 b.m.s. can record on a spectrograph up to 1130 mμ with an exposure of 3 hours.

778. Direct photographic methods

The first direct infra-red photographs were made by Abney using a special collodion emulsion (which probably contained colloidal silver). Ritz(5) was able to reach 1400 mμ using the same method.

Alizarin blue bisulphite and *nigrosine* sensitize gelatino-silver bromide emulsions and enable the sodium line at 816 mμ to be recorded with an exposure of a few seconds whilst the 860 mμ Ca line can be recorded in one minute.

Colour sensitization with cyanines has resulted in the abandoning of the old methods.(6) The synthesis of *dicyanine* (1905) then *kryptocyanine* (1919) and *neocyanine* (1925) and finally the *di-*, *tri-*, *tetra-* and *pentacarbocyanines* enabled the near infra-red to 1300 mμ, and even further, to be easily and rapidly recorded. The general sensitivity of emulsions is considerably diminished by the infra-red sensitizers.

779. Applications

The applications of infra-red photography are very numerous.

We will first note the *determination of chemical functions* by studying their spectral absorptions; every change in the molecule is accompanied by a change in the spectrum.

Spectrographic analysis, the differentiation of isotopes and stellar spectrography.

In *astronomy* it has been shown that certain stars, such as Acturus, emit a large amount of infra-red radiation, and that the hydrogen of the hot stars gives two groups of characteristic lines: the Balmer group in the ultra-violet and the Paschen group between 820 and 880 mμ. The recording of the calcium lines between 850 and 870 mμ has also enabled important observations to be made. Again using spectrographic methods, it has been possible to show that carbon dioxide is present in Venus's atmosphere, and that methane and ammonia gas are present in those of Saturn and Jupiter.

In *photography*, infra-red radiation is hardly affected by fog and smoke. This enables detailed pictures to be made, and the previously diffused long-distance shots become clear. Aerial photography is an important application of this phenomenon.

The *reflecting power* of different substances varies with their nature; the appearance of infra-red photographs is therefore very different from normal ones; thus it has been shown that the sky, which transmits little infra-red, appears dark and that the green substance in plants appears very light, chlorophyll and its cellulose support do not absorb long wavelength radiations (700–870 mμ). The mountain plants which grow in strong light reflect twice as much infra-red as the plants of the valleys.(7)

Night effects in photographs taken in broad daylight are therefore easily made with an infra-red sensitive film and a colour filter.

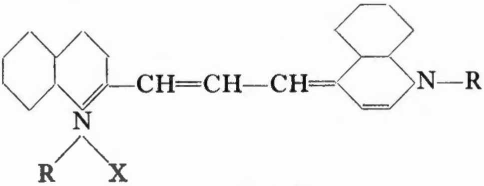
We would finally point out the applications of variations in absorption and reflection of infra-red in the photography of *biological* and *anatomical* specimens (the blood vessels are transparent whilst the fibres of the nervous system are opaque), in *biological investigations* (canker in potato plants, for example), in *paleontology*, *metallography*, and the examination of *manuscripts*, *fabrics*, etc. For cinematography, 500 W projector lamps can be used with suitable filters (see 3rd part). The illumination on the subject is between 10,000 and 40,000 lux. The focus must be corrected.(8)

2:4′ AND 4:4′-CARBOCYANINES

The 2:4′- and 4:4′-carbocyanines are related to the true carbocyanines, differing from them in the positions of the nucleus as the linkage in 2:4′ then in 4:4′ further increases the distance between the two nitrogen atoms. This increase in the chain length between the two nitrogen atoms results in a displacement towards the infra-red and consequently gives sensitizers for the region from the far red to 900 mμ (Fig. 132).

780. Dicyanines

The dicyanines are the 2:4′-carbocyanines.(9)



Dicyanine

These dyes were the earliest infra-red sensitizers; they were prepared in 1905 by König and Philips. The dicyanines have the disadvantage that they *do not keep well* and are difficult to use (the nitrate is used rather than the iodide).

The absorption spectrum of the dicyanines comprises a principal band with a sharp maximum at about 670 mμ, and two secondary bands. The *sensitizing*

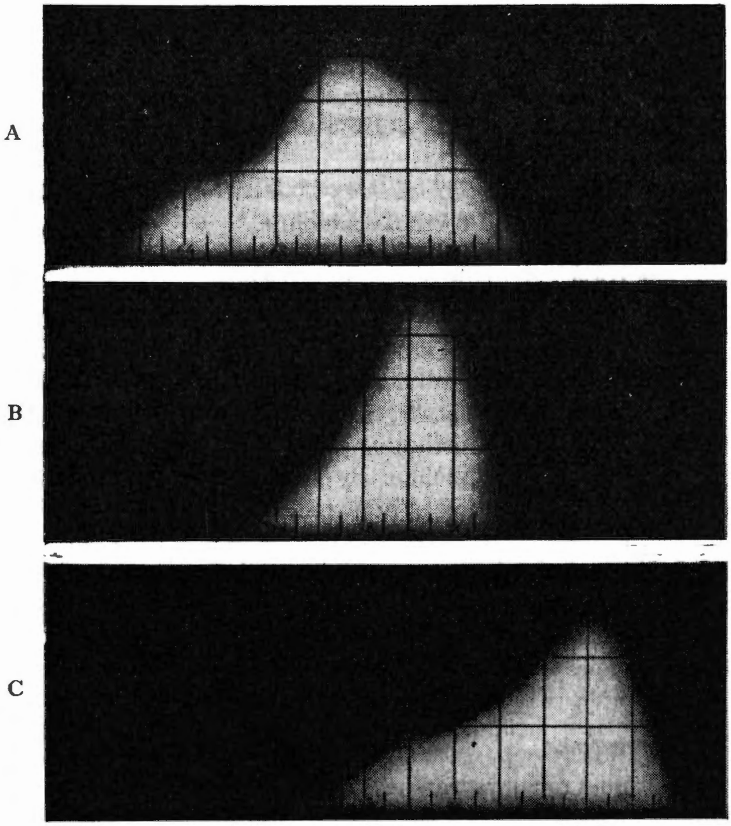


Fig. 132. Sensitization:
A. Dicyanine A; B. Kryptocyanine; C. Neocyanine.

action extends to 810 mμ (for dicyanine A) but the maximum is only at 715 mμ.

Preparation

(*a*) Condensation at room temperature of a *2:4-dimethylquinoline* ethiodide or ethyl nitrate with sodium in absolute methanol, and in the presence of a current of air. Reaction time 16–60 hours. Temperature 10°C. The dye is recrystallized from methanol.

(*b*) Condensation of *2:4-dimethylquinolines* with *ethyl orthoformate* in *pyridine*.

(*c*) Condensation of *quinaldine alkyl iodide* with *diphenylformamidine* at 100°C then further condensation of this product with a *lepidine alkyl iodide* in the presence of 4 molecules acetic anhydride and 1 molecule sodium acetate (25 minutes).

(*d*) *di-o-formylmethylaminodiphenyl disulphide* is treated with a mixture of quinaldine and lepidine ethyl nitrates. In addition to the carbocyanines, a thiopseudocyanine and a thioisocyanine are produced.

The following dicyanines have been prepared:

1:1′-diethyl-2:4′-carbocyanine from quinaldine and lepidine.

1:1′-diethyl-2′:4-dimethyl-2:4′-carbocyanine from 2:4-dimethylquinoline.

2′:4:6:6′-tetramethyl-1:1′-diethyl-2:4′-carbocyanine (dicyanine) obtained using 2:4:6-trimethyl quinoline.

1:1′-diethyl-2′:4-dimethyl-6:6′-diethoxy-2:4′-carbocyanine or dicyanine A. Prepared with 2:4-dimethyl-6-ethoxyquinoline.

Mileska and Adams(10) have also prepared the derivatives of 2:4:6:8 , 2:4:5:7- and 2:4:5:8- tetramethylquinoline without any particular advantage, however.

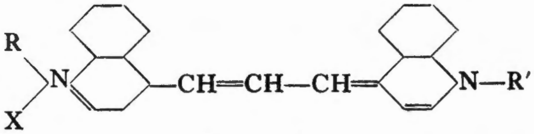
The starting *quinoline bases* are most frequently methylated in the 4-position. The condensation of ethylidene acetone with aniline, discovered by Baeyer(11) was modified by Mikeska, Stewart and Wise for the preparation of 2:4-dimethylquinoline. By substituting p-toluidine for aniline, Pfitzinger(12) obtained 2:4:6-trimethyl quinoline. By starting with p-phenetidine, 2:4-dimethyl-6-ethoxyquinoline can be prepared.(13) The 2:4-dimethylquinolines give better dicyanines than the simple bases.

The ethiodides of the bases, treated with silver nitrate in hot absolute alcohol, yield the corresponding *ethyl nitrates* by precipitating silver iodide which is filtered off.

Bathing technique was used with dicyanines.

781. Kryptocyanines

The kryptocyanines or rubrocyanines are 4:4′-carbocyanines. They are more powerful and more stable than the dicyanines; their action, which normally extends to 790 mμ with a maximum at 743 mμ with a 1:500,000 bath, can go as far as 910 mμ with long exposures.



Kryptocyanine

The kryptocyanines were discovered by Adams and Haller by treating a *lepidine* alkyl iodide with alkali in alcoholic solution in the presence of chloroform or formaldehyde with air excluded.⁽¹⁴⁾

The kryptocyanines are also obtained by the general ethyl orthoformate method. In pyridine, the yield is 35–42%, in benzyl alcohol 67%, and in propionic acid 67%.

Preparation of 1:1′-diethyl-4:4′-carbocyanine: 5·98 g lepidine⁽¹⁵⁾ ethiodide in 400 cc 95% ethyl alcohol is boiled under reflux. When all the air has been expelled by the alcohol vapour, a freshly prepared mixture of 20 cc N sodium ethoxide and 1 cc 40% formalin is slowly added over 20 minutes. Heating is continued for 10 minutes and the stoppered flask is allowed to cool slowly. The solid which separates is sucked dry, washed with 80% alcohol, then with an alcohol-ether mixture and finally with pure ether. Yield, 0·43 g black powder.

Second method. Two molecules of the lepidine salt are treated with 4 molecules ethyl orthoformate, following the general scheme already described, but replacing the pyridine with *benzyl alcohol*. The dyestuff which is precipitated by adding water is recrystallized from alcohol.

Third method: 375 cc of an alcoholic sodium sulphide solution containing 20·4 g Na_2S are heated to 50°C. 11·55 g lepidine ethiodide is added with stirring followed by 33 g chloroform. Heating at 50°C is continued for 30 minutes and the solution filtered. After 13 days 5·9 g of the crude dye (yield, 63%) is obtained which can be used as it is.

Kryptocyanine is also obtained as a by-product in the filtrate from the preparation of diethylthiaisocyanine with di-o-formylmethylaminodiphenyl disulphide.

Kryptocyanine is dried at 100°C and 15 min.

Absorption: double band with maxima at 690 and 693 mμ and a lesser band at 640 mu.

Sensitizing action in the far red or near infra-red from 650 to 790 mμ with maximum at 743 mμ.

Other kryptocyanines:

1:1′-dimethyl-4:4′-carbocyanine. Feeble sensitization accompanied by fog.

1:1′-dialkyl-4:4′-carbocyanine. Strong sensitization especially with bathing. Maximum at 755 mμ.

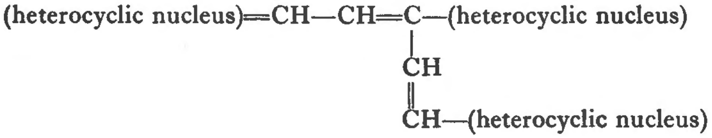
1:1′:6:6′-tetramethyl-4:4′-carbocyanine. Obtained from p-tolulepidine. Similar action to ordinary kryptocyanine.

For the preparation of lepidine, see para 262.

782. Neocyanines

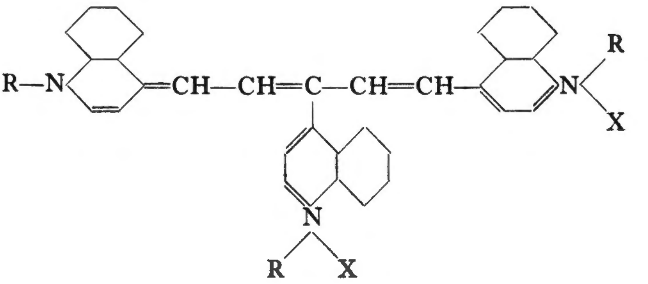
The neocyanines (or allocyanines) are chain-substituted dyes. They were prepared by Ogata in 1924, then isolated by T. Clarke in 1925, from the less soluble products in the preparation of kryptocyanine. They are very stable, and this enables them to be incorporated in the emulsion. Their sensitizing action in the near infra-red extends from 680 to 880 mμ for moderate exposures, and up to 900 mμ for long exposures. By hypersensitizing, 1160 mμ can be reached. The sensitization maximum for ordinary neocyanine is at 824 mμ. Absorption maximum at 760 mμ.

Constitution. Kendall (*J.C.S.*, 1948, 690) considered the neocyanines as 4:4′-carbocyanine substituted in the chain by a third heterocyclic nucleus with the formula:



$$\begin{array}{l}\text{(heterocyclic nucleus)}{=}CH{-}CH{=}\overset{}{C}{-}\text{(heterocyclic nucleus)}\\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad |\\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad CH\\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad \|\\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad CH{-}\text{(heterocyclic nucleus)}\end{array}$$

According to Miss Hamer, the neocyanines are *dicarbocyanines* in which the chain (with 5 links) is substituted by direct contact with a third nucleus (*J.C.S.*, 1947, 1434). They have three extreme resonance forms of which the most characteristic is the following:



Neocyanine (after Miss F. M. Hamer)

The two conceptions result from the two different methods of preparation which give equally good results. Kendall's method, for example, in the preparation of a benzthiazole neocyanine, is to condense 3:3′-diethylthiacarbocyanine iodide with 2-methylbenzthiazole methiodide in the presence of ethyl trithio-orthoformate in acetic anhydride. In this way, unsymmetrical neocyanines can be obtained with three different nuclei. However, Miss Hamer has also prepared neocyanines starting with dianil derivatives containing the group $=CH-\overset{\|}{C}-CH=$ (especially the thiazole and selenazole neocyanines) which appears to confirm her formula.

Preparation. Many neocyanine type dyes have been prepared by Miss Hamer⁽¹⁶⁾ by the general method using ethyl *orthoformate*: by reacting the orthoester on *lepidine ethiodide* in the presence of pyridine, 42% kryptocyanine and 17% neocyanine are obtained. But if the condensation is carried out with *lepidine p-toluene-sulphonate*, the yields are altered: 7% kryptocyanine and 26% neocyanine. By precipitating the dye with ammonium bromide, the neocyanine yield is increased to 37% for the ethyl derivative and 41% for the methyl.

The solvent plays an important part. A reduction of solvent favours the formation of neocyanine.

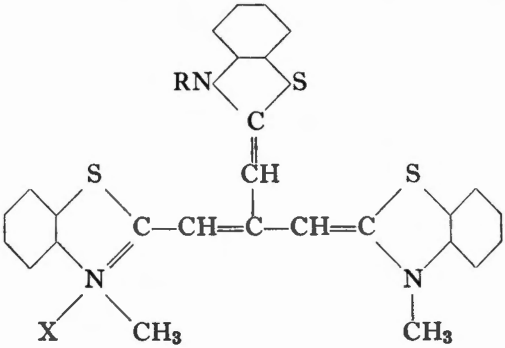
Ethylneocyanine:⁽¹⁷⁾ 56 g lepidine (2 mol) and 78·3 g ethyl p-toluene-sulphonate $CH_3—C_6H_4—SO_3 . C_2H_5$ are heated to 140–150°C for 3 hours. The product is then poured into a boiling solution of 130 cc ethyl orthoformate and 270 cc pyridine for 3 hours. This is then poured into a boiling solution of sodium bromide (37 g in 200 cc water). The precipitated dye is extracted three times with 100 cc boiling alcohol and the residue is recrystallized from 3 litres alcohol (yield, 35%). The first alcoholic solution yields 5% kryptocyanine (bromide) and the two following, 2% neocyanine. The ethylneocyanine bromide is obtained as small bronzed dark green crystals M. Pt. 291°C with decomposition.

Mesomethylcarbocyanines can be condensed with heterocyclic bases bearing an *aldehyde* or *anil* reactive chain: the resulting products are neocyanines (Miss Hamer).⁽¹⁸⁾

The *dicarbo-neocyanines* have dissimilar nuclei when a *dianilisopropylidene* base is condensed with two molecules of quaternized, methyl base of other type.⁽¹⁹⁾ They are poor sensitizers, or even desensitizers.

Another method of synthesis of neocyanines is to react the quaternary salt of a methyl base, with the quaternary salt of a base having a *vinyl chain, substituted in β with a heterocyclic nucleus*, in the presence of sodium ethoxide.

Synthesis of neocyanines by means of ethyl *trithio-orthoformate* was disclosed by Kimura in 1937:⁽²⁰⁾ an intermediate ethylthiovinyl compound is formed, first. Van Dormaël and Ghys⁽²¹⁾ found it simpler to react the salt of a cycloammonium base having a reactive *alkylmercapto* group, and a mesomethylcarbocyanine. In that case, the resulting dye has the following structure:



For other operating methods, see ⁽²²⁾.

DICARBOCYANINES

783.

The *dicarbocyanines* (pentacarbocyanines according to German nomenclature) have a chain with fine methine —CH= groups —CH=CH—CH= =CH—CH= (or $—(CH=CH)_2—CH=$).

The *increase in the length of the carbon chain* by inclusion of a further vinyl chromophore —CH=CH—, results in a deepening of the colour by *displacement of the absorption bands towards the infra-red* compared with the simple carbocyanines.

We know that to prepare the latter compounds, two molecules of a methyl heterocyclic base are condensed with a compound which provides the central —CH= group in the chain. With the dicarbocyanines, the problem is to introduce the group —CH=CH—CH=. This can be done by four methods of synthesis.

(*a*) König disclosed in 1922 that *malonic dialdehyde* $CHO—CH_2—CHO$, or better still, *β-ethoxyacrolein acetal* $C_2H_5O—CH=CH—CH=(OC_2H_5)_2$ can be condensed with two molecules of a *nitrogenous heterocyclic base* containing a *reactive methyl group.*⁽²³⁾ β-ethoxyacroline acetal is considered, in short, as a homologue of ethyl orthoformate $C_2H_5O—CH=(OC_2H_5)_2$. The condensation is carried out by heating the constituents in pyridine.

(*b*) *Propargylic* (or propiolic) *aldehyde* $CH\equiv C—CHO$ gives *propargylic* acetal $CH\equiv CH=(OC_2H_5)_2$ which can condense with two molecules of a methyl heterocyclic base in pyridine. One H from a methyl group of the base becomes attached to the central carbon atom which therefore frees one of the bonds of the $CH\equiv$ which becomes —CH=.

(*c*) *Malonic dialdehyde* $CHO—CH_2—CHO$ indirectly produces α-bromo-β-anilidoacrolein anil $C_6H_5N=CH—CBr=CH—NH . C_6H_5$ which is a homologue of diphenylformamidine $C_6H_5N=CH—NH . C_6H_5$. The anil is obtained when mucobromic acid CHO—CBr=CBr—COOH is treated with aniline in alcoholic solution.⁽²⁴⁾

Beattie, Heilbron and Irving⁽²⁵⁾ obtained dicarbocyanines by condensing two molecules of quinaldine (or other base) alkyl iodide with a molecule of this anil in *pyridine* in the presence of piperidine or in acetic anhydride in the presence of potassium acetate.

$$\text{Base—CH}_3 + C_6H_5N{=}CH—CBr{=}CH—NH—C_6H_5 + CH_3\text{—Base} \longrightarrow$$
$$\longrightarrow \text{Base—CH=CH—CH=CH—CH=Base} + HI + 2C_6H_5NH_2$$

(*d*) The preceding reaction can be carried out in an identical manner with non-halogenated β-anilinoacrolein anil $C_6H_5N=CH—CH=CH— —NH . C_6H_5$ which is obtained by heating propargylic aldehyde with aniline hydrochloride following the reaction

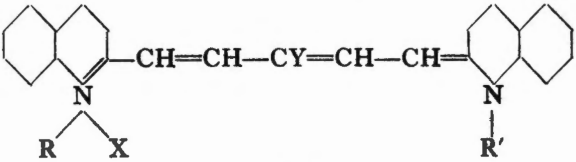
$$CH\equiv C—CHO + 2C_6H_5NH_2HCl \longrightarrow$$
$$C_6H_5NH—CH{=}CH—CH{=}NC_6H_5 + H_2O + HCl$$

To obtain the *unsymmetrical dicarbocyanines* the base alkyl iodide is first condensed with a molecule of anil by warming (as with diphenyl formamidine). The compound Base—CH=CH—CH=CH—(NHC$_6$H$_5$) will combine with another molecule of a heterocyclic base in the presence this time of an excess of acetic anhydride (4 mol) and sodium acetate or in pyridine in the presence of piperidine.

Mucobromic acid which is used to prepare the brominated acrolein anil is obtained by Simonis' method(26) starting with furfural treated with bromine. 100 g of bromine is slowly added to 10 g furfural, while the flask is gradually heated to gentle boiling. When all the bromine is in, boiling is continued 15 minutes more. After cooling, the solid mucobromic acid is dissolved in ether. The latter is evaporated and the crude product is recrystallized from hot water and dried. It is further purified by dissolving in anhydrous ether then precipitated by addition of ligroin. M. Pt. 125°C.

784. Principal dicarbocyanines

The following *dicarbocyanines* have been prepared by the above methods. They have the general formula:



Dicarbocyanine

in which the quinoline nuclei may be replaced by thiazole, selenazole, oxazole or indoline and Y by H, a halogen or other substituent.(27)

1:1'-diethyl-11-bromo-2:2'-dicarbocyanine, obtained by treating 20 g quinaldine ethiodide and 8·5 g α-bromo-β-anilidoacrolein anil with 3 cc piperidine in 70 cc pyridine. After refluxing for 1 hour, the dye precipitates on cooling and is recrystallized from alcohol.

Absorption maximum 700 mμ (pinacyanol 607 mμ). Very active far red and infra-red sensitizer with maximum at 755 mμ.

The *4:4'-diphenyl derivative* is not such a strong sensitizer (absorption maxima at 730 and 700 mμ).

1:1'-diethyl-2:2'-dicarbocyanine: prepared by heating quinaldine ethiodide with an excess of propargylic aldehyde acetal or β-ethoxyacrolein acetal for 3 hours in pyridine. This is removed by distilling at reduced pressure and the dye is recrystallized from alcohol.

Sensitizing action from 640 to 760 mμ.

1:1'-diethyl-11-bromo-4:4'-dicarbocyanine. This corresponds to kryptocyanine. It is obtained from lepidine, 10 g lepidine ethiodide, 7·2 g α-bromo-β-anilino-acrolein anil (hydrobromide), 2·5 cc piperidine and 75 cc pyridine are boiled for 2 mins.

The 4:4′-position again displaces the maximum absorption towards the longer wavelengths (800 mμ). Sensitization maximum at 840 mμ.

1:1′-diethyl-6′-ethoxy-4:4′-dicarbocyanine. Obtained starting with p-ethoxy-lepidine, following the general method for unsymmetrical dicarbocyanines. Strong sensitization from 740 to 915 mμ (Fig. 133).

3:3′-diethyl-10-bromothiadicarbocyanine. Absorption maximum at 645 mμ. Sensitization maximum at 690 mμ. The simple thiadicarbocyanines are effective only in the far red region.

Better results are obtained with the substituted derivatives:

3:3′-diethyl-5:6:5′:6′-tetramethoxythiadicarbocyanine.(28) Strong sensitizing action from 630 to 790 mμ (Fig. 133).

3:3′-diethyl-6:6′-dimethoxythiadicarbocyanine. Powerful sensitizing from 610 to 765 mμ.

3:3′-diethyl-4:5:4′:5′-dibenzothiadicarbocyanine. Obtained starting with 2-methyl-β-naphthothiazole. Sensitizes 70 mμ further into the infra red

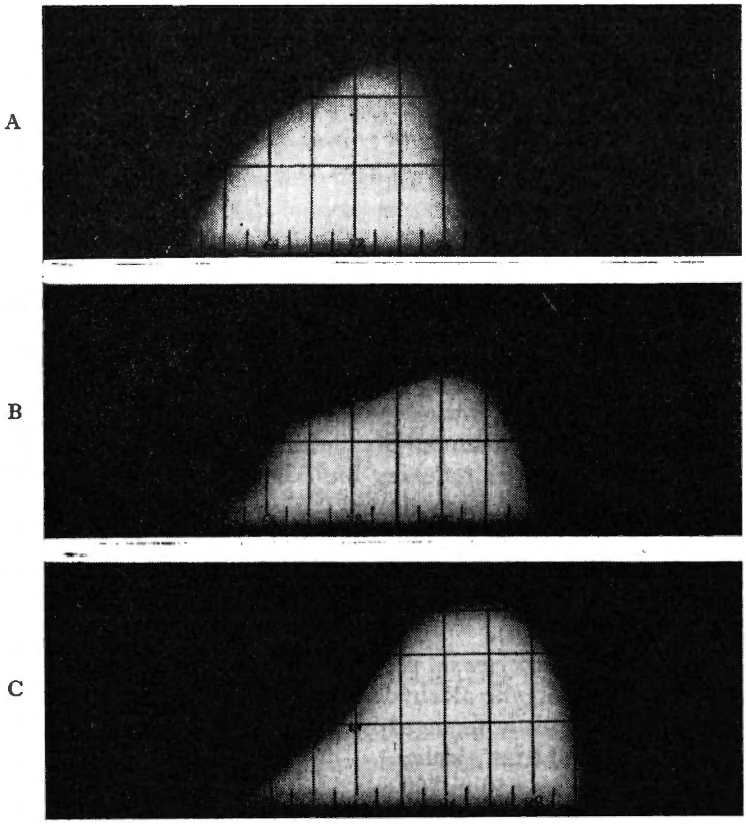


Fig. 133. Sensitization by dicarbocyanines.

(A) 2 . 2′ diethyl 4 : 5 : 4′ . 5′ tetramethoxy . thio . dicarbocyanine;
(B) 2 . 2′ diethyl 3 : 4 : 3′ . 4′ . dibenzothiodicarbocyanine;
(C) 1 . 1′ diethyl 6 ethoxy 4 : 4′ dicarbocyanine (scale displaced to the left).

than the simple thiadicarbocyanine. Its action extends from 630 to 820 mμ (Fig. 133). That of the 6:7:6′:7′- derivative is more restricted—from 650 to 780 mμ.

3:3′-diethyl-6:6′-dimethoxy-4:5:4′:5′-dibenzothiadicarbocyanine.(29) Action extends as far as 825 mμ.

3:3′-diethyl-10-chlorooxadicarbocyanine. 10 g 2-methylbenzoxazole ethiodide are added in 5 minutes to a stirred, boiling solution of 4·4 g α-chloro-β-anilinoacrolein anil and 1·7 g sodium acetate in 100 cc acetic anhydride. The dye is recrystallized after cooling.

Absorption maximum at 580 mμ. Sensitizes in the yellow and red with maxima at 560 and 615 mμ.

3:3′-diethylselenadicarbocyanine. Sensitization from 640 to 760 mμ with maximum at 685 mμ.

1′-methyl-2-ethylselenadicarboquinocyanine. Sensitizing action extends to 840 mμ.

Other dicarbocyanines contain a selenazole nucleus and a thiazole nucleus and also one or two indoline nuclei. Finally the dyes analogous to the *neocyanines* with a heterocyclic substituent at the central carbon atom can also be obtained.

The dicarbocyanines with a meso methyl substituent have been prepared by Hamer and Rathbone (*J.C.S.*, 1945, 595), after the I. G. Farben, Kendall (B.P. 390,808 and 553,144) and Sitnik and Steingardt (*Jl. Appl. Chem.*, U.S.S.R., 1936, 1842). The intermediates are: β-anilido-α-methylacraldehyde-anil hydrochloride, for γ-substituted dicarbocyanines, and the crotonaldehyde derivative, for β-substituted dicarbocyanines.

TRICARBOCYANINES(30)

785.

The *tricarbocyanines* have a chain of 7 —CH= groups:

$$\text{—CH=CH—CH=CH—CH=CH—CH=}$$

giving one vinyl group —CH=CH— more than the dicarbocyanines:

$$\text{—(CH=CH)}_3\text{—CH=}$$

Prepared independently by Wahl(31) (1928), Piggot and Rodd, and Misses Hamer and Fisher, the tricarbocyanines are compounds unstable to heat which have absorption bands displaced towards the long λ relative to the dicarbocyanines, which results, as we know, from an increase in the length of the chain. The displacement is about 200 mμ relative to the monocarbocyanines. Whilst the dicarbocyanines are effective more or less up to 910 mμ, the *tricarbocyanines sensitize up to 1100 mμ.*

786. Preparation of the tricarbocyanines

Two molecules of a quaternary salt of a nitrogenous heterocyclic base are condensed with a compound capable of providing a chain of five —CH=

groups, the other two links being provided by the reactive methyl groups of the base. These condensing compounds comparable with diphenylformamidine or β-anilinoacrolein anil are *2:4-dinitrophenylpyridinium chloride* and *glutaconic aldehyde dianil hydrochloride.*

2:4-dinitrophenylpyridinium chloride, $C_5H_5N \cdot Cl{-}C_6H_3(NO_3)_2$ is prepared by heating 100 g 2:4-dinitrochlorobenzene with 80 cc pyridine at 100°C for 12 minutes then crystallizing the solid from boiling absolute alcohol.

The pyridine nucleus of this compound can be split by the action of an alkali to produce, in the enolic form, glutaconic aldehyde or the hydrochloride of its dianil.

The glutaconic dialdehyde dianil hydrochloride has the formula

$$C_6H_5N{=}CH{-}CH{=}CH{-}CH{=}CH{-}NHC_6H_5 \cdot HCl$$

It is prepared by heating 80 g of aniline with 80 g of 2:4-dinitrophenylpyridium (chloride) in 160 cc alcohol. The solid obtained is washed with acetone and dried under reduced pressure at 60–80°C. The aniline can be replaced by toluidine, naphthylamine, etc.

The *condensation* to the tricarbocyanine can be carried out in six different ways:

(*a*) *Dinitrophenylpyridinium chloride* dissolved in absolute alcohol is treated with 1 mol sodium also dissolved in absolute alcohol. The alkyl iodide of the base (in alcohol) is added to the product which is heated for 10–20 minutes. The dye precipitates on cooling and is washed with water, then extracted with ether and acetone and recrystallized from methanol.(32)

(*b*) One mol of *glutaconic aldehyde dianil hydrochloride* is dissolved in boiling alcohol with two mols of the alkyl iodide of a heterocyclic base containing a reactive methyl group. One mol sodium (in absolute alcohol) is then added with stirring. After boiling for a few minutes the solution is allowed to cool.(33) Better yield than previous method: 45–50% instead of 25–28%.

(*c*) The alkyl iodide of the base is dissolved in boiling acetic anhydride; the dianil is added with 2 mols anhydrous sodium acetate. After boiling for 10–20 minutes, the liquid is poured into a solution of potassium iodide. The precipitate is washed with ether and recrystallized from methanol.

(*d*) The same scheme as (*c*) is used but the alkyl halide of the base is replaced by the corresponding methylene derivative: 1:3:3-trimethyl-2-methylene-indoline, 3-alkyl-2-methylene-benzothiazole, etc.

(*e*) Two mols of the alkylhalide of the base are condensed with 1 mol of the dianil in *pyridine* with an excess of *piperidine.* The reaction can be carried out at 18–20°C, leaving until the precipitate is formed.

(*f*) The *unsymmetrical tricarbocyanines* are prepared by condensing 1 mol of the alkyl iodide of the base with 1 mol of the dianil in hot alcohol, acetic anhydride, or even without solvent. The reaction product is treated with 1 mol of another base in the presence of anhydrous sodium or potassium acetate in acetic anhydride. The methylene base can also be used.

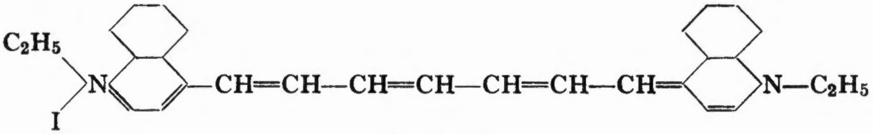
787. Principal tricarbocyanines

The following *tricarbocyanines* are among those which have been prepared:(24)

1:1′-diethyl-6:6′-dimethyl-2:2′-tricarbocyanine.(35) Absorption maximum at 820 mμ.

1:1′-diethyl-2:2′-tricarbocyanine. Absorption at 810 mμ. Sensitizes from 700 to 915 mμ.

1:1-diethyl-4:4′-tricarbocyanine (Brooker's Xenocyanine(36) and Agfa 960). Prepared from lepidine ethiodide in *pyridine* at room temperature in the presence of piperidine.



Xenocyanine

Its solutions are very unstable. The crystals are kept in ether. Powerful sensitization (by incorporation) up to 1060 mμ with maxima at 980 and 860 mμ.

The diallyl, dibutyl and dipropyl derivatives have also been prepared.

3:3′-diethylthiatricarbocyanine. Remarkable sensitization, superior to that of kryptocyanine extending from 680 to 870 mμ with maximum at 810 mμ. Absorption maximum at 765 mμ (Fig. 134).

3:3′-diethyl-6:6′-diethoxythiatricarbocyanine(37) prepared from 2-methyl-6-ethoxybenzothiazole. Strong sensitization from 650 to 835 mμ with maximum about 818 mμ.

3:3′-diethyl-5:6:5′:6′-tetraethoxythiatricarbocyanine. Good sensitizer from 680 to 920 mμ with maximum at 828 mμ. The 5:5′-dimethyl, 5:5′-diethyl, 6:6′-diethyl, 5:6:5′:6′-tetramethyl, 5:6:5′:6′-tetraethyl, etc., derivatives have also been prepared.(38)

3:3′-diethyl-6:6′-diacetylaminothiatricarbocyanine. Sensitization from 700 to 880 mμ (Fig. 134).

3:3′-diethyl-4:4′-bis-diethylaminothiatricarbocyanine. Weak sensitization extending from 750 to 915 mμ. With certain thiatricarbocyanines, the 6 and 7 positions of the benzene nucleus are substituted by dihydroxymethylene or dihydroxyethylene, the central carbon of the chain ultimately containing a methyl group.(39)

3:3′-diethyl-6:7:6′:7′-dibenzothiacarbocyanine. Prepared from 2-methyl-α-naphthothiazole. Remarkable sensitization from 800 to 900 mμ with a maximum at 860 mμ (Fig. 134). Similar results are obtained with 4:5:4′:5′-dibenzo compound prepared with 2-methyl-β-naphthothiazole.

3:3′-diethylthiazolintricarbocyanine. The absorption maximum is reduced, due to the lighter nucleus, to 645 mμ. The sensitization is then situated at 600–760 mμ with a maximum at 700 mμ.

A whole series of *unsymmetrical tricarbocyanines*(40) can be prepared by method (*f*). They are generally very active sensitizers.

The *selena derivatives* are prepared like the thiatricarbocyanines.

3:3'-diethylselenatricarbocyanine sensitizes from 660 to 800 mμ, and *3:3'-diethyl-5:6:5':6'-tetramethylselenatricarbocyanine* from 720 to 890 mμ.

3:3'-diethyl-5':6'-dimethylselenathiatricarbocyanine. Prepared from one molecule of 2-methylbenzothiazole and one molecule of 1:4:5-trimethylbenzoselenazole. Sensitizes up to 885 mμ. The benzothiazole can be replaced by a thiazole or α-picoline.

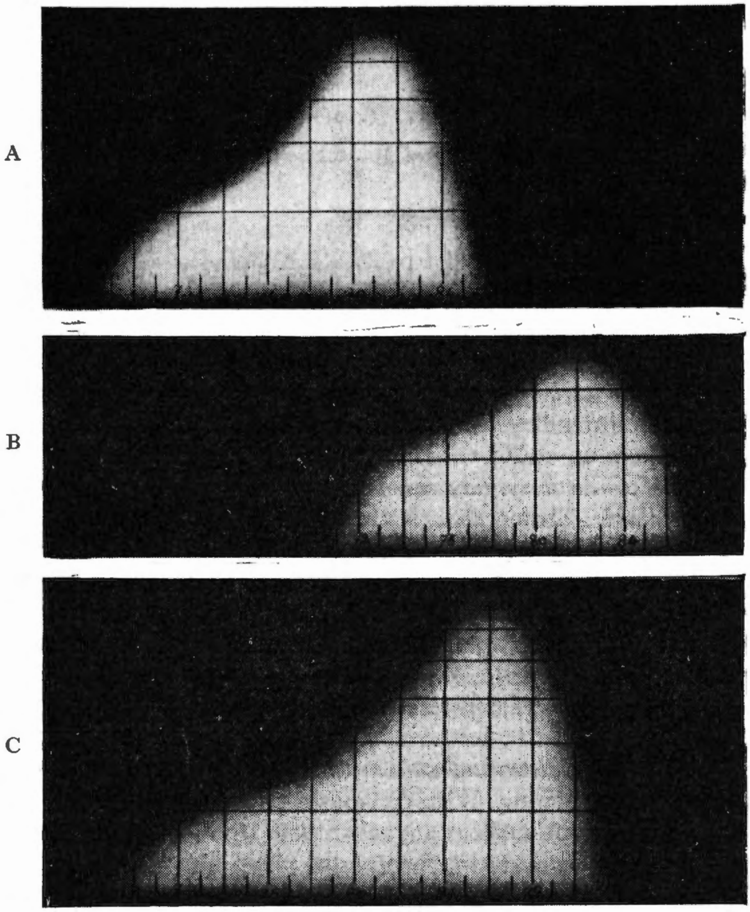


FIG. 134. Sensitization by tricarbocyanines.

(A) 2 . 2' diethyl thiotricarbocyanine;
(B) 3 . 3' diethyl 6 . 6' diacetylaminothiatricarbocyanine;
(C) 3 . 3' diethyl 6 : 7 : 6' : 7' dibenzothiatricarbocyanine.

1:1':3:3:3':3'-hexamethylindotricarbocyanine.(41) Absorption maximum at 740 mμ. Sensitizing action from 750 to 850 mμ with maximum at 795 mμ.

The *oxatricarbocyanines* have been described by G. H. Keyes (F.P. 848,215). They are obtained from a methylbenzoxazole salt treated with a dianil in the presence of acetic anhydride, the resulting product being condensed with a second molecule of a methylbenzoxazole quaternary salt. Maximum action about 750 mμ.

Tricarbocyanines with methyl in the chain. Hamer and Rathbone have prepared tricarbocyanines with a methylated chain starting with the methyl pyridines: α-picoline (or α-methylpyridine) reacts with cyanogen bromide, then with aniline in the presence of hydrobromic acid, giving the compound (*J.C.S.*, 1947, 960)

$$\mathrm{(Ph)N{-}C(CH_3){=}CH{-}CH{=}CH{-}CH{-}N(Ph)H\ .\ HBr}$$

which is condensed in piperidine at a low temperature with methyl benzthiazole ethiodide to give the corresponding thiatricarbocyanine

$$\underset{\mathrm{Et}}{\mathrm{(Benzthiazole)}}\mathrm{{=}CH{-}C(CH_3){=}CH{-}CH{=}CH{-}CH{=}CH{-}}\underset{\mathrm{Et\ I}}{\mathrm{(Benzthiazole)}}$$

With αα-lutidine, β-picoline, γ-picoline and γ-lutidine respectively, the following substitutions are obtained

$$\mathrm{{=}CH{-}C(CH_3){=}CH{-}CH{=}CH{-}C(CH_3){=}CH}$$

$$\mathrm{{=}CH{-}CH{=}C(CH_3){-}CH{=}CH{-}CH{=}CH{-}}$$

$$\mathrm{{=}CH{-}CH{=}CH{-}C(CH_3){=}CH{-}CH{=}CH{-}}$$

$$\mathrm{{=}CH{-}C(CH_3){=}CH{-}C(CH_3){=}CH{-}CH{=}CH{-}}$$

The action of these substituents is:

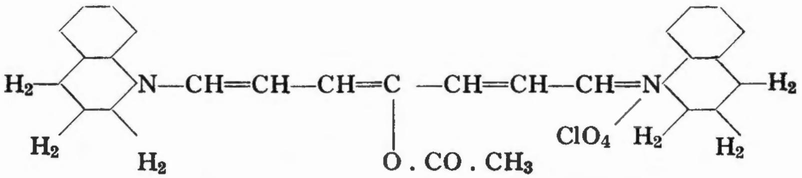
	Absorption					
Substituent	*None*	β	γ	δ	ββ	βδ
Thiatricarbocyanine	762	765	761	790	772	706
Tetramethoxythia	800	—	—	—	790	—
Dibenzothia	797	—	—	825	820	—
Selenatricarbocyanine	770	—	770	800	797	—
Thiazolinotricarbocyanine	645	—	—	675	—	658

TETRACARBOCYANINES (or nonacarbocyanines)

788.

The tetracarbocyanines have a 9-carbon atom chain $\mathrm{{-}CH{=}CH{-}CH{=}CH{-}CH{=}CH{-}CH{=}CH{-}CH{=}}$ or $\mathrm{{-}(CH{=}CH)_4{-}CH{=}}$. The absorption maxima are shifted towards the longer infra-red wavelengths compared with the tricarbocyanines.

The possibility of obtaining the tetracarbocyanines was noted by Eggert.⁽⁴²⁾ The reactive compound must contain a very long chain of 7 carbon atoms joined by conjugated double bonds. For this purpose, 4-acetoxy-$\Delta^{3.5}$-heptadiene-1:7-dial-di-tetrahydroquinolide perchlorate, prepared by König(43) is used.



This compound is condensed with an alkyl p-toluene-sulphonate of the nitrogenous heterocyclic base:

(*a*) By reacting in alcoholic solution in the presence of *piperidine* after Brooker and Keyes.(44)

(*b*) By a similar reaction in *pyridine.*

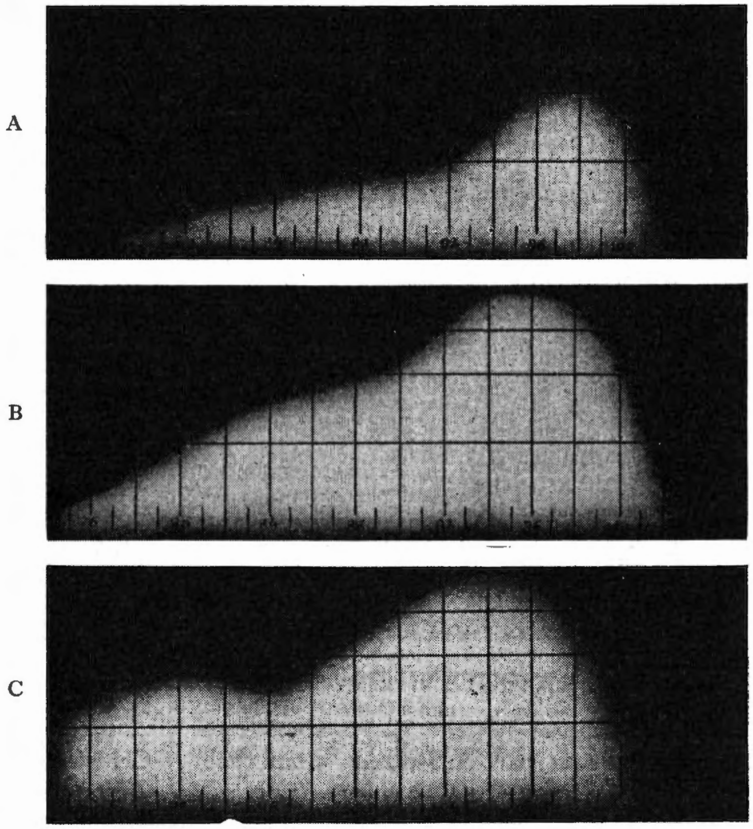


FIG. 135. Sensitization by tetra and pentacarbocyanines.

(A) 1 . 1′ diethyl (13) acetoxy 2 : 2′ tetracarbocyanine;
(B) 3 . 3′ diethyl (12) acetoxy 6 : 7 : 6′ : 7′ dibenzothiatetracarbocyanine;
(C) 3 . 3′ diethyl (12) acetoxy 6 : 7 : 6′ : 7 dibenzothiapentacarbocyanine.

(*c*) The solvent is *acetic anhydride*, and the condensing agent *anhydrous sodium acetate.*

The optimum conditions vary with the dye. Generally, room temperature is used or in the neighbourhood of the setting temperature. The dye can only be partially purified after precipitation with sodium perchlorate, due to its instability.

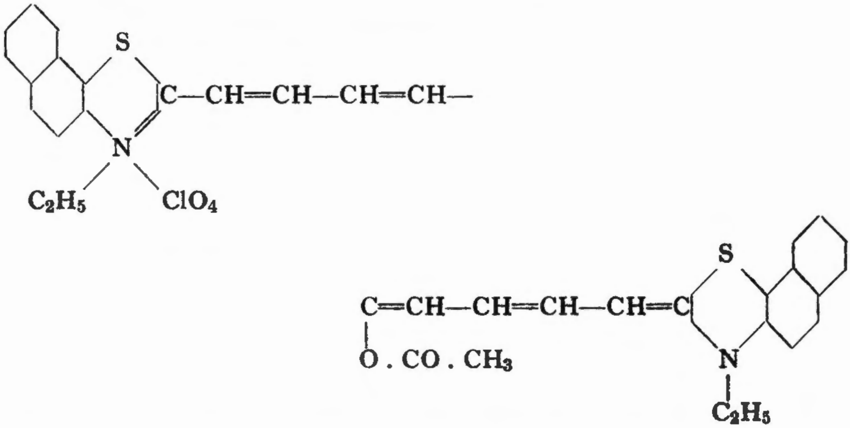
789. Principal tetracarbocyanines

The following tetracarbocyanines can be prepared in this way:

1:1′-diethyl-13-acetoxy-2:2′-tetracarbocyanine: sensitizing action to 1030 mμ with maximum about 980 mμ (Fig. 135).

3:3′-diethyl-11-acetoxythiatetracarbocyanine: strong sensitization from 760 to 1000 mμ with sharp maximum at 940 mμ.

3:3′-diethyl-11-acetoxy-6:7:6′:7′-dibenzothiatetracarbocyanine:



Strong sensitization to 1030 mμ with maximum at 950 mμ (Fig. 135).

PENTACARBOCYANINES

790.

The pentacarbocyanines, prepared by Brooker and Keyes, have an 11-carbon atom chain:

$$—CH{=}CH—CH{=}CH—CH{=}CH—CH{=}CH—CH{=}CH—CH{=}$$

$$\text{or } —(CH{=}CH)_5—CH{=}$$

The large number of conjugated double bonds gives a great displacement to the absorption maximum compared with the more simple carbocyanines. The pentacarbocyanines normally sensitize from 1000 to 1160 mμ. With sufficiently long exposures 1300 mμ can be reached.

The pentacarbocyanines are prepared in the same way as the tetracarbocyanines. The reactive compound being in this case *4-acetoxy-*$\Delta^{3,5,7}$*-nonatriene-1:9-dial-di-tetra-hydroquinolide* perchlorate.(45)

The purification of these dyes is difficult due to their great instability. The sensitizing action extends into the visible red because of the presence of other cyanines formed by rupture of the chain. They should not be recrystallized.

1:1′-diethyl-13-acetoxy-2:2′-pentacarbocyanine: pronounced action up to 1200 mμ with an indefinite maximum at 1120 mμ.

3:3′-diethyl-11-acetoxy-thiapentacarbocyanines. Strong sensitization up to 1120 mμ with a maximum about 1050 mμ.

3:3′-diethyl-11-acetoxy-6:7:6′:7′-dibenzothiapentacarbocyanine: Powerful sensitizer up to 1140 mμ. Maximum at 1065 mμ (Fig. 135). The 4:5:4′:5′ derivative has a maximum at 1090 mμ.

It should be mentioned that the carbon chain can be lengthened still further (*hexacarbocyanines*), but the instability of the dye increases as the chain becomes longer, and the general sensitivity of the emulsion decreases.

Thiohexacarbocyanines, obtained by D. W. Heseltine (Kodak), has an absorption maximum at 1140 mμ and sensitizes at 1170 mμ.

791. Stabilization of infra-red sensitized emulsions

The loss of sensitivity caused by the infra-red sensitizers can be avoided by adding to the emulsion a reducing agent containing several NH_2 groups such as hydrazine or semicarbazide or their reaction products with aldehydes or ketones. The amount used is about 0·35 g.p.l. (A. P. H. Trivelli and B. H. Carroll, F.P. 865,260).

L. G. S. Brooker and L. Smith, on the other hand, increased the sensitivity by replacing the alkyl groups attached to the nitrogen atoms with ether, ester, or nitrile groups (F.P. 847,660). The benzyl radicals also give good results; 1:1′-dibenzyl-4:4′-tricarbocyanine is prepared from the base treated with benzyl bromide (F.P. 846,415).

1. Columbium nitride superconducting bolometers for the infra-red: see Fuson: *J.O.S.A.*, Oct. 1948, 845–853.
2. Lehmann W.: *Phot. Korr.*, July 1951, 5–10.
3. Czerny: *Sci. et Ind. Phot.*, 1938, 93; Gobrecht and Weiss: *Zeits. Angew. Physik*, June 1953, 207.
4. Suza and Yosihara: *Sci. of Light*, Aug. 1955, p. 1–6.
5. Ritz: *Compt. Rend. Ac. Sc., Paris*, 1906, **143**, 167.
6. Note, however, sensitization by *silver sulphide* (by immersing the plate in 1 : 1000 sodium sulphide). Limit of sensitivity reached: 1,190 mμ.
7. Obaton F.: *Compt. Rend. Ac. Sc., Paris*, 1944, **218**, 721.
8. Rieck J.: *Naturwiss. Rundsch.*, July 1953, 289–293.
9. The first quinoline nucleus can be replaced by a thiazole or other nucleus: thia-, selena-, oxa-, or indo-dicyanines sensitizing in the red and orange.
10. *J.A.C.S.*, 1920, **42**, 2394.

11. *Jl. prakt. Chem.*, 1886, **33(2),** 401.
12. *Jl. prakt. Chem.*, 1888, **38(2),** 41.
13. Palkin S. and Harris M.: *Jl. Ind. and Eng. Chem.*, 1922, **14,** 704.
14. Adams and Haller: *J.A.C.S.*, 1920, **42,** 2661.
15. By replacing lepidine (γ-methylquinoline) by γ-picoline, Rosenhauer and Barlet obtained the pyrido-4 : 4'-carbocyanines. Absorption maximum at 600 mμ. Weak sensitization in the orange red.
16. Hamer F. M.: *J.C.S.*, 1928, 1472.
17. Preparation of lepidine: see para. 673.
18. Hamer F. M.: *J.C.S.*, 1952, 3197–3211.
19. Hamer F. M., Rathbone R. J. and Winton B. S.: *J.C.S.*, 1948, 1872.
20. Kimura: *Chem. Zentr.*, II, 1937, 4187.
21. Gevaërt: F.P. 867,415.
22. *J.C.S.*, July 1947 and Nov. 1947, 1434; Zanabe Y.: *J. Pharm. Soc., Japan*, 1954, 98 and 162.
23. König: *Ber.*, 1922, 3309; and G.P. 410,487 (1922).
24. *J.C.S.*, 1932, **123,** 260; and B.P. 353,589 (1930).
25. Dickmann and Platz: *Ber.*, 1904, **37,** 4638.
26. *Ber.*, 1899, **32,** 2084.
27. For the preparation of the bases see para. 685.
28. F.P. 754,746 and add. 43,895 (1934).
29. F.P. 731,508 (1932); 774,028 (1934) and B.P. 388,204 (1933).
30. Heptacarbocyanines using German nomenclature.
31. G.P. 499,967 (1928).
32. B.P. 388,204 (1933) and F.P. 731,508 (1932).
33. Hamer: B.P. 351,555 (1930) and 354,826 (1930).
34. For chain substituted polycarbocyanines see F.P. 777,034 and Beilenson and Hamer: *J.C.S.*, 1936, 1225.
35. Hamer and Fisher: *J.C.S.*, 1933, 1889.
36. F.P. 731,508 (1932).
37. F.P. 754,746 and add. 43,895 (1934).
38. F.P. 767,190 (1934) and 767,189 (1934).
39. G.P. 708,345.
40. F.P. 773,648.
41. Piggott and Rodd: B.P. 355,693 (1930).
42. *Chemiker Zeitz.*, 1934, **58,** 398.
43. *Ber.*, 1934, **67,** 1274.
44. *Brit. Jour. Phot.*, 1935, 191.
45. König: *Ber.*, 1934, **67,** 1274.

Chapter XLI

COLOUR SENSITIZING TECHNIQUE AND THEORY

792. Sensitizing by direct incorporation

Industrially, photographic emulsions are colour sensitized by adding small quantities of dye directly to the emulsion at the end of *after-ripening.*

The choice of sensitizing dyes naturally depends on the required sensitization spectrum, that is, its position and extent. This must be restricted in the case of emulsions for colour processes.

The dyes having the most powerful sensitizing properties are the *meso-substituted carbocyanines* derived from *benzoxazole,* thiazoline, *benzthiazole* and *benzselenazole,* and the *complex merocyanines.* The latter have the valuable property of sensitizing for the red but not the green.

The quinoline cyanines and the non-cyanine dyes (except erythrosin) generally reduce the overall sensitivity of the emulsions. This is also true of the non-meso-substituted carbocyanines, or those with a heavy meso substituent.

The introduction of electronegative substituents such as nitro, acetyl and cyano, lowers the sensitizing power. This also happens when electron-accepting groups such as halogen or phenyl are placed close to a chromophoric group.

The optimum concentration of dye depends on the dye itself, and upon the grain size of the emulsion. *Fine grains are sensitized more efficiently*: they need, therefore, less dye than larger grains. For fast emulsions an average concentration is 16 mg per litre.

The dyes are first dissolved in ethanol or methanol at a concentration of 1:2,500. *They must not be kept for long* as the solutions are unstable. If the solubility of the cyanine iodide is too low to enable a solution of suitable concentration to be prepared (for example 4:5:4′:5′-dibenzothiacarbocyanine) it is better to use the corresponding bromide, or preferably the p-toluene-sulphonate or the perchlorate.

Permanent staining of the gelatin is a disadvantage for papers, therefore large molecules which diffuse slowly must be avoided. It has been recommended that the alkyl groups attached to the nitrogen atoms should be made acid (para. 745).

In the case of *multilayer materials* it is, on the contrary, essential to avoid diffusion from one layer to another. Long-chain nuclear substituents will prevent this diffusion. It has also been suggested that the diffused dye should be precipitated by adding, to the non-sensitized emulsion, a soluble salt whose anion forms an insoluble salt with the dye (2·5 g.p.l. sodium perchlorate for example)(1) or to make the diffused dye ineffective by saturating the unsensitized emulsion with 100–200 mg. per litre of a substantially colourless cyanine.

The removal of the colour sensitizer and the consequent reduction of its effect is sometimes brought about by the *coupler*, for example, the substituted amide of 1-hydroxy-2-naphthoic acid.(2) The basicity of the heterocyclic nuclei of the sensitizer also has some effect on the stability towards colour couplers.

Fogging action. The cyanines produce more emulsion fog as their chains become longer. In addition, the quinoline nuclei, particularly those used in the 4-position (lepidine derivatives) fog much more than the thiazole, selenazole and oxazole nuclei. Heavy substituents often reduce this tendency but their action is chiefly pronounced on the non-quinoline nuclei.

It has been disclosed that *hydroxyalkyl* groups attached to the nitrogen atoms, particularly with the polycarbocyanines, reduce the high fog produced by these dyes.(3)

The fogging tendency of the cyanines has been attributed to their reducing powers (Mecke and Semerano), to their tendency to form complexes with silver salts (Calzavara)(4) and to the solubility product of these complexes (Natanson);(5) the fog increases with the solubility product of the resulting complex.

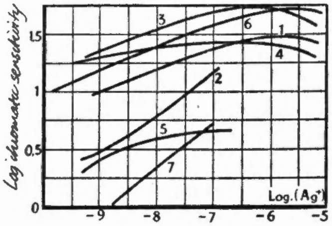


FIG. 136. Variation in sensitivity as a function of silver ion concentration. (After Carroll and Hubbard). 1. Erythrosin (neutral emulsion). 2. Erythrosin (ammoniacal emulsion). 3. Pinaverdol (neutral emulsion). 4. Pinaflavol (neutral emulsion). 5. Pinaflavol (ammoniacal emulsion). 6. Pinacyanol (neutral emulsion). 7. Pinacyanol (ammoniacal emulsion).

793. Sensitizing before digestion

When a sensitizing dye is added to an emulsion before digestion it has the effect of *slowing down chemical ripening*. With the carbocyanines the speed is only noticeably increased if the pH is above 7, whilst with the isocyanines, the effect is greatest in neutral media.

An excess of bromide ions prevents the dye from being adsorbed to the surface of the crystal lattice; because of this, the colour sensitivity is depressed by the addition of bromides. This is shown in the curves of the variation of sensitivity as a function of the pAg in Fig. 136.

Organic stabilizers behave like bromide, but their particular effect on any dye depends on the two compounds.

The adsorption of a dye is almost complete at a silver ion concentration of 3×10^{-6} and is halved at $[Ag^+] = 1{\cdot}2 \times 10^{-9}$.

To encourage *second order sensitizing* (see para. 799) it has been suggested that the colour sensitized emulsion should be digested in the presence of a certain quantity of *ammonium chloride*—about 7 cc of a 20% solution per litre of emulsion.

794. Sensitizing by bathing

Sensitizing by bathing is only used for experimental work. The photographic plates are bathed in an aqueous-alcoholic solution of the dye at a concentration of 1:20,000 to 1:100,000 and drained in a vertical position. *The sensitized plates can be exposed in the spectograph without drying.*

If the dye flocculates in the gelatin layer, as with pinacyanol for example, the electrolytes present in the emulsion (bromide, alum, etc.) must be removed by a *previous wash.*

In general, the gelatin is stained after treatment in the sensitizing solution. If the staining is to be reduced, rinse with alcohol before drying.

The *preparation of the sensitizing bath* is very simple: for example, 4 cc of 1:2500 dye solution is added to 100 cc of a water-alcohol mixture containing 40% alcohol to obtain a 16 mg per litre bath. The water must be distilled.

Immersion in the hydroalcoholic solution of the dye is adequate for spectrographic tests; but to obtain the maximum effect it is usual to add 2% *ammonia* (or even more) or some *triethanolamine.*

The treatment time in the solution is usually about 2 mins.

For infra-red sensitizing to 900 mμ without producing fog, treat for one minute in:

Distilled water	75 cc
Methanol	25 cc
Neocyanine 1:2000 (or polycarbocyanines)	1 cc

Rinse in alcohol and dry. For films, reduce the alcohol content.

Important note. Photographic emulsions which are colour sensitized by bathing do not keep well, especially when an ammoniacal bath has been used. Fog increases rapidly on storage, whilst sensitivity falls.

795. Colour sensitization with inorganic compounds

A certain number of *inorganic compounds* can impart colour sensitivity to photographic emulsions. The results, however, are very inferior to those obtained with dyes, and their interest is primarily theoretical.

In most cases the extension of sensitivity appears to be due to the formation of *colloidal silver* on the surface of the silver bromide crystals.

Colour sensitization with *colloidal silver* and with *silver sulphide* has been demonstrated by many workers. The phenomenon has been explained by the formation of an ionic absorbing layer which, by losing electrons, leads to the formation of development centres. Fajans and Frankenburger put forward the hypothesis that the absorption of the longer wavelengths is due to the deformation of the electron orbits, a hypothesis which has also been applied, as we have seen, to the sensitizing dyes. The comparison of photoelectric effects of alkali metals with those of halide crystals accompanied by colloidal particles also supports the possibility of a photoelectric sensitizing mechanism (Sheppard).

Among the inorganic sensitizing methods are:

(*a*) The addition of *colloidal silver* to the emulsion (Luppo-Cramer).

(*b*) Washing photographic plates for several hours (Capstaff and Bullock).

(*c*) Treatment with *sodium sulphide* solution (infra-red sensitizing).

(*d*) Bathing in 1:20,000 *potassium iodide* (extension in the green and red).

(*e*) Bathing in very dilute *potassium cyanide* (slight extension).

(*f*) Bathing in 5% *sodium bisulphite*. After 5 mins. the plates are washed for 10 mins. in a 5 g.p.L. solution of sodium carbonate and again washed for 5 mins. 800 mμ can be reached.

(*g*) *Sodium thiosulphate*: very weak red sensitization; may be due to the formation of traces of silver sulphide.

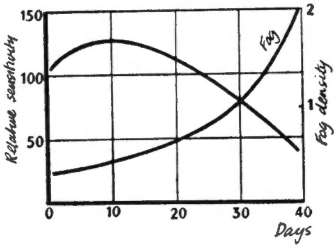


FIG. 137. Storage of a hypersensitized emulsion.

796. Hypersensitizing

1. *Ammonia*, in a very dilute solution, increases both the inherent and induced sensitivities of photographic layers. Thus a panchromatic plate treated for 4 mins. in a solution of 75 cc water, 25 cc alcohol and 3·5 cc ammonia has its general sensitivity doubled, and its colour sensitivity increased from two to eight times. The increase in sensitivity obtained by increasing the alkali is limited by the formation of intense fog. The action of the bath is greater *without alcohol* but drying takes longer and the risk of fog is increased (an alcohol-free bath can be used followed by an alcohol rinse).

Hypersensitization produces only a negligible effect with emulsions which are not colour sensitized.

Hypersensitized emulsions can only be *stored* for a short time, from two days to two weeks depending on the degree of treatment and the emulsion type. At first the speed increases slightly, then it drops, whilst the fog increases (Fig. 137).

2. *Mechanism of hypersensitization*: the action of ammonia is not due to its alkalinity, as soda is ineffective. The ammonia dissolves a little of the silver bromide, and silver hydroxide may be formed. The net result is a *considerable increase in the silver ion concentration* within the emulsion; this concentration increases linearly with the concentration of ammonia. Now a high silver ion concentration increases the sensitivity, and at the same time, the instability of the emulsion, that is, its tendency to fog. Thus a hypersensitized emulsion may have a pAg of 5 whilst for six months' keeping, the pAg must be kept above 8·7.

3. *Other ammonium bases. Hydrazine hydrate* in a concentration of 0·1 % (pH 11·3) produces a hypersensitizing effect similar to that of ammonia, but inferior with carbocyanines.

Pyridine has only a moderate action, whilst 0·5 % *triethanolamine* is as effective as dilute ammonia.⁽⁶⁾

4. *Hypersensitization with hydrogen peroxide.* The red sensitivity is increased with the following bath: distilled water 1000 cc, 1 % silver nitrate 10 cc, 12 vol. hydrogen peroxide 2·5 cc. The plates are treated in this bath, washed for 10 mins. in distilled water and dried. With ammonia, the action is stronger:

Water	1000 cc
Ammonia	2·5 cc
Hydrogen peroxide 12 vol.	4 cc or more
Silver salt containing	0·06 g silver

Silver nitrate gives a fog density of 0·2; silver tungstate gives 0·1, a figure which is maintained for 4 days, but which increases to 0·4 after 12 days. The plates can be treated first in 1:4000 ammoniacal silver tungstate, then in 0·08 % hydrogen peroxide.⁽⁷⁾

The active materials in these solutions are the silver salt and the ammonia, for hydrogen peroxide alone behaves as a desensitizer, and added to a solution of ammonia it reduces the hypersensitizing power.

Kikuchi and Tomoda⁽⁸⁾ used various methods to hypersensitize infra-red sensitive plates: 0·12 g Ag per litre silver tungstate (pH 10) increases the sensitivity by 2·5 to 3·6; 1 % pyridine gives a 4 × increase, rising to 5·4 × when 0·01 % silver nitrate is added.

The effectiveness of hypersensitization is only at a maximum with chemically ripened ammoniacal emulsions. The degree of speed increase is to some extent dependent on the gelatin and on the sensitizing dye to a greater extent.

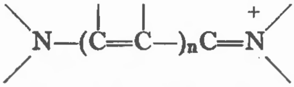
5. *Ultrasensitizing* is hypersensitizing using a bath similar to the preceding one but without the hydrogen peroxide. Used with slow positive plates in

the presence of a colour sensitizer, an increase of 30–40 times the initial sensitivity is achieved with the production of slight fog. With pinaverdol the following formula can be used:(9) distilled water 40 cc, alcohol 40 cc, ammoniacal silver chloride 2:1000, 10 cc, pinaverdol 1:1000, 4 cc. Pinacyanol gives intense fog.

THEORY OF COLOUR SENSITIZING

797. Aggregation, and absorption spectra of the cyanines

The cyanines, as we have seen, have the characteristic of two strongly basic nitrogen atoms linked by a polymethine chain



in which the alternating single and double bonds is the cause of a continual electron transfer. In addition to the electrons σ belonging to each atom, there are the electrons π common to the chain which can easily pass from one atom to another travelling between the two nitrogens.

The structure of the cyanine molecule is in this way subject to an incessant change of the conjugated double bonds, limited by the two extreme *resonance* structures. The colour results from this electronic movement through the molecule.

The merocyanines are superficially electrically neutral, being internally ionized systems (see para. 671 and end of 672).

The reduction of the basicity of a nitrogen, by the introduction of an acetyl group for example, prevents the change in the resonance structures.

The inclusion of nuclear substituents in the cyanines, especially in the 6-position has a bathochromic effect. On the other hand, removal of symmetry has a hypsochromic effect compared with the average of the two corresponding symmetrical cyanines.

The *solvent* has an important influence on the absorption of a dye. On changing from a polar to a non-polar solvent, a displacement of the absorption maximum towards the longer or the shorter wavelengths can occur. The most intense coloration results from the solution of a compound having a predominantly polar structure in a non-polar solvent, or from the solution of a predominantly non-polar compound in a polar solvent.

The most interesting phenomenon appears in aqueous solution: when the concentration of a cyanine in water is increased, the absorption spectrum changes. First, a new band, called the *H band*, appears in the short wavelengths then, at higher concentrations, a narrow but intense band appears at longer wavelengths—the *J band*—accompanied by a short-duration fluorescence. The reason for the appearance of these new absorption bands is that the dye polymerizes in *aggregates*—as shown by Scheibe and his collaborators.(10) This polymerization is enhanced by the van der Waal's forces brought into play by the movement of the π electrons of the conjugated chain.

The J band, discovered by Jelley,(11) is a characteristic of the second stage of aggregation. In this stage the cyanine molecules are oriented parallel to each other, and the whole has a *fibrous* appearance. Examination with X-rays has shown that with pseudocyanine chloride, the molecules are inclined to 35° on the fibre axis.(12b) When an aggregate is oriented, in order to absorb light in the J band, the electrical component of the light must be parallel to the fibre. The reflected light is polarized.

The degree of aggregation can be determined by measuring the *osmotic pressure* of the dye solution behind a collodion membrane contained in a solution of potassium chloride.(13) It is also determined by measuring the electric conductivity or by diffusion.

Aggregation results in an increase of viscosity: a 0·01 M solution can turn into a gel.(13b)

The ease of aggregation is dependent on the structure of the dye. Small changes in structure have a great influence.

798. Aggregation of cyanines on gelatin

The aggregation of the cyanines is greatly enhanced by their adsorption on gelatin. This phenomenon has been studied by many authors.(14) Dickinson(15) showed that the J band only appears at a critical optimum concentration—0·01% in the case of triethyl-4:5:4′:5′-dibenzothiacarbocyanine.

The simple thiacarbocyanines show the J band only if heavy nuclei are linked to their molecules or if they have halogen substituents. The simple mesothiacarbocyanines only produce an H band.

The J band only appears above the isoelectric point of the gelatin, with a maximum in alkaline media.

The gelatin-dye complexes can be isolated and analysed. Those giving an H band are precipitated in the presence of an electrolyte such as ammonium nitrate. The H complex is decomposed with alcohol more easily than the J complex.

Sheppard attributed the reason for the formation of aggregates adsorbed by the gelatin to the presence of special points, 4Å apart along the gelatin micelles.

799. Adsorption of sensitizing dyes on the silver halides

Sensitizing dyes added to a photographic emulsion are *adsorbed on the crystal surface* of the silver halide. Doubtless, the *gelatin* influences this adsorption but nothing definite is known on the subject. It can reasonably be supposed that the dye is located at the silver halide-gelatin interface. As we have already seen, gelatin favours the polymerization of cyanines into H and J aggregates. These aggregates have the identical spectral absorptions as the same dyes adsorbed on *glass*.(16) They are more strongly retained by the silver halide than the monomers and play an important part in colour sensitizing.

Because of the polymerization of the sensitizing dye adsorbed on the crystal surface, the *sensitization spectrum* corresponds not to the adsorption spectrum in alcoholic solution, but to the absorption spectrum of the dyed silver halide. This accounts for the shift of from 20 to 90 mμ towards the long wavelengths observed between the absorption and sensitization maxima.

To achieve optimum colour sensitizing, the whole surface of the grain need not be covered with dye. It is enough to have 30–65% of the total area covered.

Sheppard, Lambert and Walker(17) have shown that the dye molecules are attached to the crystal surface *on edge*, due to the reciprocal repulsion of the two heterocyclic nuclei. Sherlack(18) has attached a pseudocyanine to mica in this way.

If excess dye is adsorbed it can be present in strata of superimposed oriented stratified layers, as with fatty substances when they are melted or pressed on to a support.

The sensitizing dye does not form a permanent compound with the silver salt. A prolonged wash brings about desorption. To achieve complete extraction,(19) the emulsion is dissolved in warm water and centrifuged. The solid is suspended in water containing hypo and is extracted with n-butanol which removes almost all the dye.

800. Second order sensitization

We have already seen that the absorption band of dyed silver halide can vary from that of the dye in dilute alcoholic solution, depending on the dye's susceptibility to polymerization. Schwarz(20) gave this the name '*second order sensitization*', the sensitization produced by the aggregation producing a *J absorption band*. The sensitizing spectrum of an emulsion, thus sensitized, always ends with a steep slope from a raised peak whose maximum is greatly shifted towards the red compared with the normal absorption of the dye.

The non-polymerizing dyes gradually sensitize the emulsion more and more as the concentration is increased, up to an optimum point. On the contrary, dyes which do have a polymerizing tendency only show weak sensitizing if their concentration is below the polymerization level: the sensitivity increases abruptly with the formation of the aggregate.

Levkoev and Natanson(21) found that at concentrations below 4×10^{-6} mol/mol. AgX, all dyes exhibit normal (or first order) sensitizing, characterized by a single absorption band. At an increased, though still moderate, concentration, a shorter wavelength band, due to the H aggregate, may appear. Then at high concentrations the dyes which are prone to form J aggregates, produce new high intensity absorption bands towards the longer wavelengths; the maximum is well defined, followed by a steep fall at the end.

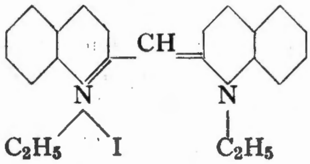
Of the mesosubstituted thiacarbocyanines, the ethyl derivative has the least tendency to second order sensitizing, whilst the mesoethyl selenacarbocyanine, on the contrary, is very prone to sensitize in this way. The naphthothiazole thiacarbocyanines, as we have seen, produce second order sensitizing more easily than the thiacarbocyanines with lighter nuclei. The most effective substituents, in decreasing order, are C_6H_5CO—, CH_3O—, CH_3—, C_2H_5O—, Cl—. The group NR_2— is the least effective.

The tendency of a dye to aggregate can be checked by salting out: ammonium sulphate is added to a boiling saturated solution of the dye. On cooling, aggregation is shown by a blue fibrous precipitate with a sharp absorption band in the red.(22)

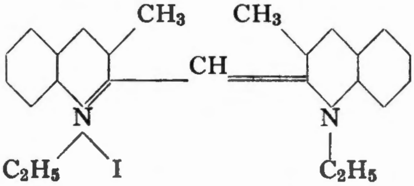
801. Effect of the molecular planarity of a dye on its sensitizing efficiency

Pauling(23) has shown that all resonance in a conjugated chain, between limiting mesomeric forms, can only take place if the different atoms are in the same plane. The effect of the planarity of the molecule on its sensitizing power has been demonstrated by Sheppard, Lambert and Walker, then by Brooker and his collaborators.

Non-planarity prevents sensitization. For example, the planar diethylpseudocyanine is a strong sensitizer, whilst 3:3′-dimethyl-diethylpseudocyanine is only a weak sensitizer, as the 3:3′-methyl groups prevent the nuclei from being coplanar.

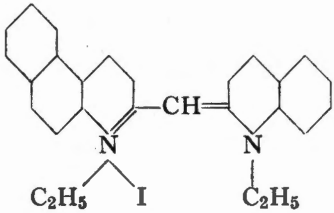


1:1′-diethylpseudocyanine

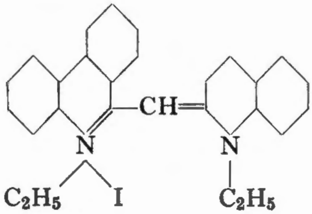


1:1′-diethyl-3:3′-dimethyl pseudocyanine

The effect of *steric prevention* is even more pronounced with the two cyanines derived from 9-methyl phenanthroline:(25)



Strong sensitizer



Non-sensitizer

With the mesophenyl thiacarbocyanines the phenyl group is pushed into a plane different from the main one, because of the impossibility of the ortho hydrogens of the phenyl group to come alongside the benzthiazole S atoms. Similarly with the weak sensitizer, isoquinoline red, whose benzyl group is pushed away. The distortion is even more pronounced when an acridine nucleus is included.

The structure of diethyloxacarbocyanine is, on the other hand, sufficiently free for a phenyl group to be introduced without distortion.

With a planar molecule, however, *a dye forms aggregates more easily as it becomes more compact*. In this case it can become a powerful sensitizer.

Each distortion restricts the transfer of energy and, in consequence, reduces the sensitizing power.

When the distortion produced by introducing a group is relative to the conjugated chain this influence shifts the absorption maximum towards the red. In the case of a very asymmetrical dye whose absorption maximum is lower than the arithmetic mean, non-planarity due to a substituent shifts the maximum towards the blue.(26)

The non-planarity diminishes the *adsorption* of the dye. Strong adsorption does not necessarily mean a high sensitizing action, however; thus the dimethylcarbocyanines are adsorbed better than the diethylcarbocyanines but are poorer sensitizers.

802. Anti-sensitization

A dye with a non-planar molecule can reduce or cancel the sensitization produced by another dye. For example, 10% of 1:1′:3:3′-tetramethylpseudocyanine (non-planar) reduces the sensitizing power of 1:1′-diethylpseudocyanine by 20%.

This phenomenon has been studied by West and Carroll.(27)

The J aggregates of dye which result in second order sensitization are most prone to anti-sensitization. The H aggregates are less sensitive.

The anti-sensitization takes place by intercepting the flow of excitation energy and dissipating it by torsional molecular vibration.

A dye with a non-planar molecule only behaves as an anti-sensitizer if its absorption maximum is at a longer wavelength than that of the sensitizer, exceeding it by at least 70 mμ for it is the electronic excitation of the sensitizer which brings about the electronic excitation of the anti-sensitizer.

In the opposite case, the anti-sensitizer can produce weak sensitizing.

803. Desensitization by sensitizers

Desensitization, which must not be confused with anti-sensitization, is a reduction in the general sensitivity by the sensitizer despite a strong colour sensitizing action, for sensitization and desensitization are two quite distinct phenomena.

The desensitizing properties of many sensitizers were studied from 1909 by König, Luppo-Cramer,(28) Heisenberg,(29) Breido and Gorokhovski,(30) Spence and Carroll.(31) The latter compared the activity of thiacarbocyanine (ethiodide) with that of phenylthiazocarbocyanine (ethiodide): the two dyes produce the same colour sensitization but the thiazocarbocyanine reduces the general speed of the emulsion considerably.

The optimum quantity of sensitizing dye is consequently limited by this desensitizing action: 15 mg for the thiacarbocyanines and 3 mg for the phenylthiazocarbocyanine.

804. Internal photoelectric effect of sensitizing dyes

A semi-conductor such as ZnO, CdO, TlCl, placed as a dielectric between two plates of a condenser, and treated with various dyes, shows an internal photoelectric effect when it is irradiated intermittently over the range of 400–1000 mμ. This technique due to Bergman was used by Putseiko and Terenin(32) with thallous iodide sensitized with methylene blue or malachite green. Under the influence of the quanta absorbed by the dye, the electrons in the semiconductor are raised to the conductivity level.

West and Carroll,(33) who studied the photo-conductivity of silver bromide dyed with sensitizers, have shown a parallel between this phenomenon and colour sensitivity.

More recently Meir(34) measured the photoconductivity of the sensitizing dyes in an electric field, for example the effects of a potential difference of 800 V on an irradiated layer of pinacyanol.

805. Mechanism of colour sensitization

The luminous energy absorbed by the colour sensitizer is transferred from it to the silver salt. Although the complete transfer mechanism is still in a hypothetical state, we do know that the *dye is not decomposed* by the light quanta, but passes to an *activated state*.

$$\text{Dye} + h\nu \longrightarrow \text{activated dye}$$

This gives rise to an internal transformation which converts the dye to a metastable state with a short life. The dye then transfers its energy to the silver bromide crystal and itself returns to its original condition. Following a hypothesis by J. Perrin, Bodenstein showed that this transfer is due to a resonance coupling between the energy pulses of the activated dye and the halide ions. Frenkel in 1931(35) then Peirls in 1932(36) developed the idea of an excitation wave, or *exciton*, characterized by the displacement of an electron-positive hole couple, which can pass through molecules, staying in each one for only a small number of vibrations. Frank and Teller(37) then Frank and Livingstone(38) applied this theory to the propagation of energy in systems based on silver halides, showing that the excitation wave is associated with the J spectrum of the aggregates of polymerized dye.

Simpson(39) has shown that the transmission of energy is due to a process of conserving the spin of the electron. Umano,(40) on the other hand, noted that there is a potential barrier between the dye and the crystal which necessitates the excited electron having a life greater than 10^{-9} sec. in this level. It is therefore probable that the electrons of the dye, excited to the $1\pi\mu$ level first pass into the *triplet* state $3\pi_g$ before passing through the potential barrier, due to thermal energy, to finally arrive at the silver bromide crystal.

As the energy levels of the dye molecule are below the conductivity level of the crystal, Mott(41) found the necessary complementary energy, with the natural colour sensitivity of silver bromide. Hautot and Sauvenier(42) brought in the effect of the bromine acceptors, and Stepanov and Meiklyar(43) the 'fluctuation' energy of the dye.

In any case the bromine liberated during the reaction is capable of decomposing the dye by a secondary action, but the gelatin absorbs it before it can react.

SUPERSENSITIZATION

806. Theory of supersensitization

Supersensitization is the term applied to the increase in colour sensitivity due to a dye when certain other compounds are added.

The reciprocal action of dye mixtures was the subject of a thesis by Daur in 1908.(44) Ten years later, Renwick and Bloch(45) disclosed the supersensitizing action of auramine. The matter was again taken up by Agfa about 1930,(46) then by Eastman Kodak and Gevaert in particular. At the present time the number of patents disclosing miraculous action of various compounds—dyes and otherwise—is considerable.(47) Actually, the really effective (and commercially interesting) substances are few. Their compositions are kept secret or carefully camouflaged by an immense number of patents. This is why supersensitizing tests, carried out with practical objectives, often lead to disappointing results.

Another reason for failure is due to ignorance of the fact that ***supersensitization is only possible if the sensitizing dye is in an aggregated state*** especially a J aggregate (see para. 796). In other words, only emulsions showing second order sensitizing can be effectively supersensitized. In the majority of experimental work on supersensitization the reference dye is ***diethylpseudocyanine*** which polymerizes very easily.

The supersensitizer generally shifts the sensitizing maximum of the J band 10–20 mμ towards the shorter wavelengths, together with a broadening of the band.(48)

If the supersensitizer is itself a colour sensitizer, it must be of a different type to the main sensitizer, but must be capable of forming a solid solution with it.

The supersensitizer plays the part of an interrupter in the path of the excitation wave. The aggregated sensitizer is itself incapable of transferring its surplus energy to the silver bromide crystal, and dissipates this energy as fluorescence. The supersensitizer facilitates the transfer of energy with the elimination of this fluorescence.(49) Carroll and West have stated that the addition of a supersensitizer to a colour sensitizer considerably increases its photoconductivity. This proves that the supersensitizer increases the number of electrons liberated in the crystal for each unit of luminous energy absorbed by the dye.

The concentration of supersensitizer depends on its nature, on the nature of the sensitizer, and upon the degree of aggregations. If the sensitizer polymerizes at a low concentration, only a small amount of supersensitizer is needed. Usually, however, an amount equal to, or greater than, the amount of sensitizer, is needed.

According to a Kodak patent (F.P. 963,682), an emulsion containing 1% silver cyanide (compared with the silver bromide) shows double the chromatic sensitivity of an ordinary emulsion. The silver cyanide is washed by decantation, and dispersed in 20% gelatin containing ammonia, which is again washed after shredding. It is then added to the emulsion before colour sensitizing. Kodak's U.S.P. 2,221,805 discloses the addition of silver thiocyanate, and U.S.P. 2,222,264 the addition of sodium thiocyanate.

807. Supersensitizing compounds

A list is given below of the principal groups of substances which have been proposed as supersensitizers.

Mesosubstituted thiocarbocyanines such as 9-methyl-diethylthiacarbocyanine (Kodak: Ital. P. 352,126—Ilford 2,430,072).

Mixture of mesomethylthiacarbocyanine and the thiacarbocyanine from β-naphthothiazole (Kodak: B.P. 498,289) or mesomethylthiadicarbocyanine (Ilford: U.S.P. 2,422,080). The mesomethylthiacarbocyanine can be replaced by triethyl-4:4′-dichlorothiacarbocyanine. A mixture of mesomethylthiacarbocyanine and tetraphenylthiazocarbocyanine was disclosed in F.I.A.T. Final Report No. 354.

Mesoalkoxythiacarbocyanines (Gevaert: U.S.P. 2,158,883).

Carbocyanines with complex nuclei (I.G.F.: F.P. 886,431—Gevaert: F.P. 891,013).

Asymmetrical carbocyanines with a 4-quinoline nucleus (Kodak: U.S.P. 2,158,883).

4:4′-carbocyanines (Kodak: B.P. 514,375).

Mesosubstituted oxacarbocyanines (Kodak: U.S.P. 2,132,856).

Various carbocyanines (B.P. 498,290 and 516,468).

Pseudocyanines. West and Carroll have disclosed ethyl-methylthiapseudocyanine as a supersensitizer for 3:3′-dimethyl-9-ethylthiacarbocyanine, whose J band at 630 mμ is shifted to 610 mμ. Borin and Trokhimovitch(50) successfully used diethylthiapseudocyanine with mesoethyl-thiacarbocyanine and benzthia-carbocyanine; the supersensitizer is added in aqueous solution after the sensitizer.

Acid selenapseudocyanines — non-diffusing (Gen. Aniline: U.S.P. 2,481,464).

Thiazinocyanines (cf. para. 743) and the thiazolinothiazinocyanine (Kodak: U.S.P. 2,206,076 and B.P. 515,789). Thiazinocyanines from cyclo 1:3-dihydrothiazine (Kodak: C.A. 51,482 to F.P. 840,957).

Cyanines substituted with an azole residue (Gen. Aniline: U.S.P. 2,504,616). Cyanines derived from 5-aryl-benzoxazole (Gevaert: F.P. 968,558).

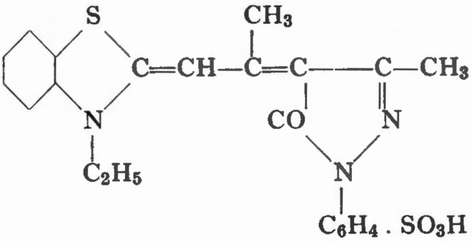
Styryl cyanines—particularly those derived from thiazole and benzthiazole (I.G.F.: Ital. P. 378,868—Kodak: Canad.P. 389,718; B.P. 498,031; U.S.P. 2,218,230; 2,533,426; 2,533,427; F.P. 867,410; 840,957).

Styrylcyanines produced by condensing 5-acetyl-methyl-3-phenyl-1:2:4-oxodiazole with p-dimethylaminobenzaldehyde, and 2[2(acetanilidovinyl)] benzoxazole (or benzthiazole) with p-dimethylaminoaniline sulphate (Gevaert B.P. 656,515).

Condensation product of cyclohexanone and p-dimethylaminobenzaldehyde (Gevaert: F.P. 969,505 and G.P. 810,458).

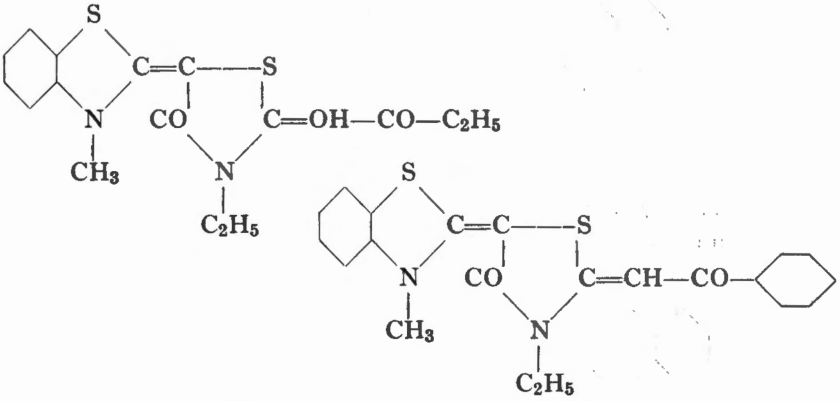
Anilinovinyl derivatives (cf. para. 696) having a para auxochromic group.(51)

Merocyanines. The merocyanines which show supersensitizing properties are those having a chain with at least one =CH—CH= group, for example, the compound below, derived from pyrazolone and α-substituted with



which Carroll and West increased the induced sensitivity produced by diethylpseudocyanine seventeenfold. This type of merocyanine was the subject of a study by Schouwenaars,(53) the colour sensitizer used being either diethylpseudocyanine, thiapseudocyanine or 9-methyl-4:5:4′:5′-benzothiacarbocyanine.

According to F.P. 969,827 (Gevaert) supersensitizing can be carried out with simple merocyanines (without a chain link) by including a keto substituent in the rhodanine nucleus. For example:



(A) (B)

of which 30 mg per litre of emulsion is used. The compound (A) is obtained by the action of ethyl propionylpyruvate and (B) by the action of benzoylacetic ester on the corresponding simple merocyanines. As the sensitizer, 9-ethyl-5:5′-ditolyl-3:3′-diethyloxacarbocyanine can be used.

Another Gevaert patent (F.P. 994,762) again discloses merocyanines with an acid group such as $—CH_2—C_6H_4—COOH$ attached to the nitrogen.

Polymethine dyes of the *oxanol* type (Gevaert: F.P. 882,245).

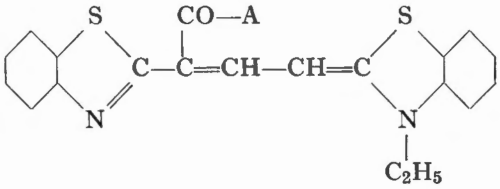
Non-sensitizing dyes formed from a furfuryl nucleus and a ketomethylene nucleus (pyrazolone, thiohydantoin) joined by a methine group —CH= (Gevaert: F.P. 954,247.)

Sensitizing dye bases.

Dequaternized cyanines (para. 737b) are frequently more active than the corresponding cyanines as supersensitizers: their two nitrogen atoms are trivalent as with the merocyanines.

Carbocyanine bases (Kodak: F.P. C.A. 51,363—Gevaert: Belgian P. 440,739).

Carbocyanine bases with an α-substituent, carbalkoxy, carbamido or carbhydrazido (Van Dormael and Nys).⁽⁵⁴⁾ For example:

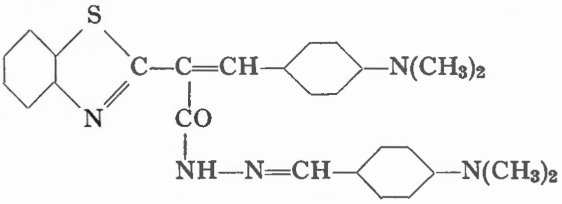


Pseudocyanine bases (I.G.F.: F.P. 630,317).

Thiazinopseudocyanine bases (Kodak: B.P. 518,478).

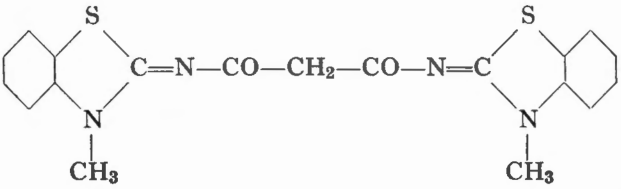
Styrylcyanine bases (I.G.F.: F.P. 870,980—Kodak: F.P. C.A. 50,775).

The cyanine bases having a hydrazide α-substituent in the chain, such as



were disclosed by Gevaert (F.P. 970,548) (para. 742).

Azacyanines of the type (Gevaert: G.P. 812,872).



Heterocyclic bases. Very many heterocyclic bases, with or without a vinyl chain, have been proposed as supersensitizers. Apart from the anilinovinyl derivatives noted above, we would mention the following types:

Acetylmethylene bases such as 2-acetylmethylene-3-ethylbenzthiazolidine or -naphthothiazolidine (para. 738–740) (Kodak: F.P. 856,351).

The methylene derivatives of the heterocyclic bases were investigated by Van Dormael and Nys,(55) and, amongst others, the cyanomethylene bases obtained by condensing ethyl cyanopyruvate with methylmercaptobenzthiazole quaternary salts.(56)

Amino quinolines and related compounds (Kodak: F.P. 841,631 and U.S.P. 2,177,635) such as 6-dimethylaminoquinaldine or lepidine, 2-aminobenzthiazole, 2-methyl-6-aminobenzthiazole, 7-dimethylaminobenzthiazole, etc.

2-thioquinolines and benzthioquinolines (Kodak: U.S.P. 2,395,846).

2-phenylmercapto quinolines and derivatives of 2:4-dimethyl-β-naphthoquinoline, 2:3:3-trimethylindoline, etc. (Kodak: F.P. 941,852).

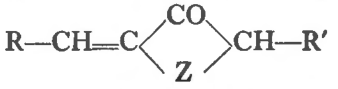
Pyridine bases with alkyl, alkoxy, aryl, etc., substituents at a concentration of 0·1–0·3 g per litre (Kodak: F.P. 942,920 and U.S.P. 2,478,369).

Benziminazole bases (Kodak: U.S.P. 2,398,778 and 2,556,167).

Bases with carbarmyl nuclei condensed with heterocyclic nuclei (Kodak: U.S.P. 2,398,778).

2-methyl-β-naphthothiazole having an hydroxyl substituent and a hydrazine, hydroxylamine, or carbamyl substituent (Kodak: U.S.P. 2,411,546). For example, the semicarbazone of 6-hydroxy-7-acetyl-2-methyl-β-naphthothiazole (termed 4-hydroxy-3-acetyl-2-methyl-naphthothiazole).

Aromatic *ketones*, such as o- and p-methoxyacetophenones, anisylacetophenone, etc. (Kodak: F.P. 944,283 and U.S.P. 2,373,659).

Cyclic ketones of the type  $\mathrm{R{-}CH{=}C}\overset{\mathrm{CO}}{\underset{\mathrm{Z}}{\langle\quad\rangle}}\mathrm{CH{-}R'}$ (Gevaert: F.P. 969,505).

p-dimethylaminobenzalacetone, p-dimethylaminocinnamylidene-acetophenone, and derivatives of p-dimethylaminocinnamaldehyde, including the hydrazones and semicarbazides (Kodak: B.P. 584,381 and U.S.P. 2,432,710).

Nitriles (Kodak: F.P. 959,732): benzonitrile, 2:5-dimethoxybenzonitrile, γ-phenoxybutyronitrile.

Esters (Kodak: F.P. 944,282 and U.S.P. 2,361,928): benzyl benzoate, benzyl phenylacetate, o-cresol benzoate, gaicolates, pyridine-carboxylates, etc. Concentration in the order of 10 g per litre of emulsion.

Mercaptan derivatives (Gevaert: F.P. 885,376, B.P. 615,430 and U.S.P. 2,546,642) similar to p-chloro mercaptoisovalerianic anilide or mercaptophenylacetanilide.

Silanes (Kodak: U.S.P. 2,500,110): bispyridylalkoxy silanes.

808. Supersensitizers derived from gelatin

The action of the basic dyes on gelatin was first studied by Sheppard(57) who noted that the gelatin favoured the formation of J aggregates (see para. 797). L. Michaelis(58) made the short wavelength bands of pinacyanol disappear by treating with an aqueous solution of nucleic acid. More recently

H. W. Wood⁽59⁾ gave evidence of the effect of gelatin *arysulphonate* on colour sensitization.

One of the most interesting sulphonyl gelatins is ***naphthalene sulphonyl gelatin*** or N.S.G. It was prepared by Wood, by treating 100 g of gelatin as a sol with 40 g naphthalene-2-sulphonyl chloride dissolved in benzene at a pH of 10. The product is purified by precipitating several times in acid medium. N.S.G. is used in soda solution at a pH of 6–8.

The aryl acid chlorides react with gelatin in the same way, to give aroyl-gelatins; whilst the ureidogelatins are obtained by a technique of Hopkins and Wormall.⁽60⁾

The addition of N.S.G. to a cyanine solution prevents its aggregation. The α-band, due to the monomer, is predominant. Now the opposite phenomenon occurs with gelatin, which, as we have seen (para. 797) favours the aggregation of certain dyes. This is explained by the fact that N.S.G. has many more adsorbing points than gelatin, and can attract the dye molecules individually. The concentration of N.S.G. to dissociate the aggregates is about 0·1 % whilst they predominate at 0·001 %.

When added to the gelatin of a photographic emulsion, N.S.G. *reduces the inherent sensitivity* to the blue, but increases the induced sensitivity in the region of the M band, and reduces it in the H and J bands.

1. Kodak: F.P. 863,743.
2. Levkoev I. I. and coll.: *Otdel. Khim. Nauk.*, 1954, **2,** 17–27.
3. Brooker and Smith: F.P. 836,155.
4. Calzavara E. (Electrometrie des cyanines): *Sci. et Ind. Phot.*, Feb. 1932.
5. Natanson S.: *Acta. Phys. Chem. U.S.S.R.*, 1946, 430.
6. Mees C. E. K.: *Sci. et Ind. Phot.*, 1932, 91.
7. *Phot. Ind.*, 1930, 445 and 472.
8. Kikuchi S. and Tomoda Y.: *Jl. Soc. Sci. Phot., Japan,* March 1945, 55–59 and 65; *Sci. et Ind. Phot.*, 1951, 11.
9. Monpillard: *Bull. Soc. Fr. Phot.*, 1922, 91; Guilleminot P.: *Bull. Soc. Fr., Phot.* 1927, 234.
10. Scheibe G.: *Zeits. angew. Chem.*, 1936, **49,** 563; Scheibe G.: Koll. Zeits. 1938, **82,** 1; Scheibe G. and Kanfler and Ecker H.: *Naturwiss.*, 1937, **25,** 75; Scheibe G., Mareis H. and Ecker H.: *Naturwiss.*, 1937, **25,** 474; Scheibe G. and Zimmermann: *Zeits. Elektrochem.*, 1950, 566.
11. Jelley E. E.: *Nature*, 1936, **138,** 1009.
12. West W. and Carroll B. H.: *Jl. Chem. Phys.* 1951, 417–427.

12b. Hoppe W.: *Kolloid Zeits.*, 1944, **109,** 21.

13. *Trans. Faraday Soc.*, 1947, **43,** 486–491.

13b. Kempl: *Thesis*, Munich, 1952.

14. Block and Hamer: *Phot. Jour.*, 1928, **68,** 21–33; Sheppard, Houck and Dittmar: *Jl. Phys. Chem.*, 1942, 158–176; Sheppard, Brigham and Newsome: *Rev. Mod. Phys.*, 1942, 303–340; Soloviev S.: *Acta Physiochim. U.S.S.R.*, 1946, **19,** 592–601; Klotz: *Chem. Rev.*, 1947, **41,** 373.
15. Dickinson H. O.: *Sci. et Ind. Phot.*, 1954, 311–319.
16. Soloviev S.: *Zh. obsh. Khimii*, 1946, 1405.
17. Sheppard, Lambert and Walker: *Jl. Chem. Phys.*, 1939, **7,** 265.
18. Skerlak: *Koll. Zeits.*, 1941, **95,** 265.

19. Davey E. P.: *Trans. Faraday Soc.*, 1940, **36,** 323.
20. Schwarz G.: *Sci. et Ind. Phot.*, 1939, **10,** 233–241.
21. Levkoev and Natanson: *Acta Physicochim. U.S.S.R.*, 1946, **21,** 437–450 (in English).
22. Dickinson H. O.: *Sci. et Ind. Phot.*, 1949, 49.
23. Pauling: The nature of the chemical bond, New York 1940.
24. Brooker, White, Heseltine, Keyes, Dent and Van Iare: R.P.S. Cent. Conf., London 1953.
25. Sheppard, Lambert and Walker: *Nature*, 1940, 386.
26. Brooker and Coll.: *Chem. Rev.*, 1947, **41,** 325–351.
27. West and Carroll: *Jl. Chem. Phys.*, 1951, 417–427.
28. Luppo-Cramer: *Sci. et Ind. Phot.*, **8R(1),** 5.
29. Heisenberg: *Sci. et Ind. Phot.*, **5(II),** 73.
30. Breido and Gorokhovski: *Sci. et Ind. Phot.*, **16(II),** 204.
31. Spence and Carroll: *Sci. et Ind. Phot.*, **19(II),** 372.
32. Putseiko E.: *C.R.Ac.Sc. U.S.S.R.*, 1948, **59,** 471; Putseiko and Terenin A.: *Doklady Ak. Nauk. S.S.S.R.*, 1951, 401; *Sci. et Ind. Phot.*, 1951, 352.
33. West and Carroll: *Jl. Chem. Phys.*, 1947, 529.
34. Meier H.: *Zeits. Electrochem.*, 1954, 859–867; see also: *Sci. et Ind. Phot.*, 1953, **24,** 180.
35. Frenkel: *Phys. Rev.*, 1931, **37,** 17.
36. Peierls: *Ann. d. Phys.*, 1932, **13,** 905.
37. Frank and Teller: *Jl. Chem. Phys.*, 1938, **6,** 861.
38. West and Carroll: *Jl. Chem. Phys.*, 1951, 417–427.
39. Simpson W. T.: *Jl. Chem. Phys.*, 1947, 414.
40. Umano S.: Symposium Phot. Sensitivity, Hakone (Japan), 1953.
41. Mott, N. F.: *Phot. Jour.*, 1948, 119.
42. Hautot: *Bull. Soc. R. Soc., Liege*, 1949, 147; *Sci. et Ind. Phot.*, 1950, 16.
43. Stepanov B. I. and Meiklyar P. V.: *Zh. fiz. Khimii*, 1947, **21,** 15–25.
44. Daur G.: *Thesis*, Munster, 1908; *Brit. Jl. Phot.*, July-Aug. 1909.
45. B.P. 133,769 and 133,770 (1918).
46. I.G.F.: G.P. 630,317 (1931).
47. See a review work of M. Mudrovcic: *Sci. et Ind. Phot.*, 1953, **24,** 47–56.
48. Dickinson H. O.: *Phot. Jour.*, 1950, **90B,** 142.
49. Carroll and West: *Sci. et Ind. Phot.*, 1951, 337.
50. Borin and Trokhimovitch: *Zh. Prikl. Khimii, U.S.S.R.*, 1946, 931.
51. Van Dormael A., Jacken J. and Nys J.: *Bull. Soc. Chim. Belge.*, 1949, **58,** 477–486; *Sci. et Ind. Phot.*, 1951, **22,** 48.
52. Carroll and West: *Jl. Chem. Phys.*, 1951, 417.
53. Schouwenaars (Gevaert): *Sci. et Ind. Phot.*, 1944, **15,** No. 5 and *K. Belg. Acad., Kl. d. Wetens*, 1943, 126; see also: Van Dormael, Nys and de Leuw: *Bull. Soc. Chim. Belge.*, 1948, 355–363.
54. Van Dormael and Nys: *Chim. et Ind.*, **63,** No. 3 bis XXI Cong. Chim. Ind. Bruxelles 1948, March 1950, 483–488.
55. Van Dormael and Nys: *Bull. Soc. Chim. Belge.*, 1950, **59,** 593; *Sci. et Ind. Phot.*, 1951, **22,** 175.
56. *Bull Soc. Chim. Belge.*, 1950, **59,** 588.
57. Sheppard, Houck and Dittmar: *Jl. Phys. Chem.*, 1942, 158; Sheppard S. E.: *Rev. Mod. Phys.*, 1942, **14,** 303–340 and *Sci. et Ind. Phot.*, 1949, **20,** 102.
58. Michaelis L.: *Jl. Phys. Coll. Chem.*, 1950, **54,** 1.
59. Wood H. W. W.: *Sci. et Ind. Phot.*, 1954, **25,** 465–475.
60. Hopkin and Wormall: *Biochem. Jl.*, 1933, **27,** 1706.

Chapter XLII

DESENSITIZATION

THE PHENOMENON OF DESENSITIZATION

809. The desensitization of photographic materials with dyes$^{(1)}$ was first noted in 1920 by Luppo-Cramer who used the *safranines*. A. and L. Lumière and A. Seyewetz found a similar effect with *chrysoidine*, *aurantia*, *picric acid*, etc. König later prepared materials with no pronounced affinity for fibres, but possessing strong desensitizing properties, the *pinakryptols*, which have the advantage that they stain neither the gelatin nor the skin.

The number of desensitizers today is very great but they are not all used in practice for various reasons: destruction of the dye by the developer sulphite or alkali, destruction of the latent image, slowing down of development, emulsion fog, staining of the gelatin, toxicity, or insufficient action. On the other hand, very few of the dyes described later are commercially available and this limits the scope of experimenters.

Desensitizers are used in a *bath* preceding development or are added to the developer. The sensitivity to green and red must be practically destroyed and that to blue greatly reduced, for example 800 times with 1:2000 *safranine*. With 1:1000 *neutral red*, the blue sensitivity is reduced 400 times and the colour sensitivity 3000 times. The desensitization in the colour sensitized region is still greater with *pinakryptol yellow*. *Picric acid* reduces the blue sensitivity 2000 times, but that to the red only 200 times. Chrysoidine is less effective; it only reduces the general sensitivity 100 times for a concentration of 1:5000.

810. Mechanism

The desensitizers are *adsorbed* to the silver bromide in the same way as colour sensitizers.

The dye, adsorbed to the surface of the crystals, takes no part in the reaction with the photosensitive salt except under the influence of light. Desensitization requires a greater concentration of dye than sensitization.

Size of grains: The larger the grains, the more effective is desensitization (the opposite effect of sensitization); a grain five times bigger is desensitized 15 times as strongly.

Sensitivity centres: Desensitization is more effective if the emulsion contains many sensitivity centres and is therefore more rapid.

Sensitization by desensitizers. A coarse grain emulsion whose sensitivity centres have been removed by chromic acid treatment becomes more sensitive when treated with 1:100,000 phenosafranine or Janus green. If centres are produced again by ripening, the dye then acts as a desensitizer.

Desensitization by sensitizers. Many colour sensitizers, such as the quinoline cyanines, reduce the general sensitivity of the emulsion.

Colour sensitizers for silver bromide act as desensitizers towards *silver iodide*, which is the least easily decomposed silver salt. Pinachrome, pinacyanol, erythrosin, rhodamine B at a concentration of 1:200,000 reduce the sensitivity 6–16 times.

Absorption spectrum. Desensitization is independent of the absorption spectrum, unlike colour sensitization. The desensitizers can be of any colour or even colourless.

Process of desensitization. Whilst with colour sensitization the cyanine receives the luminous energy and passes it on to the silver salt, in this case, the cyanine passes the energy to the desensitizer which can be decomposed to the leuco base by reduction. In fact, in an atmosphere of hydrogen, desensitization is prevented, whilst it is accelerated in an oxygen atmosphere which regenerates the desensitizer.

The desensitizers are essentially *oxidizing agents*: this explains, for example, the desensitizing influence of the NO_2 group on the cyanines and the fluoresceins. *Depending on the redox potential, a sensitizing dye can therefore behave at the same time as a colour sensitizer and a desensitizer.* On the contrary, a substance with a low redox potential, such as a thiacarbocyanine, does not reduce the general emulsion sensitivity.

Tamura and Tutihasi(1b) have suggested a mechanism based on the formation of aggregates of desensitizer on the sensitivity centres. They then interfere with the movement of photoelectrons in the crystal without reference to the presence of colour sensitizer, however effective.

Horvitz and Friedman(1c) admit that when the desensitizer is close to an electron and to a silver ion acting as an electrode, it is reduced to a stable form by resonance. Therefore, oxygen would have negligible influence. Substances, such as pinakryptol yellow, inhibit chain reactions.

811. The desensitizing bath

1. The desensitizer, which can be added to the developer or used in a prebath, must not stain the gelatin permanently. Furthermore, the dye attached to the colloid fulfills no useful purpose. *Phenosafranine* gives a strong red stain if it is too concentrated; basic scarlet and neutral red are simpler to use although they still have a high staining power. Some compounds on the other hand hardly stain or are readily eliminated; these include *pinakryptol green*, *yellow* and *white*, the *isosafranines*, *sodium-nitroanthraquinone-2-carboxylate*, *sodium anthaquinone-2-sulphonate*, the *furylvinylquinolines*, etc.

2. *Concentration of the bath.* This varies from 1:100 to 1:25,000 depending on the desensitizer. Examples: *picric acid* 1:100, *sodium 1-nitro anthraquinone-2-carboxylate* 1:400; *neutral red* 1:2000; *pinakryptol yellow* 1:2000; induline

scarlet 1:2000; *isosafranines* 1:5000; *chrysoidine* 1:5000; *pinakryptol green* 1:10,000; *phenosafranine* 1:20,000; *Nile blue 2B* 1:20,000.

3. *Treatment time.* Desensitization increases with the time of immersion. The speed with which the dye is adsorbed is rapid for the *first two minutes*, then becomes slower and finally ceases. The penetration of the liquid in the layer depends on the hardness of the gelatin (*temperature* of bath, 18°C (65°F)).

4. *Effect of developer.* The developer can destroy or diminish the desensitizing action in two ways:

(*a*) The dye is destroyed by the alkali or the sulphite. The desensitizer then permits, at the most, the examination of the plate before development: this is the case with derivatives of *triphenylmethane*, certain *carbocyanines*, the *anils*, the *chrysoidines*, *styrylbenzopyrylium*, etc.

(*b*) Some developers produce a precipitate with the dye-stuff: hydroquinone precipitates *pinakryptol green*; and concentrated metol-hydroquinone, *phenosafranine*. *Pinakryptol yellow* must not be added to the developer.

Desensitization is enhanced by the presence of *bromide ions*; conversely, it is retarded by the presence of silver ions.

Sodium sulphite slightly increases the power of safranine and pinakryptol green. In high concentrations it checks the desensitization of fine grain emulsions.

5. *Destruction of the latent image.* When a desensitized plate is exposed to light, the dye oxidizes the centres which tend to form: the action of the light then becomes much less efficient. But if the oxidation is too strong, the centres already present which comprise the latent image will be attacked; this results in loss of shadow detail.

The *anils* destroy the latent image. With *chrysoidine* and basic scarlet (which contains some chrysoidine), this attack is complete at 1:1000 and only becomes negligible with less than 1:5000. *Pinakryptol yellow* also results in some loss. The loss is insignificant with *pinakryptol green* and *phenosafranine*. It is practically nil with *anthraquinone derivatives* and with *phenylaminostyrylquinolines*.

6. *Retarding development.* The retarding of development which occurs in the presence of a desensitizer is tied up with the oxidation of the silver salt by the dye. The effect is not, however, constant, depending on the working conditions.

With *chrysoidine*, the development time is quadrupled. It is multiplied by 5 or 6 with *benzene-6-azo-2-chloro-3:5-toluylene diamine*.

7. *Fog.* Fog depends on the nature of the desensitizer, and on its concentration. With *phenosafranine* it is negligible. It is stronger with *flavinduline* and *sodium-1-nitroanthraquinone-2-carboxylate*.

The *rhodulines*, *methylene blue*, *Victoria blue*, the *indulines*, *ester yellow*, *Janus yellow* and *malachite green* produce an intense fog. This can be reduced by adding *anti-fogging dyes* such as *auramine*, *auracine*,(2) *acridine yellow*, *acridine orange*, *cachou brown* or *benzoflavine*.(3)

8. *Reversal of the latent image.* A rapid plate, immersed for 2½ minutes in a 1:10,000 solution of phenosafranine containing 2% bromide and then dried, gives, after fogging for a few seconds 6 feet from a 20 W lamp, a reversed image when exposed through a negative (solarization). The order of the exposures can be reversed.

CHEMICAL CONSTITUTION OF THE DESENSITIZERS

812. Azines

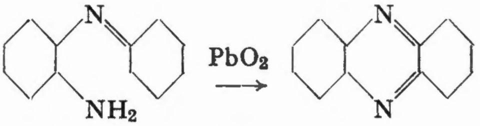
The azine dyes are derived from ***phenazine***, which is formed by oxidizing ***phenyl-o-phenylene diamine***.⁽⁴⁾ To prepare the dyes from the phenazine nucleus, amino or hydroxyl groups must be added.

The simple amino or hydroxyl azines are named respectively ***eurhodines*** and ***eurhodols***.

A nitrogen atom can have an alkyl or aryl group attached to it, giving, for example, ***phenylphenazonium***. The monoamino derivatives of phenylphenazonium are the ***aposafranines***, the diamino derivatives are the ***safranines*** and ***isosafranines***.

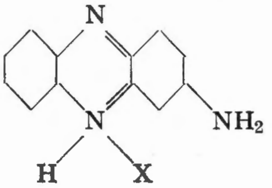
An aposafranine with a naphthalene nucleus gives the ***rosindulines***.

The substitution of an NH_2 group by —NH . C_6H_5 gives the indulines

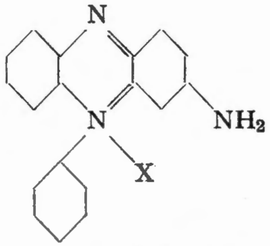


Phenyl-o-phenylene diamine

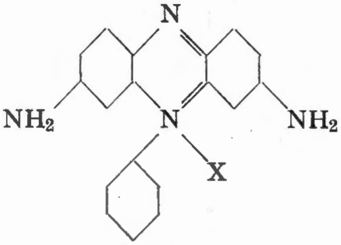
Phenazine



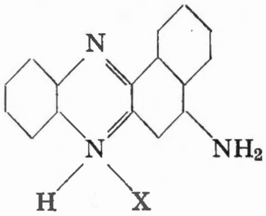
Eurhodine



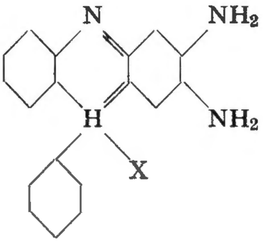
Aposafranine
(amino-phenylphenazonium)



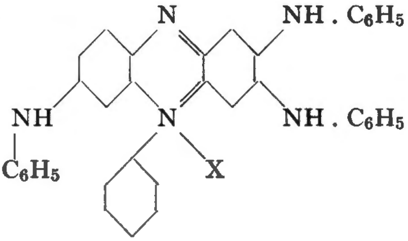
Safranine
diamino-phenylphenazonium



Rosinduline



Isosafranine



Induline

The azine dyes have a remarkable ***desensitizing action.*** This property is a result of the phenazine nucleus, but also depends on the nuclear amino substituents; however, the relation between the number of amino groups and the desensitization is not well defined. The replacement of the amino groups by hydroxyl, —OH, destroys the desensitizing properties. The replacement of the phenyl group attached to the nitrogen by alkyl groups has no effect. On the contrary, acetylation and diazotization destroy the activity of the azine. The presence of more than two amino groups reduces the photographic activity. The substitution of NH_2 by $NH . C_6H_5$ has the same effect (indulines).

813. Eurhodines

Neutral red (or toluylene red) has a phenazonium nucleus with a dimethylamino substituent on one part and an amino substituent on the other with an ortho methyl group. It is prepared by oxidation of a mixture of dimethyl-p-phenylenediamine and m-toluylenediamine. At a concentration of 1:1000 it reduces the red sensitivity 3000 times and the blue 400 times.

Neutral violet containing 3 amino groups (the third being an $—NH . C_6H_4 . . N(CH_3)_2$ group) is much less active.

814. Safranines

Phenosafranine is the simplest of the safranine (diamino-phenylphenazonium) dyes. It is basic. It is prepared by oxidation of equimolecular parts of aniline and p-p′-diaminodiphenylamine or by oxidation of a mixture of p-phenylenediamine and aniline.

Phenosafranine is the best known desensitizer as it is the easiest to obtain. It must be used in dilute solutions (1:20,000) or it stains the gelatin and the skin. It slows down the appearance of the image and precipitates with metol hydroquinone in strong solutions.

The other safranine desensitizers are:

Safranine (or tolusafranine) with methyl groups ortho to the amino ones. It is the main constituent of safranine T.

Basic scarlet N is a mixture of safranine and chrysoidine. It reduces the image slightly and delays its appearance. It can be used only as a forebath. The desensitized plates are slightly sensitive from 380 to 510 mμ with a maximum at 460 mμ. Panchromatic emulsions are developed in orange-red light.

The naphthosafranines such as *Magdala pink* also have desensitizing properties.

Dimethylsafranines. Fuchsia has a dimethylamino and an amino group. It is a desensitizer (particularly the bromide).

Safranine MN is similar to fuchsia but has a further methyl group ortho to the amino. It is a strong desensitizer, but fogs. *Safranine 6B*, *clematine* and *brilliant heliotrope 2R* are the same as safranine MN.

The *rhodulines* are safranines with one of the NH_2 groups dialkylated. They produce intense fog.

Giroflé and *tanin heliotrope* are safranines having a dimethylamino group on the first nucleus and an amino and two methyl groups (ortho and meta) on the second and two methyl groups on the phenyl radical. Desensitizers producing fog.

Tetramethylsafranine has two dimethylamino groups. It is prepared by oxidation of equimolecular proportions of dimethyl-p-phenylenediamine, dimethylaniline and aniline. Tetramethylsafranine is a powerful desensitizer constituting *pinasafrol* and *desensitol.* Tetraethylsafranine (amethyst violet or iris violet) has similar properties.

815. Alkyl phenazoniums

These are safranines in which the phenyl radical attached to the nitrogen is replaced by an alkyl radical. The best known dye is *neutral violet B*, dialkylethylamino-ethylphenazonium chloride—a fairly active desensitizer.

816. Aposafranines

These contain only a single amino group with the exception of the rosindulines which contain a naphthalene nucleus; they are inferior to the safranines as desensitizers.

Induline scarlet—aminoethyl-tolunaphthazonium chloride is a desensitizer which is as strong as phenosafranine. It is prepared by heating the azo derivative of monoethyl-p-toluidine with α-naphthylamine hydrochloride in the presence of a diluent such as phenol.

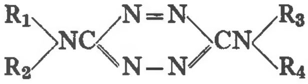
817. Isosafranines

The isosafranines are dyes which are isomeric with the safranines having the two amino groups in the same nucleus. They are good desensitizers which can be used as a 1:5000 forebath or in the developer (1:5000 to 1:20,000). They have the advantage that they do not stain gelatin. The principal isosafranines are *2:3-isophenosafranine* (nitrate) and *1:3-isophenosafranine.* The former is obtained by oxidizing a mixture of 3:4-dinitrodiphenylamine and aniline; the dinitroazine derivative which is produced is reduced to the diamine which is converted, after re-oxidation of the leuco base, to the nitrate.

Pinakryptol green was prepared, in a similar way to the quinoxalines, by reducing with stannous chloride the condensation product of o-aminodiphenylamine and picric acid. It is frequently given in the literature as a flavinduline obtained by the action of aminodiphenylamine on 2-aminophenanthraquinone. It has no pronounced affinity for fibres, and can be used as a 1:10,000 forebath. The desensitized plate must be washed prior to development in red light. Stock solutions must be kept in the dark. It can not be added to hydroquinone developers.

818. Tetrazines

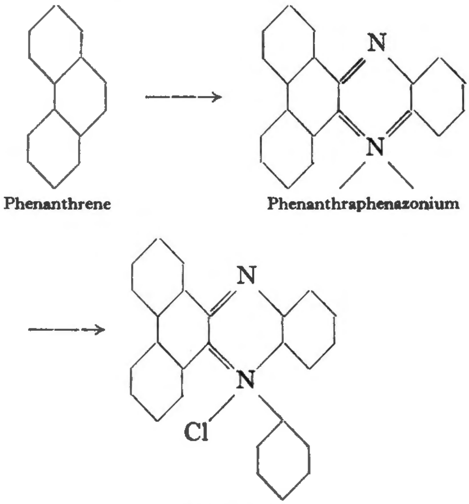
The tetrazines⁽⁵⁾ have the general formula:



They are strong desensitizers, although less powerful than the pinakryptols: such is *3:6-diaminotetrazine.*⁽⁶⁾

819. Quinoxalines

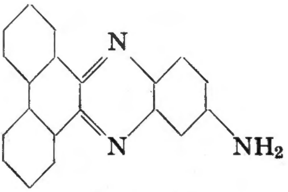
The quinoxalines are the phenazines derived from *phenanthrene.* The simple and the amino derivatives are all powerful desensitizers.



Phenanthrene

Phenanthraphenazonium

Flavinduline O



Aminoquinoxaline

Flavinduline O is phenylphenanthraphenazonium chloride and is prepared by reacting phenanthraquinone with o-aminodiphenylamine, C_6H_5—NH—C_6H_4—NH_2, in acetic acid.(6b)

Flavinduline O gives orange solutions which produce emulsion fog. To prevent the latter, the dye is mixed with *acridine yellow.*

Aminoquinoxalines. The amino quinoxalines are obtained in the same way as flavinduline. The o-aminodiphenylamine is replaced by 2:5-diaminodiphenylamine or the phenanthraquinone by an aminophenanthraquinone.

820. Nitro derivatives

The principal nitro derivative desensitizers are *picric acid*, *naphthol yellow* and *aurantia.*

Naphthol yellow (sodium salt of 2:4-dinitro-1-naphthol-7-sulphonic acid) has only a slight desensitizing action. *Picric acid* (trinitrophenol) is superior to it. At a concentration of 1%, the latter reduces the blue sensitivity 2000 times and the colour sensitivity 200 times.

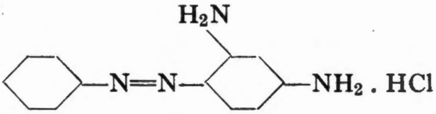
Aurantia is hexanitrodiphenylamine. It is a yellow substance which when used at 1:1000, reduces the blue sensitivity 800 times and the red sensitivity 400 times. Its toxicity is a disadvantage.

821. Azo dyes

Some azo dyes owe their desensitizing power to the presence of nitro groups. These include the *indian yellows*, also called azoflavine, citronine, azo yellow, brilliant yellow, curcumene. They are mixtures of the mono- or di-nitro derivatives of *orange IV* and of dinitrodiphenylamine, the orange itself being an azo dye of one molecule of diphenylamine and one of sulphonated aniline.

The indian yellows used at about 1%, reduce the natural sensitivity 50 times without affecting the induced sensitivity, a large part of this action being due to the absorption of blue light by the dye.

Chrysoidine is benzene-azo-m-phenylenediamine hydrochloride



Chrysoidine

It is prepared by reacting one mol of diazobenzene with one mol of m-phenylenediamine.

Used as a 1:5000 prebath (yellow solution) it gives a negligible loss of image, but slows down development two to four times more than phenosafranine. The desensitization is rather weak (100 times).

Chrysoidine R (methyl chrysoidine) delays the appearance of the image less.

Bromochrysoidine (benzene-5-azo-1-bromo-2:4-phenylenediamine hydrochloride). This dye is as powerful as phenosafranine. At 1:5000 it retards the appearance of the image only slightly. To prepare it, diazobenzene hydrochloride $C_6H_4N{=}NH\,.\,HCl$ is coupled with 1-bromo-2:4-phenylenediaamine. The latter is prepared by nitration and reduction of bromobenzene.

Chlorochrysoidine (benzene-5-azo-1-chloro-2:4-phenylenediamine hydrochloride) is obtained from diazobenzene hydrochloride and 1-chloro-2:4-phenylenediamine. The desensitizing action of this dye is greater than that of phenosafranine, but the developing time two or three times longer.

Benzene-6-azo-2-chlorotoluylene diamine and benzene-3-azo-5-chloro-2:4-toluylene diamine are also very powerful desensitizers but retard the appearance of the image even more.

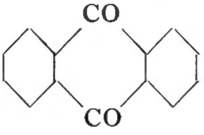
822. Anthraquinone derivatives

A great number of desensitizers are derived from *anthraquinone*. The anthraquinone nucleus has in fact oxidizing properties, and suitable substituents enable it to be adsorbed on silver bromide.

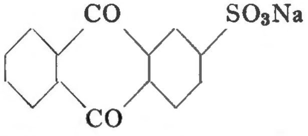
The acid derivatives of anthraquinone are strong desensitizers with but little effect on the latent image. They are resistant to sodium sulphite and developer alkalis. Furthermore, they are often almost colourless.

Sodium anthraquinone-2-sulphonate. Colourless compound obtained by controlled sulphonation of anthraquinone. Used in a 1:400 solution, it is a weak desensitizer used only with slow orthochromatic emulsions.

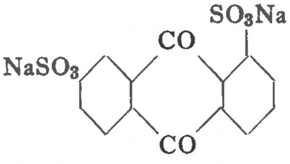
A more active product is obtained by introducing two sulphonic acid groups: sodium anthraquinone-1:7-disulphonate which constitutes *pinakryptol white*. The properties of this compound are partly due to the sulphonate groups. Pinakryptol white has been recently replaced by the Agfa *Denixan*.



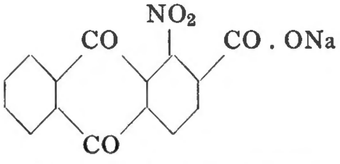
Anthraquinone



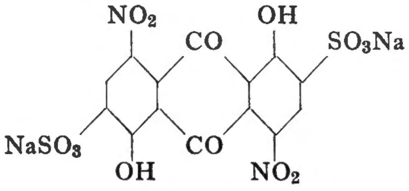
Sodium anthraquinone-2-sulphonate



Sodium anthraquinone-1 : 7 disulphonate



Sodium nitroanthraquinone-2-carboxylate



Sodium 1 : 5 dihydroxy-4 : 8 dinitroanthraquinone-2 : 6-disulphonate

Sodium nitroanthraquinone-2-carboxylate is an almost colourless powerful desensitizer. At 1:400 it is more active than phenosafranine at 1:5000 but it produces some fog. Residual blue sensitivity. It is obtained from 1-nitroanthraquinone which is sulphonated and converted to the nitrile. The latter is then hydrolyzed. Methylanthracene can also be nitrated, then oxidized with chromic acid.

Sodium 1:5-dihydroxy-4:8-dinitroanthraquinone-2:6-disulphonate is obtained by sulphonating 1:5-dihydroxyanthraquinone (anthrarufin) then nitrating the sulphonate. Very active desensitizer, but produces oxidation fog and stains the gelatin strongly when an M.Q. developer is used.

The basic anthraquinone derivatives are also desensitizers but they fog emulsions.(7)

823. Di- and triphenylmethane derivatives

The diphenylmethane and triphenylmethane derivatives often have sensitizing and desensitizing properties simultaneously. These include *auramine*, *methyl violet*, *crystal violet*, *coralline*, *fuchsine*, *Victoria blue*, *malachite green*, and *brilliant green*.

They can be used together with acridine yellow which reduces fog, but they do not resist alkalis or sulphite.

We would add to this group the *nitro derivatives of fluorescein*, for example *eosine scarlet* (or dinitrodibromofluorescein).

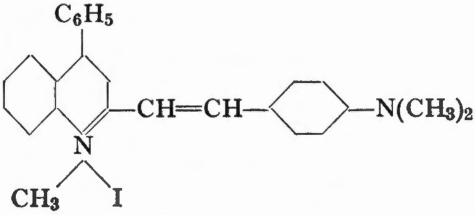
824. Carbocyanines

Some carbocyanines, such as *1:1′-dimethyl-4:4′-diphenyl-2:2′-carbocyanine* are very weak desensitizers. To increase the desensitizing action the cyanine must be nitrated: thus *nitrated diethylcarbocyanine* has a vigorous action, unfortunately destroyed by alkalis. The same effect is obtained with nitrated dicarbocyanines.

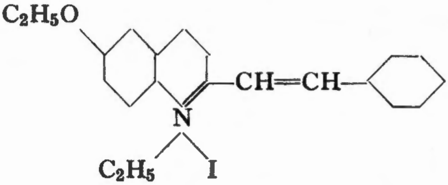
825. Styryl derivatives

These correspond to the hemicyanines.

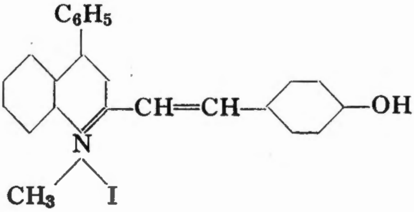
The pinaflavols obtained from quinaldine are weak sensitizers. The introduction of a phenyl group in the quinoline nucleus and a methyl group at the quaternary nitrogen atom results in powerful desensitizing properties. For example, *4-phenyl-2-(p-dimethylaminostyryl)-quinoline methiodide* obtained by the general method for preparing pinaflavols. This compound does not destroy the latent image.



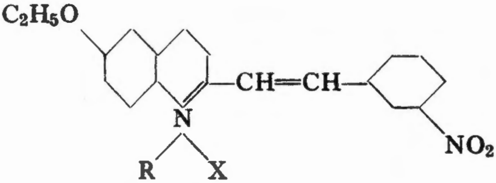
4-phenyl-2 (p-dimethyl aminostyryl)-quinoline



6-ethoxy-2-styryl quinoline



4-phenyl-2-(p-hydroxystyryl)-quinoline



2-(m-nitrostyryl)-4-ethoxyquinoline

By condensing p-ethoxyquinaldine ethiodide with benzaldehyde in alcohol in the presence of piperidine(8) 6-ethoxy-2-styryl quinoline is obtained in which the dimethylamino group is missing. Strong desensitizing action.

The combination of a phenyl group in the quinoline nucleus with an hydroxyl group in the benzene nucleus results in strong desensitizers; example, *4-phenyl-2-(p-hydroxystyryl)-quinoline* (methiodide), obtained by condensing 4-phenylquinaldine with p-hydroxybenzaldehyde in alcoholic solution in the presence of pyridine or piperidine.

Used as a forebath, this compound desensitizes ordinary emulsions strongly. It has quite a small effect in the red.

Nitrated styryl derivatives. By replacing benzaldehyde with ***m-nitrobenzaldehyde*** in the preceding condensations, very active nitropinaflavols are produced, particularly *pinakryptol yellow* which is 2-(m-nitrostyryl)-4-ethoxyquinoline.

Pinakryptol yellow is recommended for desensitizing panchromatic emulsions as it reduces the red and green speed greatly. It is used only as a forebath at a concentration of 1:2000. On exposure to light the solution turns brown and turbid.

In all the styryl derivatives the halogen radical can be advantageously replaced by a p-toluene-sulphonate radical —SO_3—C_6H_4—CH_3.

826. Styryl vinyl (or cinnamylidene) derivatives

By condensing cinnamaldehyde C_6H_5—CH=CH—CHO with quaternary salts of heterocyclic bases, desensitizers of moderate activity are obtained. For example, cinnamylidene-6-ethoxyquinaldine—a 6-ethoxy-2-styrylquinoline with a longer chain:

$$\text{—CH=CH—CH=CH—}$$

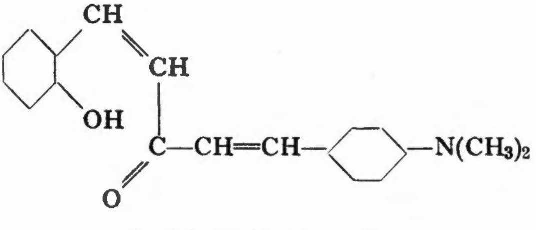
We note finally that by heating a quinaldine ethiodide with glyoxal in dry pyridine, dyes with a divinyl chain —CH=CH—CH=CH— joining two quinoline nuclei are formed which are devoid of sensitizing power.

827. Styryl derivatives of benzopyrylium

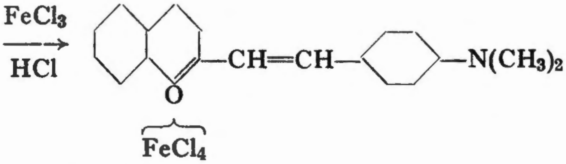
There is a direct analogy between the styryl derivatives of quinoline and those of benzopyrylium.

Some are weak sensitizers, but the majority show a marked desensitizing action. They have the disadvantage that they are destroyed by alkalis and sulphite.

One of the most important of these compounds is the *ferric chloride salt of p-dimethylaminostyryl-benzopyrylium*, a more energetic desensitizer than phenosafranine. It is prepared by condensing o-hydroxystyryl-methylketone OH . C_6H_4—CH=CH—CO—CH_3 with p-dimethylaminobenzaldehyde CHO—C_6H_4—$N(CH_3)_2$ in alcoholic solution in the presence of soda.⁽⁹⁾ The p-dimethylamino-2-hydroxystyrylketone, thus produced, is cyclized in warm hydrochloric acid and then treated with ferric chloride.



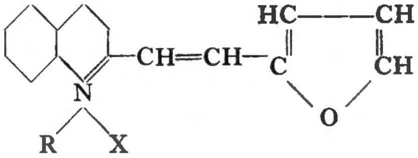
p-dimethylamino-2-hydroxystyrylketone



p-dimethylaminostyryl-benzopyrylium (ferric chloride salt)

828. Furylvinylquinolines

Furfural condenses with the alkyl halides of nitrogenous heterocyclic bases to give vinylquinolines of the general formula



Furylvinylquinoline

These compounds are very active, producing negligible fog, almost colourless, but destroyed by sodium sulphite. *2-β-furylvinyl-6-nitroquinoline methiodide* is more powerful than phenosafranine.

The quinoline and furyl nuclei can carry various substituents.(10)

829. Methine-anthraquinone derivatives

R. Dupont condensed anthraquinone derivatives with p-dimethylaminobenzaldehyde and m-nitrobenzaldehyde, obtaining a number of desensitizers. Many of them produced fog.(11)

830. Anils

We have seen that the pinaflavols are prepared by condensing p-dimethylamino benzaldehyde with a quaternary salt of a nitrogenous heterocyclic base. If the aldehyde is replaced by p-nitrosodimethyl aniline NO—C_6H_4——$N(CH_3)_2$, a ***p*-*dimethylaminoanil*** is produced(12) with the general formula

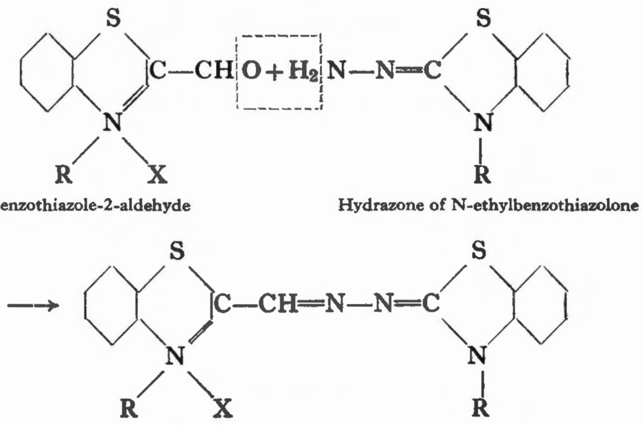
[Quaternary nitrogen base]—CH=N—C_6H_4 . $N(CH_3)_2$

The azamethine group —CH=N— confers marked desensitizing properties. The anils are in every case destroyed by alkalis and sulphite, and furthermore, they attack the latent image. Finally they produce fog when they contain acid substituents. Some of these compounds—in particular those obtained from the quinolines, naphthoquinolines, acenaphthopyridines and benzthiazoles are more active than the safranines.

831. Azacyanines

2:3:3-trimethylindoline methiodide, treated with a nitrite in the presence of acetic anhydride,(13) produces an azacyanine analogous to an indocarbocyanine but having a chain —CH=N—CH=. This azacyanine is a yellow desensitizing dye. An azathiacyanine can be similarly obtained.

Another group of azacyanines with a chain —CH=N—N= was disclosed by Fuchs and Grauaug.(14) Except for the chain, their structure is identical with that of the carbocyanines. They are very powerful desensitizers. They can be prepared by condensing a heterocyclic aldehyde with the hydrazone of a heterocyclic ketone (perchlorate) in boiling water. Their colour is from yellow to red.



Benzothiazole-2-aldehyde

Hydrazone of N-ethylbenzothiazolone

X.N-ethylbenzothiazole-1-aldehyde
N-ethyl-1-benzothiazolone-hydrazone

To prepare the *hydrazone of N-ethylbenzothiazolone*, ethylphenylthiourea $(C_2H_5)(C_6H_5)N—CS—NH_2$ is treated with bromine in chloroform;(15) this gives N-ethylimidobenzothiazoline by cyclization (the sulphur is joined to the phenyl group). This compound is nitrosated by sodium nitrite in acetic acid, then reduced with zinc to N-ethylnitrosoimidobenzothiazoline, then N-ethylbenzothiazolone hydrazone.

Benzothiazole-2-aldehyde is obtained by treating methylbenzothiazole perchlorate with p-nitroso-dimethylaniline, and decomposing the resulting anilide with perchloric acid.

Mann and Haworth have described azadimethine cyanines obtained by condensing 1:2-substituted-3-nitroso-indols with quaternary salts of heterocyclic bases containing a reactive methyl group. These azadimethines are vigorous desensitizers. They do not affect the latent image, but produce a little fog (*J.C.S.*, 1944, 670).

832. Triazoles

Steigmann's *Desensit N* is a phenazinotriazole which is prepared from o-phenylenediamine. 1–2 cc of a (hot saturated) isopropyl alcohol solution is used in 100 cc of developer; this can be replaced by 0·5–1 cc of a 1:1000 solution of the sodium salt (*Brit. Jour. Phot.*, 1946, 256).

833. Dipyridine compounds

The *γ-γ′-diquaternary* derivatives of *dipyridylium* are efficient desensitizers (B.P. 714,290, 1954).

1. Among the desensitizers which are not dyes, *apomorphine hydrochloride* (alkaloid), after aerial oxidation of its solution, has a strong desensitizing action: at 1 : 1000 it destroys the colour sensitivity and reduces that to blue 200 times, giving a slight fog. *Sodium hydrosulphite* which is a developer is also a desensitizer (see para. 67–2). Potassium chromate also reduces the sensitivity 40 times.

1b. Tamura M. and Tutihasi S.: *R.P.S. Cent. Conf.*, 1953, London.

1c. Horvitz and Friedman (Ansco): *Phot. Sci. and Techn.*, May 1955, p. 68–75.

2. *Auracine*: diamino-dimethylacridine formate.

3. *Benzoflavine*: diamino-dimethyl-phenylacridine hydrochloride.

4. Phenyl-o-phenylenediamine is o-amino diphenylamine. Fukushima and Suzuki have stated that the *amino-diphenylamines* are active desensitizers. The amino derivatives of cyclised *thiodiphenylamine* (analogous to the azines) are also desensitizers) (producing fog): such is methylene blue.

5. Described in *Gazz. Chim. Ital.*, 1913, **43** (2), 162 and —, **45**, 182 .

6. F.P. 866,741. Red solutions with low tinctorial power without action on the latent image. Densensitizing power is 300 times at 1 : 2,000. It is reduced by sulphite (E. B. Knott).

6b. Dye discovered by Homolka, see: *Phot. Ind.*, 1925, 347.

7. See R. Dupont: *Recherches sur les derivés anthraquinoniques*, Gevaert, Brussels. The rayon and acetate anthraquinone dyes were studied by this author, also the anthrasoles. Some of these compounds sensitize and desensitize simultaneously.

8. B.P. 262,816.

9. Heilbron and Buck: *J.C.S.*, 1921, **119**, 1500; 1922, **121**, 1198; 1923, **123**, 1935; 1927, —, 14 and Bullock: *Brit. Jour. Phot.*, 1927, 590.

10. There are also carbocyanines from quinazoline devoid of all activity, also the *styrylquinazolines* with weak desensitizing power. These desensitizers, of uncertain constitution, are obtained by condensing sodium o-hydroxyquinolinesulphonates with certain amines such as dimethyl-p-phenylenediamine in the presence of an oxidizing agent. These substances are destroyed by sulphite.

11. Dupont R.: *Bull. Soc. Chim. Belge.*, 1942, **51**, 209–224.

12. Hamer F.: *Phot. Jl.*, 1930, 374; Kaufmann and Valette: *Ber.*, 1912, **45**, 1736.

13. Wahl: G.P. 459,616 (1926) and B.P. 291,888 (1927).

14. *Ber.*: 1928, **61**, 57.

15. Besthorn: *Ber.*, 1910, **43**, 1519.

APPENDIX

Summary of Fundamental Chemical Laws

Chapter XLIII

THE ATOMS

834. Structure of atoms

The atoms of the different elements are all formed of the same materials following a similar scheme. Only the proportions of the various constituents and their geometrical positions vary. This is why the so-called elements which were once thought to be permanent can be converted from one to the other.

The atom can be represented by a miniature spherical or elipsoidal planetary system. At the centre of the system, a positive *nucleus*. Around the nucleus, one or more negatively charged bodies—the *electrons*—which revolve around the nucleus at high speeds. The complete atom is electrically neutral.

The size of an atom varies between one and ten ten-millionths of a millimetre. The nuclei are extremely small compared with the atoms, their diameters being 10,000 to 100,000 times smaller. This indicates the immense *vacuum* which exists, the solid particles being infinitesimal particles in empty space.

Almost the whole mass of the atom is concentrated in the nucleus. The cloud of electrons accounting for only a two-thousandth part of the mass. A hydrogen atom, having a diameter of one ten-millionth of a mm, weighs $1{\cdot}6 \times 10^{-24}$ g and has a single electron with 1/1,847 of this mass.

The number of electrons turning around the nucleus is different for each of the 98 known configurations. *It is the number of electrons which determines the chemical properties of the element* and therefore its characteristics. There are therefore as many elements as there are electron groupings. The simplest of all these is hydrogen: as we shall see, it has but one electron revolving around the nucleus. Helium has two electrons, lithium 3, carbon 6, chlorine 17, bromine 35, silver 47, lead 82, uranium 92. The number of electrons furnishes the *atomic number* of the particular element. It provides a classification of the different elements into groups having similar chemical properties.

835. The nucleus

The nucleus of an atom has a complex structure. It is made up of two kinds of particles with very different properties: *the neutrons*—electrically neutral—and the positive electrons or *positrons*.

The neutrons are the heavy particles accounting for the major part of the atom's mass. Being very small, they are therefore very heavy. The union of a neutron with a positron gives a positively charged *proton*. The proton is the nucleus of hydrogen. A positron in the nucleus is always united with a neutron. This indicates that there are at least as many neutrons as positrons: this gives, in each nucleus, a certain number of protons (formed from a neutron-positron union) plus a certain number of *free neutrons* joined to the protons.

How many protons are there in the nucleus of an atom? The answer is simple: there are as many protons as there are orbital electrons. In fact, for the atom to be neutral, the negative charges of the electrons must be balanced by an equal number of positive charges, that is by an equal number of protons (each containing a positively charged positron). Silver, for example, having 47 electrons, must necessarily

PERIODIC TABLE OF ELEMENTS

			1 H	2 He	3 Li	4 Be	5 B										
6 C	7 N	8 O	9 F	10 Ne	11 Na	12 Mg	13 Al										
14 Si	15 P	16 S	17 Cl	18 A	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga
32 Ge	33 As	34 Se	35 Br	36 Kr	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In
50 Sn	51 Sb	52 Te	53 I	54 X	55 Cs	56 Ba	57 to 71 *	72 Ct	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl
82 Pb	83 Bi	84 Po	85 At	86 Rn	87 Ml	88 Ra	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	

* *Rare earths metals*: La (57), Ce (58), Pr (59), Nd (60), Pm (61), Sm (62), Eu (63), Gd (64), Tb (65), Dy (66), Ho (67), Er (68), Tm (69), Yb (70), Lu (71).

have in its nucleus 47 protons. Hydrogen, having only a single electron, has but one proton.

This is not all; for there are, in addition, free neutrons attached to the protons. How many free neutrons are there in the nucleus? The only indication of this is given by the mass of the nucleus, the *atomic weight* which must be found. If, for convenience, we take arbitrarily chosen figures such that the mass of a proton or a neutron is equal to unity, *the figure giving the atomic weight of each element gives the total number of neutrons present in the nucleus.* A simple subtraction gives the number of free neutrons. For example, the atomic weight of oxygen is 16; the atom therefore has 16 neutrons in all. Its atomic number is 8: the number of electrons is 8 and therefore there are 8 protons, and this gives us the number of free neutrons, 16—8 = 8 neutrons. The result is written $O = 8_p + 8_N$. For lead, whose weight is 207, we have $Pb = 82_p + 125_N$ as the atomic number of lead is 82.

The neutron, although without an electrical charge, attracts the positron over a small distance (to form a proton) whilst it repels an electron. The positively charged proton attracts the electron over a greater distance, but if the electron wanders too close to the nucleus, the neutron repels the electron more strongly than the proton attracts it, and the electron must move away. We would finally state that a proton cannot be accompanied by more than two free neutrons, otherwise the neutrons repel each other. The recent discoveries of the *antiproton* (negative) and the *antineutron*, perhaps will bring some explanation of these phenomena.

836. Isotopes

We have said that there are 98 known configurations. This is understood from the 98 electron systems which determine the different chemical properties. But in fact, for each orbital system (or, if preferred, for each element) there are many different nuclei with different atomic weights, that is containing different numbers of neutrons. The sodium orbit of 11 electrons can be associated with 23 or 24 neutrons forming the combinations $11_p + 12_N$ and $11_p + 13_N$. This means that there are two sodium elements with the same chemical properties but with the different atomic weights 23 and 24. They are termed *isotopes* as they occupy the same position in the atomic number classification. More than 2000 are known. All elements have isotopes: mercury has 8, lead 11, carbon 4, uranium at least 4 whose atomic weights are respectively 234, 235, 236 and 238. The elements encountered in nature are *mixtures of isotopes*: this is why their atomic weights are rarely whole numbers. Chlorine, atomic weight 35·46, is a mixture of the two principal isotopes—78 % of chlorine 35 and 22 % of chlorine 37. Bromine, with an atomic weight of 79·92 contains the isotopes 79 and 81, similarly with iodine 126·93 (principally 127). As for silver, atomic weight 107·88, it also is a mixture of two isotopes (107 and 109) having the same chemical properties.

Hydrogen whose mass is 1 has two isotopes with masses 2 and 3 called deuterium and triterium. The deuterium atom has one electron turning round a nucleus composed of one proton and one neutron. In combination with oxygen it forms 'heavy water' of which there is 0·2 g in each litre of ordinary water. The deuterium nucleus is termed *deuton* (2 neutrons +1 positron).

Helium with the atomic number 2 (2 electrons) has a neucleus with a mass of 4 containing 4 neutrons and 2 positrons. This nucleus is called *helion* or an α-particle.

Helion, deuton and the proton are very stable nuclei which are found associated in various proportions in the heavy atoms such as mercury, lead, and radium.

The nuclei can be disintegrated by bombardment with α-particles or better, with neutrons:

Nitrogen (14 neutrons) + α-particle (4 neutrons) → Hydrogen (1 neutron) + Oxygen (17 neutrons).

Beryllium (9 neutrons) + α-particle (4 neutrons) → Carbon (12 neutrons) + 1 free neutron.

The second reaction enables neutrons to be obtained. These neutrons can in their turn be used to bring about other disintegrations. The neutron being electrically neutral is not moved out of its path by the electric charges of nuclei and electrons. This is the reason for its high penetrating power. Silver, bombarded by neutrons, gives a radioactive isotope of natural silver. It can also happen that the bombarded nucleus breaks into 2 large fragments; uranium can in this way be divided into strontium and xenon.

Some unstable natural nuclei disintegrate spontaneously by emitting a helium nucleus; the original nucleus by losing 4 neutrons provides a lighter nucleus. For example, radium (88_p+138_N) is transformed to radon (86_p+136_N). At the same time it emits three different radiations: α-particles or helions, β-particles or electrons (corresponding to the α-particles), and a natural oscillatory radiation which is very penetrating and similar to X-rays, called 'γ-rays'. The radon decomposes in the same way, and following a series of successive disintegrations a stable nucleus is finally left, generally lead. This is the characteristic known as *'radioactivity'* possessed by many elements such as thorium and uranium.

837. The electron

1. Electrons are constituents of matter. They exist, in the free state, in β-rays emitted by radioactive substances; they also form the cathode rays emitted by the negative electrode of discharge tubes in which there is a high vacuum. They constitute the flow of particles emitted by a heated filament towards an electrode having a positive charge (radio valves). They are also found liberated in flames of incandescent gas.

For convenience the electron is generally represented as a geometric particle limited by a well-defined surface like a billiard ball. In fact it is not at all like this. At the same time material and abstract, the electron is a manifestation of energy localized in space tied up with a field of forces which extend it; it can in no way be given a fixed volume. There is no line of separation between the electron and the vacuum which surrounds it, for it is more like a node in space. All that can be calculated is the volume in which its energy is concentrated, probably in a sphere 1/100th of a billionth of a millimetre, that is 1×10^{-11} mm. The mass of the electron is 9×10^{-28} g, that is about a billionth of a billionth of a billionth of a gram, for an electric charge of $4{\cdot}7\times10^{-10}$ electrostatic units. This charge is equal to that of a hydrogen nucleus but of opposite sign.

The electron can be deviated from its orbit under the influence of a magnetic or electrostatic field. This happens in cathode ray tubes used in television. It also explains why the electrons are displaced in metallic conductors in electric fields giving rise to a flow of current.

2. Now let us consider the movement of the electron in the atom. The theory of *undulatory movement* shows that the electron is a *corpuscle associated with a wave motion.* By wave motion is meant a succession of waves moving in a certain direction at a determined speed; this gives periodic variation whose time of variation or frequency is given by the time of the wave from one crest to another. The *length of the wave* is measured by the distance separating the two crests.

In the atomic scale, the classic mechanism can no longer be applied to calculate the movements of such small corpuscles. To explain this anomaly, Planck admitted that the corpuscular movements in closed orbits do not happen following a continuous series of values as in dynamics, but following a discontinuous series representing fixed steps or *quanta.* A quantum is definitely a whole number, and 'quantum mechanics' is based on the values represented by whole numbers (without intermediate values). In other words, corpuscular movements take place in jumps without a transition. Now we have already stated that *molecules are discrete particles of matter* and this characteristic is again found in the atom formed from separate corpuscles. It is logical to think that the discontinuity must be found again in the movements of these particles and that only these jerky (or quantum) movements are compatible with the energies brought into play.

Thus the electron does not describe a smooth orbit but one with an undulatory movement which is ultimately associated with it and whose wavelength can only have certain well-defined values. The vibration of the electron can be compared with that of a vibrating string which can only be based on a limited number of oscillations corresponding to its fundamental, the frequency of these vibrations being necessarily a whole number. Mathematically the electronic wave is represented by a function with four components, corresponding to four partial equations and depending on a first order equation system.

If m is the mass of an electron and v its speed, the associated wavelength λ is given by the formula

$$\lambda = \frac{h}{\mathrm{mv}}$$

h being Planck's constant equal to $6{\cdot}55 \times 10^{-27}$. When v is many thousands of kilometres per second, wavelength is of the order of 1 Å (the Angström unit having a value of one ten-millionth of a mm).

3. In addition to the orbit which it describes, *the electron has its own rotatory movement called spin.* Spin is a property bound up with the existence of the electron. This rotation gives rise to a magnetic moment (or magnetic quantity) and a kinetic moment. The quantity of magnetism being one magneton of Bohr, the amount of movement (kinetic) will be half the quantum unit $\frac{h}{2\pi}$ (h being Planck's constant). The spin can only have two opposite values, $+\frac{1}{2}$ and $-\frac{1}{2}$, depending upon the direction of rotation. In the atom, the spins of all the electrons are added algebraically in such a way that the total spin determines the external properties of the element. The nuclei also have a rotation formed from the sum of the spins of the neutrons and positrons.

The movement and the distribution of the electrons can be forecast *statistically.* But apart from statistics, the individual track of a corpuscle cannot be determined in advance. Heisenberg has shown that two components x and y of the movement of a corpuscle cannot be measured simultaneously with precision, for the product of two *incertitudes* (or errors) relative to these two simultaneous measurements is equal to or greater than the constant h:

$$\Delta \mathrm{x} \times \Delta \mathrm{y} \geqslant h$$

This principle is true only for the atomic scale, for with a normal scale the measurement error is insignificant compared with the size measured.

As far as the electron is concerned, its exact position can never be known. We only know in which limits of *probability* a certain position corresponds to a given velocity.

Chapter XLIV

FUNDAMENTAL CHEMICAL PRINCIPLES

838. Symbolic representation of chemical substances

To represent the substances composed of simple elements, it is customary to place side by side the symbols of the different constituents: we know that HCl, hydrochloric acid, shows a compound of hydrogen and chlorine, and that KBr, potassium bromide, is a compound formed of potassium and bromine.

The smallest possible unit being the *atom*, a discrete particle of material, as we have already seen, we suppose that each symbol represents an atom. The result of this is that the formula of a composite substance represents a molecule: HCl and KBr will be the molecules of hydrochloric acid and potassium bromide.

HCl and KBr are substances each composed of two atoms. But there are other compounds formed of more than two atoms: water, H_2O, is made up of two atoms of hydrogen and one atom of oxygen; silver nitrate, $AgNO_3$, is composed of one atom of nitrogen, three atoms of oxygen and an atom of silver.

From these first statements we can form two general rules.

1. *Compounds are formed by the combination of elements in fixed proportions by weight* (Proust's law of constant proportions). In other words the formula of a chemical substance is always the same and characteristic of the substance.

2. *When two elements combine together to form more than one compound, there is a simple ratio between the different weights of one element which will combine with a fixed weight of the other element* (Dalton's law of multiple proportions). It is evident that a formula will always contain a whole number of atoms (1, 2, 3, 4, etc.) and never 1·23 or 2·8 since an atom cannot be divided without being destroyed: this is a consequence of the discontinuity of matter and the presence of whole numbers in compounds is in accordance with the quantum theory where the electron movements also take place in definite steps.

If two elements form, combining between themselves, several different compounds, the number of atoms of one of the elements which unites with a fixed number of atoms of the second element will be simple multiples of the same number following Dalton's rule. With nitrogen and oxygen we therefore have the following compounds:

NO_2—nitrogen peroxide.
N_2O_2 (or NO)—nitric oxide.
N_4O_2 (or N_2O) nitrous oxide.

839. Atomic weights

We have seen that the atomic mass of an element represents the *number of neutrons* contained in the nucleus, the mass of a neutron being arbitrarily chosen as 1. The mass of the neutrons is practically equal to the mass of the atom, those of the electrons and positrons being negligible in comparison.

The mass is a measure of the inertia of a body. In the case of chemical elements, the atomic mass expresses a *relationship* between the absolute masses of the atoms of different elements. It is therefore wrong to designate these relationships by the expression *atomic weights* (which is relative to the earth's gravity). We will retain, however, the established use of the latter term which in practice has no effect on calculations.

If instead of considering the formulas of chemical substances as representing individual molecules (just as we have done in the preceding paragraph) we regard them more as groups of molecules containing a number n (n being a constant number and equal for all substances), we can choose n sufficiently great for the weight of the substance represented by a formula to be measured in practice.

Taking for the weight of each symbol of an element a number of grams equal, in absolute value, to the corresponding atomic mass (more exactly to the *number of neutrons*) we have the weight of a *gram atom* represented by its symbol. An example will make this easier to understand.

The silver atom has 107 neutrons in its nucleus; its atomic mass (or atomic weight) is therefore 107. The symbol Ag represents a 'gram atom' of silver whose weight is exactly 107 grams. The result of this is that each time the symbol Ag is written in the formula of a compound it is understood by this that 107 grams of silver is used; and each time there is Ag then each time one takes 107 grams. In reality, natural silver being a mixture of isotopes, the atomic weight of this metal given by the tables is 107·88 and this is the figure which we use in calculations.

The formula of a molecule represents consequently the sum of the gram atoms which constitute it, and the total weight of material which it contains is equal to the sum of the atomic weights 'in grams' of each constituent element. Thus the formula of silver bromide AgBr represents a weight of substance equal (in grams) to the sum of the atomic weights of silver and bromine: $107{\cdot}88 + 79{\cdot}92 = 187{\cdot}80$ grams. We see that if an atom of silver combines with an atom of bromine in a simple ratio conforming to Dalton's Rule a weight of 107·88 grams of silver will always combine with a weight of 79·92 grams of bromine. The latter figures appear less simple as proportions but each corresponds to the number of neutrons in silver and in bromine and are therefore the fixed quantities or quanta (the decimals in these figures are due only to the presence of isotopes; with pure elements one would have the whole numbers, 108 and 80 for example, ignoring the insignificant mass of the electrons).

To go from the simple molecule to the gram molecule the former mass must be multiplied by the number N, which is the number of molecules of it equal to a gram-molecule. N is called *Avogadro's number*. It enables the reverse calculation to be made also: to find the mass of an actual molecule knowing the mass of the gram-molecule, easily calculated from the 'atomic weights' of the constituents.

$$\text{molecular mass} = \frac{\text{gram-molecule}}{N}$$

$$\text{atomic mass} = \frac{\text{gram-atom}}{N}$$

$N = 603 \times 10^{21}$, which enables the mass of a silver bromide molecule to be found from its 'molecular weight' which we have already calculated:

$$\text{molecular mass AgBr} = \frac{187{\cdot}80}{603 \times 10^{21}} = 3{\cdot}1 \times 10^{-22}\text{ g.}$$

List of atomic weights most commonly used in photography:

Element	Symbol	At. Wt.	Element	Symbol	At. Wt.
Hydrogen	H	1·0078	Cerium	Ce	140·25
Oxygen	O	16·0	Chromium	Cr	52·0
Chlorine	Cl	35·46	Copper	Cu	63·57
Bromine	Br	79·91	Iron	Fe	55·84
Iodine	I	126·93	Manganese	Mn	54·93
Sulphur	S	32·06	Mercury	Hg	200·6
Nitrogen	N	14·00	Nickel	Ni	58·68
Phosphorus	P	31·0	Gold	Au	197·2
Selenium	Se	79·2	Platinum	Pt	195·23
Carbon	C	12·005	Lead	Pb	207·20
Boron	B	10·82	Potassium	K	39·10
			Sodium	Na	23·0
Metals			Thallium	Tl	204·38
Silver	Ag	107·88	Titanium	Ti	47·9
Barium	Ba	137·37	Uranium	U	238·2
Cadmium	Cd	112·4	Vanadium	Va	51·0
Calcium	Ca	40·07	Zinc	Zn	65·38

When the elements taking part in a reaction are gases, the *volumes of the gaseous masses which appear or disappear have a simple relationship* (Gay-Lussac's Law). This relationship is the same as the molecular ratio. For example:

$2H_2$	+	O_2	=	$2H_2O$
2 molecules hydrogen		1 molecule oxygen		2 molecules water

or

2 volumes hydrogen	1 volume oxygen	2 volumes water vapour

The gaseous molecules, whatever their type, always displace the same volume. As a gram-molecule always contains N molecules, it follows that a gram-molecule of any gas always occupies the same volume, which at 0°C and 760 mm pressure is about 22·4 L. Thus 44·8 L of hydrogen combines with 22·4 L oxygen to give 44·8 L of water vapour weighing 2 gram-molecules, i.e. 36 g. In this case there is a *reduction of volume* by combination but there is no loss of weight, hence no loss of material, at least in practice. This will now be examined with the law of conservation of matter.

840. Conservation of matter

According to the law put forward by Lavoisier, the total weight of a compound is equal to the sum of the weights of the components. We have just given the example of the formation of water from oxygen and hydrogen. Similarly, the silver chloride formed from an atom of chlorine and an atom of silver will have the same weight as the sum of the weights of a gram atom of silver and a gram atom of chlorine:

	Cl	+	Ag	=	AgCl
Atomic weight in grams	35·5		108		(108 + 35·5) 143·5
	1 atom of chlorine		1 atom of silver		1 molecule of silver chloride

It is again so with carbon burning in oxygen, being transformed into carbon dioxide with no appreciable loss in weight of material

$$\begin{array}{cccccc} \mathrm{C} & + & 2\mathrm{O} & = & \mathrm{CO_2} \\ 12 & & 2\times16 & & 12+32 = 44 \end{array}$$

Theoretically this law is incorrect, for it is not the matter which is conserved but the energy, and it should be called the *law of conservation of energy*. Every chemical reaction absorbs or produces thermal energy, and the equation should be written, to be correct, using matter for producing energy

$$\mathrm{A}+\mathrm{B} = \mathrm{C}+\text{energy}.$$

This means that in each heat-producing reaction there is no loss of matter, since the energy (formed from the matter) is found elsewhere, but subtraction of matter (or addition in other cases needing a supply of energy). The difference, however, is so small that it can be ignored.

2. The *inertia* of a body is its resistance to all actions tending to alter its state of rest or of movement. If the body is in motion it resists any action tending to accelerate or slow down this movement.

The *mass* of a body is the measure of this inertia. Now the *theory of relativity* teaches us that inertia increases with the velocity of the body. At a velocity of 300,000 km/sec. the inertia becomes infinite; that is why a velocity of 300,000 km/sec. is a limit which can never be exceeded. If the inertia of a body increases, its mass increases necessarily. In this way the mass of an electron increases with its velocity following the formula:

$$\mathrm{m} = \frac{\mathrm{m_o}}{\sqrt{1-\left(\frac{\mathrm{v}}{\mathrm{c}}\right)^2}}$$

where $\mathrm{m_o}$ is the initial mass, m the mass at velocity v and c the velocity of light.

Thus when a substance receives energy, the molecular agitation becomes greater and the mass increases. The reverse phenomenon occurs when a substance loses part of its energy, most frequently as heat; it then loses mass. A striking example of loss of mass as energy is the following: the atomic mass of hydrogen is 1·0078. The union of four atoms of hydrogen produces helium whose nucleus contains 2 protons +2 free neutrons. Now the atomic mass of helium is 4 very exactly whilst $4\times1{\cdot}0078 = 4{\cdot}0312$. There is therefore a loss of mass of 0·0312 which is 3 centigrams per gram-atom of helium. If the energy lost at the moment when the four atoms of hydrogen combine is E ergs and c the velocity of light, the loss of mass Z is related by the formula $\mathrm{Z} = \frac{\mathrm{E}}{\mathrm{c}^2}$ to the loss of energy, which is approximately equal to 3×10^{19} ergs.*

841. Inert elements

The electrons which turn around the nucleus of an atom are subdivided into different concentric *shells* (themselves divided into sub-orbits) which are designated, starting from the one nearest the nucleus, by the letters K, L, M, N, O, P, Q. The complete enlarged atom can be represented as a series of spheres (or ellipsoids) each contained within another and whose respective surfaces serve as tracks for the different groups of electrons passing across them. The radii of these spheres are of different lengths depending on the nature of the atom. With uranium for example, the average radii of the shells K, L and M are respectively $0{\cdot}6\times10^{-10}$ cm and 12×10^{-10} cm.

---

* Erg: See note para 2.

Figure 138 represents the electron configuration of the atoms of hydrogen, oxygen, chlorine, bromine, silver, barium and uranium, following the increasing complexity of their shells.

Now, among the simple elements there are a certain number whose shells give the appearance of being perfectly spherical. The electron orbits of such atoms are symmetrical, and therefore the energies which must be applied to withdraw the electrons from the same shell are equal. This results in very stable and chemically inactive atoms. These are the *inert atoms*: helium, neon, argon, krypton and radon and the relatively stable *secondary inert atoms*, nickel, palladium and platinum.

It is important to know the electronic distribution of these inert atoms for this enables the chemical behaviour of all other elements to be understood. The shell arrangement of each is as follows:

Inert atom	Atomic number	Number of electrons in the shells						
		K	L	M	N	O	P	Q
Helium	2	2						
Neon	10	2	8					
Argon	18	2	8	8				
Krypton	36	2	8	18	8			
Xenon	54	2	8	18	18	8		
Radon	86	2	8	18	32	18	8	
Nickel	28	2	8	18				
Palladium	46	2	8	18	18			
Platinum	78	2	8	18	32	(8 +10)		

If, from the electron cloud of an inert element (without considering the nucleus) 1, 2, 3, or 4 electrons are removed from the outer shell, a new *unstable* but active element is obtained which will have a great affinity for external electrons until its shell is saturated.* The chemical reactions of this unstable element are due to its need to be reconverted to a stable element by acquiring one or more electrons belonging to another element. Examples:

2. Remove *one* electron from the outer shell of *argon* (distribution 2, 8, 8): an element having 7 electrons in shell M is obtained, which is *chlorine* (Fig. 138). Needing one electron to become stable, the chlorine atom will unite with all other atoms having an electron to give up.

Remove *one* electron from the outer shell of *krypton* (distribution 2, 8, 18, 8): an element is obtained with the electron distribution K : 2, L : 8, M : 18, N : 7 which is bromine (Fig. 138). Like chlorine, bromine needs one electron to become stable, and its chemical properties resemble those of chlorine.

Chlorine and bromine, together with fluorine (derived by a similar mechanism from neon) and iodine (derived from xenon) form the *halogen* group.

---

* The transformations described here are purely schematic. They are not true transmutations, for the nuclei of the atoms are not considered.

Instead of removing one electron from the outer shell of an inert atom, *two* are removed; a second group of elements with similar chemical properties is obtained:

Neon (2, 8) 2 electrons = *oxygen* (2, 6).
Argon (2, 8, 8) 2 electrons = *sulphur* (2, 8, 6).
Krypton (2, 8, 18, 8) 2 electrons = *selenium* (2, 8, 7, 8, 6).
Xenon (2, 8, 18, 18, 8) 2 electrons = *tellurium* (2, 8, 18, 18, 6).

By removing *three* electrons from the outer shell of the same elements one obtains successively: *nitrogen*, *phosphorus*, *arsenic* and *antimony*. Their electron content is that of the corresponding inert elements less 3.

By taking away four electrons in the same way and in the identical order, *carbon* (2, 4), *silicon*, *germanium*, *tin* and *lead* (from radon) are obtained.

3. Now, if instead of removing the electrons, the opposite operation is performed: *adding an electron to an additional shell* of the inert elements, the series of *alkali metals* is obtained: *lithium* (2, 1), *sodium* (2, 8, 1) and *potassium* (2, 8, 18, 1), corresponding to helium, neon and argon.

Adding *two* electrons to the empty additional shell produces a series of *alkaline earth metals*: *beryllium*, *magnesium*, *calcium*, *strontium* and *barium* (Fig. 138).

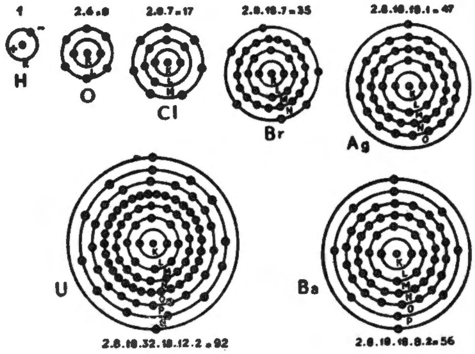


FIG. 138. Schematic representation of the atoms of hydrogen, oxygen, chlorine, bromine, silver, barium and uranium.

Three electrons added in an extra shell to the electronic system of neon gives aluminium (2, 8, 3).

Passing to the three fairly inert elements: nickel, palladium and platinum. The nickel atom has 18 peripheral electrons in shell M. If *one* electron is added to shell N, *copper* is obtained in which one electron of shell M will, together with the new electron, have the property of mobility, as we shall see later. *Two added electrons* give *zinc*.

If an electron is added to the vacant shell O of *palladium*, the electronic configuration of *silver* results (Fig. 138), whose distribution is K : 2, L : 8, M : 18, N : 18, O : 1. With another electron cadmium is formed.

By adding one, two or three electrons to the electronic arrangement of platinum, those of *gold*, *mercury* and *thallium* are obtained by the same mechanism.

4. All the elements obtained by *adding* one, two, three or four electrons to an additional shell of the inert elements tend to take up a stable configuration: because of this, they have the property of donating their new electrons to the elements requiring them (chlorine, bromine, sulphur, etc.) as we have already seen in the operation of removing electrons. The addition elements react readily with the subtraction ones.

For example, sodium combines with bromine with the exchange of an electron (from sodium to bromine) and calcium with sulphur (with the passing of two electrons from the calcium to the sulphur).

From all these considerations of the inert elements and the conversion to them of the more active elements, some very important facts result, which we shall study in the following paragraphs: ions, valency and the classification of the simple elements.

842. The ions

Each atom of an active element can, by acquiring or losing one or more electrons› again conform to the electronic configuration of the inert element from which it is theoretically derived: it is then in the state of an *ion.*

As the atom is electrically neutral, any addition or loss of electrons alters its electric charge: it becomes polarized. The ion has a negative charge (—) when it is formed by acquiring an electron (negative); it is positively charged when it results from the loss of an electron (the nuclear charge becoming stronger). For example, chlorine (derived from an inert element by removal of a peripheral electron) becomes a *chloride ion* Cl^- (negative) when it *captures* an electron. Silver (derived from the stable element palladium by addition of an electron in a supplementary shell) *loses* an electron to become a positive *silver ion* Ag^+. The union of a silver atom with a chlorine atom automatically brings about the formation of the two ions Ag^+ and Cl^-, as the electron given up by the silver is immediately taken by the chlorine.

The active elements which we suppose to be formed by the removal or addition of more than one electron are obviously converted to the corresponding ions by the transfer of the appropriate number of electrons. In this case the charge on the ion is double, treble or four times that of the ions Cl^- or Ag^+ formed by transfer of a single electron. Thus sulphur gives the doubly negative charged ion S^{--}, phosphorus P^{---}, magnesium Mg^{++}, aluminium Al^{+++} (loss of three electrons), etc.

In short, the *ion* is an atom which has acquired or lost one or more peripheral electrons.

The ions can exist in the free state. They are produced when a cathode ray beam (of electrons) passes through rarefied gas. They are also produced by the action of X-rays. The positive and negative ions produced can be reversed by an electric field. The gases escaping from a flame are also ionized, partly by the electrons liberated at the moment of combustion.

The place where the manifestation of ions is most apparent is in aqueous solution. A salt such as sodium bromide NaBr is formed from two stable ions Na^+ and Br^- bound by electrical attraction. Now in solution this mutual attraction is considerably reduced and the two ions are released, each retaining its charge.

If two electrodes are immersed in the solution, and if an electric current is passed between them, the positive ion Na^+ is naturally attracted by the negative electrode (—) and the negative ions Br^- by the positive electrode. In this way two ionic migrations in opposite directions are produced. When the ions reach the electrodes they lose their charges. The negative ion Br^- loses the electron which it has borrowed and again becomes a neutral bromine atom; the positive ion Na^+ regains the electron which it had lost to the bromine and again becomes neutral sodium. A similar result is obtained with all other salts. Any substance which in this way allows an electric current to pass by *dissociation of its molecule into its ions* is an *electrolyte*. The amount of dissociated molecules becomes greater with respect to the undissociated ones as the concentration becomes lower.

The negative ions which migrate towards the positive electrode, or anode, are called *anions* (ex: Cl^-, Br^-, I^-). The positive ions which migrate towards the negative electrode, or cathode, are called *cations* (ex: Na^+, K^+, Ag^+, Ba^{++}).

The ions of the same element provided by different compounds have exactly the same chemical characteristics: the ion Cl^- formed by ionic dissociation of the chlorides of sodium, magnesium or zinc is the same in all cases, and reacts in the same way with the customary reagents. It is this that leads, in chemical analysis, to the study and identification of each ion separately as if the constituents of the substance were completely independent.

843. Valency

Depending on whether it needs, or has an excess of 1, 2, 3, 4 (or more) electrons to again form the parent stable electronic configuration, an atom must, to produce an ion, be provided with or lose 1, 2, 3, 4 electrons. Depending on the number of these electrons, the ion will have a single, double, treble, fourfold, etc., negative or positive charge, equal to the number of electrons transferred.

The halogens: fluorine, chlorine, bromine and iodine formed from the inert elements by *removal* of a single electron, only need, to form the ions (and resaturate their external shells) to acquire a single electron per atom. The negative charge of a single electron is added to the neutral atom: F^-, Cl^-, Br^-, I^-. We say that the elements fluorine, chlorine, bromine and iodine are *monovalent*. One atom of any will combine with a single atom of hydrogen (monovalent as it has only one electron) to form the compounds HF, HCl, HBr, HI, the electron from the hydrogen being given to the halogen atom.

By similar reasoning it can be seen that the elements derived from a stable electronic configuration by the addition of *a single electron*, such as the alkali metals and silver, are monovalent, their ions possessing only one positive charge: Na^+, K^+, Ag^+. These elements combine atom for atom with the halides, both being monovalent, for example silver iodide AgI and potassium fluoride KF.

2. All active atoms derived from a stable configuration by subtraction or addition of *two electrons* are *bivalent*, and their ions have two negative or positive charges: such are oxygen O^{--}, sulphur S^{--}, selenium Se^{--}, the alkaline earths Mg^{++}, Ca^{++}, Sr^{++}, Ba^{++} (magnesium, calcium, strontium, barium), iron Fe^{++}, copper Cu^{++}, manganese Mn^{++}, nickel Ni^{++}, lead Pb^{++}, mercury Hg^{++}. For combination to take place between a monovalent element and a bivalent one, two atoms of the monovalent substance are necessary. Examples: water H_2O, silver sulphide Ag_2S, calcium chloride $CaCl_2$.

3. Elements derived from a stable configuration by the addition or subtraction of *three electrons* are tervalent. Their ions carry three charges: nitrogen N^{---}, phosphorus P^{---}, arsenic As^{---}, gold Au^{+++}, aluminium Al^{+++}. With monovalent elements they give compounds similar to NH_3 (ammonia) or $AuCl_3$ (gold chloride). Combined with bivalent atoms, they must be written in such a way that the negative and positive charges of the two ions are balanced. For example:

$$\begin{array}{cccc} 3S^{--} & + \quad 2Al^{+++} & = & Al_2S_3 \\ \text{3 sulphur ions} & \text{2 aluminium ions} & & \text{Aluminium sulphide} \\ \text{—6 electrons} & \text{6 electrons} & & \text{neutral} \end{array}$$

4. Elements formed from the stable system by the addition or subtraction of 4 *electrons* are *tetravalent*. Their ions carry four positive or negative charges. Among the tetravalent substances, the most important is *carbon*, the constituent of all organic material. Si^{----} (silicon), Ti^{++++} (titanium), Pt^{++++} (platinum), are also tetravalent, forming compounds such as $PtCl_4$ (platinic chloride).

5. In addition to the principal valency, some elements can have one or more *secondary valences*. Iron, bivalent in ferr*ous* compounds such as $FeCl_2$ is trivalent in ferr*ic* compounds like $FeCl_3$. The passage from the ferrous Fe^{++} to the ferric Fe^{+++} follows the scheme:

$$\begin{array}{ccccc} Fe^{++} & - & e & = & Fe^{+++} \\ \text{Ferrous} & & \text{Electron} & & \text{Ferric} \\ \text{ion} & & & & \text{ion} \end{array}$$

The electronic shells of the iron atom can be represented as follows, compared with those of argon (inert):

	K	L	M
Argon No. 18	2	8	8
Iron No. 26	2	8	8 +(5 +1 +2)

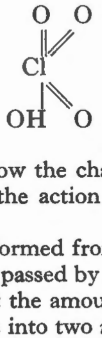
The electrons in the shell M (of iron) are divided into *separate orbits* of which the outermost contains the two electrons giving the valency of two. The electron in the next orbit is hardly more difficult to remove than the first two, which explains why ferrous salts change so readily to ferric salts. Also it is possible that a certain asymmetry in the orbits results in unequal forces attaching the electrons and hence a variation in the valency of the atom.

Among the other polyvalent metals of interest in photographic chemistry are

Valency	Metal	Atomic number	Shells					
			K	L	M	N	O	P
2, 3, 4	Titanium	22	2	8	8 +(1 +1 +2)			
2, 3, 4, 5	Vanadium	23	2	8	8 +(1 +1 +1 +2)			
2, 3, 4, 5, 6	Chromium	24	2	8	8 +(1 +1 +1 +1 +2)			
2, 3, 4, 6, 7	Manganese	25	2	8	8 +(1 +2 +1 +1 +2)			
1, 2	Copper	29	2	8	17 +(1)	(1)		
2, 4	Tin	50	2	8	18	18	(2 +2)	
3, 4	Cerium	58	2	8	18	18 +(1)	8	(3)
1, 2	Mercury	80	2	8	18	32	18	(1 +1)
1, 3	Thallium	81	2	8	18	32	18	(2 +1)

Titanium, vanadium, chromium and manganese have several successive orbits in shell M which results in a simple valency charge. For example, manganese is bivalent in the monoxide MnO, trivalent in the sesquioxide Mn_2O_3, tetravalent in the dioxide MnO_2, hexavalent in potassium manganate K_2MnO_4, and heptavalent in potassium permanganate $KMnO_4$.

6. Finally, in addition to their normal valencies as ions, the halogens and other non-metals such as sulphur, nitrogen and phosphorus can take very diverse valencies, particularly with oxygen, towards which they play the part of positive elements going as far as parting with 7 outer electrons. Example: chlorine (2, 8, 7 electrons) combines with 3 O (2, 6) and 1 OH (monovalent), donating 6 electrons to the 3 O and 1 electron to the radical OH. It retains the skeleton (2, 8) which is that of neon (inert), whilst the oxygen (2, 6) becomes (2, 8), also like neon. Result: perchloric acid with the formula



or $HClO_4$

7. Now that we know how the characteristic of valency differentiates the various substances, we can study the action of an electric current on the ions in aqueous solution.

Consider an electrolyte formed from a solution of sodium bromide NaBr through which an electric current is passed by means of two electrodes (+) and (—) immersed in the liquid. Suppose that the amount of the salt is exactly one gram-molecule. As sodium bromide dissociates into two *monovalent* ions Na^+ and Br^-, we say that NaBr contains one *gram-ion* of Na^+ and Br^- respectively. It is found that the quantity of electricity necessary to carry a gram-ion of Na^+ and Br^- to the electrodes is 96,490 coulombs (1 Faraday). In other words, one Faraday is necessary to decompose one gram valence.

To decompose cupric chloride $CuCl_2$ containing two valency bonds, 2F or 96,490 × × 2 coulombs are needed.

As in one gram-molecule there are N molecules (Avogadro's number) F coulombs will neutralize N electrons *e*. The total electronic charge of the molecule is therefore Ne. Now $F = Ne$, where the electric charge of an electron $e = F/N = 4{\cdot}6 \times 10^{-10}$ electrostatic units.

844. Classification of the simple elements

The usual classification of simple substances into two groups—*metals* and *non-metals*—is made more accurate with knowledge of the electronic mechanism.

Firstly, the terms metal and non-metal indicate chemical characteristics more than anything, for the same element can behave as one or the other according to circumstances.

When an element loses one (or more) electrons it behaves as a metal, being converted to a positive ion

H	—	e	H^+
Neutral hydrogen		Electron	Hydrogen ion

When an element receives one (or more) electrons, it behaves as a non-metal, being converted to a negative ion

H	+	e	H^-
Neutral hydrogen		electron	Negative hydrogen ion

In the first case, the ion H^+ plays the part of a metal. By combining with negative ions such as Cl^-, Br^-, I^-, S^{--}, etc., it forms acids—hydrochloric HCl, hydrobromic HBr, hydriodic HI, hydrogen sulphide H_2S. The hydrogen ion H^+ is stable as it is a proton, a simple nucleus.

In the second case, hydrogen plays the part of a halogen (non-metal) as it forms hydrides with metals, e.g. NaH, sodium hydride.

Also we have stated above that the non-metals such as chlorine can also give negative ions (Cl^-) which behave as metals towards other more negative elements by losing electrons from the outer shell.

Long ago Berzelius arranged the simple elements in order of decreasing electronegative potential: oxygen, fluorine, chlorine, bromine, iodine, sulphur, selenium, nitrogen, phosphorus, carbon, silicon, boron, hydrogen, metals. It should be noted that hydrogen is at the border of the metals and non-metals. *Each member plays the part of a metal towards the previous one.*

Generally, the simple elements are arranged in groups having similar chemical properties, and more often with the same valency.

Among the non-metals, we have already spoken of the importance of the halogens (F, Cl, Br, I) whose various members have similar properties. Then there is the sulphur, selenium, tellurium group and the nitrogen, phosphorus, arsenic group: *the oxides of the non-metals are all acidic.*

The metals are electrical conductors; they give *basic oxides* which can combine with acids to give *salts*.

In practice the metals of interest can be arranged as follows:

1. *Alkali metals*: lithium, sodium, potassium, cesium.
2. *Alkaline earths*: calcium, barium, strontium.
3. *Semi earths*: magnesium, zinc, cadmium.

4. *Aluminium.*
5. *Iron series*: iron, nickel, cobalt, manganese.
6. *Chromium series*: chromium, molybdenum, tungsten, uranium, vanadium.
7. *Tin series*: tin, titanium, zirconium.
8. *Copper.*
9. *Noble metals*: platinum, palladium, iridium, gold.
10. *Silver, thallium, lead, mercury* which form insoluble salts with most acids except nitric.

845. Acids

The acids are compounds formed from a combination of one or more *hydrogen ions* with a *negative ion*. This negative ion can be either a non-metal such as F^-, Cl^-, Br^-, I^-, S^{--}, or an *oxygen grouping* (or acid radical) such as $(SO_4)^{--}$, $(PO_4)^{---}$:

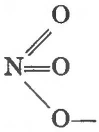
$Cl^- + H^+ = HCl$ hydrochloric acid.
$(SO_4)^{--} + 2H^+ = H_2SO_4$ sulphuric acid.
$(PO_4)^{---} + 3H^+ = H_3PO_4$ phosphoric acid.

The formula of a 'hydracid' composed only of hydrogen and a simple electronegative element, such as HCl, is simple as we see. That of an 'oxacid' containing oxygen together with the electronegative element is a little more complicated; it *depends on the secondary valency* of this element, always considering oxygen to be bivalent. Example: nitrogen N is normally trivalent, but it can also be pentavalent as represented here:

Pentavalent nitrogen

Bivalent oxygen

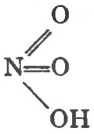
By saturating the valencies of nitrogen with oxygen we have



The last valence being insufficient to satisfy the third oxygen atom, this retains a free negative valency which can be represented by NO_3^-.

It is this radical which, saturated by a hydrogen ion gives *Nitric acid*

$NO_3^- + H^+ = HNO_3$ or



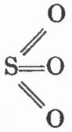
Chloric $HClO_3$, sulphuric H_2SO_4, phosphoric H_3PO_4, permanganic $HMnO_4$ dichromic $H_2Cr_2O_7$ acids can be represented with similar structures. It is enough to remember that an acid hydrogen atom is always attached to an oxygen atom which has one valency to attach it to the starting element.

An acid is also considered as the result of a combination of a non-metal oxide (or one with its characteristics) with water. Pentavalent nitrogen combines with oxygen to give the compound N_2O_5 or nitric anhydride

When treated with a molecule of water this is converted to two molecules of nitric acid

N_2O_5	+	H_2O	=	$2HNO_3$
Nitric anhydride		Water		Nitric acid

Similarly we can show how sulphuric anhydride SO_3 or



gives sulphuric acid

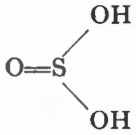
SO_3	H_2O	=	H_2SO_4
Sulphuric anhydride	Water		Sulphuric acid

gives carbonic acid (unstable)

CO_2	+	H_2O	=	H_2CO_3
Carbon dioxide		Water		Carbonic acid

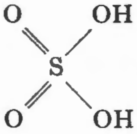
If the starting element has several secondary valencies it gives several different acids. Take sulphur: its principle valency is 2 and its secondary valencies 4 or 6. The possible combinations are

Valency 4: sulphurous acid



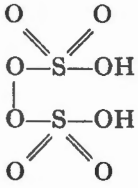
or H_2SO_3

Valency 6: sulphuric acid



or H_2SO_4

persulphuric acid

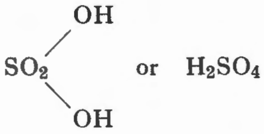


or $H_2S_2O_8$

and the corresponding anhydrides

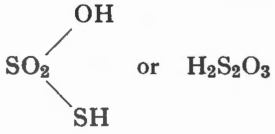
SO_2	SO_3	S_2O_7
sulphur dioxide	sulphur trioxide	persulphuric anhydride

With sulphuric acid, one of the atoms of oxygen linked to a hydrogen can be replaced with bivalent sulphur: *thiosulphuric* acid (or *hyposulphurous*) is obtained in this way and the salts are the thiosulphates.



$SO_2(OH)(OH)$ or H_2SO_4

Sulphuric acid



$SO_2(OH)(SH)$ or $H_2S_2O_3$

thiosulphuric acid

The ions corresponding to all these sulphur acids are, in order, SO_2^{--}, SO_4^{--}, $S_2O_8^{--}$, $S_2O_3^{--}$.

As we have noted, the groups of atoms have their valencies exactly like the simple elements.

846. Bases

1. Water, H_2O or H . OH is formed by the union of two ions H^+ and OH^-, respectively positive and negative (Fig. 139). The H^+ ion is the constituent of all acids. The group OH^-, named *hydroxyl*, owes its negative valency to oxygen from its structure H—O—$^-$, one of the two valencies being neutralized by the hydrogen atom. The hydroxyl group is a characteristic of bases as the hydrogen ion is a characteristic of acids.

The name base is given to the compound formed from an OH^- ion with a positive ion, such as Na^+, Ca^{++}, Al^{+++}, etc. A base is therefore a metallic *hydroxide* (or hydrate).

The alkali metals provide the strongest bases: sodium hydroxide NaOH commonly called *caustic soda*; potassium hydroxide KOH or *caustic potash*; lithium hydroxide LiOH. These compounds are very soluble in water.

The alkaline earths give strong but slightly soluble bases: calcium hydroxide $Ca(OH)_2$ or slaked lime (Ca^{++} being bivalent, $2OH^-$ are required to satisfy its two valencies); barium hydroxide $Ba(OH)_2$.

Magnesium gives hydrated magnesia or magnesium hydroxide $Mg(OH)_2$; zinc, zinc hydroxide $Zn(OH)_2$; aluminium, aluminium hydroxide $Al(OH)_3$ which are insoluble.

As a general rule, the insoluble hydroxide of a metal is obtained by adding to the solution of one of its salts the equivalent amount of caustic soda or potash: the hydroxide is quickly precipitated. Example:

$FeCl_3$	+	$3NaOH$	→	$Fe(OH)_3$	+	$3NaCl$
Ferric chloride solution		Caustic soda solution		Ferric hydroxide precipitate		Sodium chloride solution

There are four other compounds in current use which in addition to the alkali hydroxides deserve special mention: these are sodium carbonate (or the potassium salt) trisodium phosphate, borax and ammonia.

1. *Sodium carbonate.* Sodium salt of carbonic acid, its formula is Na_2CO_3. Formed by the combination of a strong base and a very weak acid, it hydrolyses in water (decomposes) into caustic soda and carbonic acid. It can crystallize with ten molecules of water.

$$\begin{array}{ccccccc} Na_2CO_3 & + & H_2O & = & 2NaOH & + & CO_2 \\ \text{Sodium} & & \text{Water} & & \text{Caustic} & & \text{Carbon} \\ \text{carbonate} & & & & \text{soda} & & \text{dioxide} \end{array}$$

2. *Trisodium phosphate.* Sodium salt of phosphoric acid H_3PO_4 in which the 3H are replaced by sodium: Na_3PO_4. It crystallizes with 12 molecules of water, and hydrolyzes like the carbonate, which gives it the properties of an alkaline compound.

3. *Borax.* Sodium salt of tetraboric acid $H_2B_4O_7$ which must not be confused with boric acid H_3BO_3, although borax can be obtained from the latter. It is a weak base with the formula $Na_2B_4O_7 . 10H_2O$.

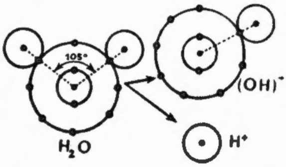


FIG. 139. Dissociation of water into ions $(OH)^-$ and H^+.

4. *Ammonia.* Trivalent nitrogen, with hydrogen forms a gas NH_3, which is very soluble in water (1 litre of water at 15°C dissolves 848 times its volume). The solution of ammonia gas has the basic properties of caustic soda. It forms salts with acids, which points to the existence of a monovalent *ammonium radical* or ion NH_4^+. The aqueous solution of ammonia will be a solution of the hydroxide NH_4OH, which can neutralize an acid with the formation of an ammonium salt.

$$\begin{array}{ccccccc} HCl & + & NH_4OH & \rightarrow & NH_4Cl & + & H_2O \\ \text{Hydrochloric} & & \text{Ammonia} & & \text{Ammonium} & & \text{Water} \\ \text{acid} & & & & \text{chloride} & & \end{array}$$

Nitrogen and hydrogen form two other basic compounds: hydrazine and hydroxylamine.

5. *Hydrazine* has the formula $NH_2—NH_2$ (or N_2H_4). It is a colourless liquid doubly basic which can combine with many organic compounds. It can be obtained by reacting ammonia with sodium hypochlorite:

$$\begin{array}{ccccccc} 2NH_3 & + & NaOCl & \rightarrow & NH_2—NH_2 . HCl & + & NaOH \\ \text{Ammonia} & & \text{Sodium} & & \text{Hydrazine} & & \text{caustic} \\ & & \text{hypochlorite} & & \text{hydrochloride} & & \text{soda} \end{array}$$

6. *Hydroxylamine* $NH_2—OH$ is also a strong base. Solid, melting at 33°C and soluble in water, it is prepared by the action of hydrogen on ethyl nitrate.

Finally, there is a whole series of organic bases which will be considered in the chapter on organic chemistry.

847. Complexes

We have just seen that trivalent nitrogen gives ammonia NH_3 which, in solution, is converted to the ammonium ion NH_4^+ which compares with a monovalent metal.

$$\begin{array}{ccccc} NH_3 & + & H^+ . (OH)^- & \rightarrow & (NH_4)^+ . (OH)^- \\ \text{Ammonia} & & \text{Water} & & \text{Ammonium} \\ & & & & \text{hydroxide} \end{array}$$

The ammonium ion is formed by the union of a neutral molecule NH_3 with a positive ion H^+, and can be written

$$(NH_3 \,.\, H)^+$$

The nitrogen always remains trivalent and there is no question of tetravalent nitrogen. We say that ammonium is a *complex ion.*

A *complex ion* is defined as a *group resulting from the union of a neutral molecule with an elementary free ion.*

The ammonium ion can be represented by a tetrahedron with the nitrogen atom in the centre and the four peaks by the four hydrogen atoms (Fig. 140).

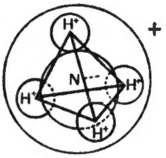
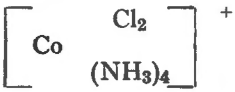


FIG. 140. Schematic arrangement of the complex ammonium ion.

How are the four nitrogen atoms retained by the nitrogen which is only trivalent? It is admitted that the forces acting on the electrons and the nuclei of a molecule have the resultant such that the distribution of the forces of attraction are divided uniformly as a type of *co-ordination* which is not the same as normal electrovalence. The number of atoms which can be held is therefore greater than with ordinary valency. The difference between covalence and electrovalence is called complementary valency.

Each element has a particular covalence: that of nitrogen is 4, that of trivalent cobalt 6; in the latter case 6 atoms or groups are around the principal element, e.g.:



$$\left[\,\mathrm{Co}\;\begin{matrix}\mathrm{Cl_2}\\ (\mathrm{NH_3})_4\end{matrix}\,\right]^+$$

The covalence has a fixed value for the elements giving perfect complexes, like nitrogen, cobalt and platinum. With others, whose complexes are readily hydrolyzed (or imperfect) the covalence can vary. The metals are more apt to form perfect complexes, the more electropositive they are, and this occurs mainly among the metals with a heavy nucleus.

848. The salts

1. A salt is a compound resulting from the *combination of an acid and a base.* The hydrogen of the acid is replaced by the metal of the base and a molecule of water is formed. With hydrobromic acid and potassium hydroxide the following reaction occurs:

$$\underset{\substack{\text{Hydrobromic}\\ \text{acid}}}{HBr} + \underset{\substack{\text{Potassium}\\ \text{hydroxide}}}{KOH} \rightarrow \underset{\substack{\text{Potassium}\\ \text{bromide}}}{KBr} + \underset{\text{Water}}{H_2O}$$

With a poly-valent acid such as sulphuric:

H_2SO_4	$+$	$2NaOH$	$\rightarrow$	Na_2SO_4	$+$	$2H_2O$
Sulphuric acid		Sodium hydroxide		Sodium sulphate		Water

Consequently, *a salt is formed from the union of a negative ion with a positive ion.* Example:

$CuSO_4$	$\rightarrow$	SO_4^{--}	$+$	Cu^{++}
Copper sulphate		Sulphate anion		Copper cation

A salt can be prepared by reacting an acid either with a hydroxide, with an oxide, with a carbonate or another easily decomposable salt:

$H_2SO_3+Zn(OH)_2 \rightarrow ZnSO_4+2H_2O$
$H_2SO_4+Ag_2O \rightarrow Ag_2SO_4+H_2O$
$H_2SO_4+Na_2CO_3 \rightarrow Na_2SO_4+CO_2+H^2O$
$H_2SO_4+\text{silver acetate} = Ag_2SO_4+\text{acetic acid}$

2. Finally there is a direct method of preparing a salt: it is to attack a metal with an acid. In this way silver nitrate can be prepared by dissolving metallic silver with hot nitric acid diluted with its own volume of water. One cannot write

$2HNO_3$	$+$	$2Ag$	$\rightarrow$	$2AgNO_3$	$+$	H_2
Nitric acid		Silver		Silver nitrate		Hydrogen

for the hydrogen, produced in the course of the reaction, decomposes part of the acid to produce nitric oxide NO which itself, in contact with the air forms nitrogen peroxide NO_2 (reddish brown vapour) and the complete reaction is summarized thus

$$3Ag+4HNO_3 \rightarrow NO+3AgNO_3+2H_2O.$$

By evaporating the solution, solid silver nitrate remains. To purify it, it is dissolved in distilled water, filtered and evaporated: colourless crystals darkening on exposure to light are obtained.

If the metal contains copper, the acid solution becomes blue-green. Heating is continued after evaporation to decompose the copper nitrate and the product changes from blue to black, with loss of nitrogen vapours; a mixture of unchanged silver nitrate and copper oxide CuO remains from which the latter is removed by filtration.

With dilute hydrochloric and sulphuric acids, decomposed by metals such as zinc or iron, the hydrogen is produced as the gas: this is a way of preparing this element:

$2\,HCl$	$+$	Zn	$\rightarrow$	$ZnCl_2$	$+$	H_2
Hydrochloric acid		Zinc		Zinc chloride		Hydrogen

3. In the case of polyvalent acids it can happen that all the hydrogen atoms are not replaced by a metal: the salt obtained is not neutral but acid.

Examples:

Sodium sulphite, Na_2SO_3, neutral.
Sodium bisulphite $NaHSO_3$ acid.
Sodium bicarbonate $NaHCO_3$.
Sodium dihydrogen phosphate NaH_2PO_4.
Disodium hydrogen phosphate Na_2HPO_4.

4. *Water of crystallization.* Many salts crystallize with a certain number of water molecules in their crystal structure. This must be borne in mind when calculating and weighing, each molecule of water weighing 18 g. Thus copper sulphate crystallizes with 5 molecules of water, ferrous sulphate with 7 molecules, alum with 24 molecules, sodium thiosulphate with 5 molecules, magnesium chloride with 6 molecules. The water content of sodium carbonate, borax and trisodium phosphate have already been given.

5. *Insoluble salts*

The halides of silver, lead, mercury and thallium are insoluble. The sulphides of these metals are also insoluble, and the salts of many other acids.

Their nitrates are soluble without exception.

Among the other insoluble salts of interest in photography is barium sulphate, $BaSO_4$, powdery white precipitate.

To prepare an insoluble salt it is generally sufficient to precipitate from the solution of a soluble salt with the desired anion. For example, sodium chloride (containing the anion Cl^-) poured into a solution of silver nitrate immediately precipitates silver chloride:

$$\begin{array}{ccccccc} AgNO_3 & + & NaCl & \rightarrow & \mathit{AgCl} & + & NaNO_3 \\ \text{Silver} & & \text{Sodium} & & \text{Silver} & & \text{Sodium} \\ \text{nitrate} & & \text{chloride} & & \text{chloride} & & \text{nitrate} \end{array}$$

The same result is obtained if sodium chloride is replaced by another soluble chloride or by hydrochloric acid.

The precipitate does not appear if it is decomposed by a strong acid produced during the course of the reaction. If we have

$$\begin{array}{ccccccc} AgNO_3 & + & \text{acetic acid} & \rightarrow & \text{silver acetate} & + & HNO_3 \\ \text{Silver} & & & & & & \text{Nitric} \\ \text{nitrate} & & & & & & \text{acid} \end{array}$$

the nitric acid produced decomposes the silver acetate (salt of a weak acid) re-forming silver nitrate and acetic acid.

6. *Salts decomposed by acids.* These are carbonates, with liberation of carbon dioxide; the sulphites with liberation of sulphur dioxide, the thiosulphates with liberation of sulphur dioxide and precipitation of sulphur, the sulphides with loss of the disagreeable smelling hydrogen sulphide, the hypochlorites giving off chlorine, the borates hot, with liberation of crystalline boric acid.

In general, all salts from weak acids, inorganic or organic, are decomposed by the strong acids such as hydrochloric, sulphuric or nitric acids.

7. *Double salts.* There are some salts like certain chlorides which have an acid reaction (antimony, tin, gold, platinum) which have the property of combining with other salts of basic reaction to form complex *chlorosalts*:

$$\begin{array}{ccccc} AuCl_3 & + & NaCl & \rightarrow & NaAuCl_4 \\ \text{Gold} & & \text{Sodium} & & \text{Sodium} \\ \text{chloride} & & \text{chloride} & & \text{chloroaurate} \end{array}$$

$$\begin{array}{ccccc} PtCl_4 & + & 2KCl & \rightarrow & K_2PtCl_6 \\ \text{Platinum} & & \text{Potassium} & & \text{Potassium} \\ \text{chloride} & & \text{chloride} & & \text{chloroplatinate} \end{array}$$

8. *Oxides.* The oxides are formed by the union of a metal with oxygen.

There are *basic oxides* like Na_2O, CuO, MgO, FeO, Ag_2O, which form salts with acids.

There are also *acidic oxides* which in fact are anhydrides. In the presence of water they form acids which combine readily with bases to form salts.

CrO_3, chromic anhydride, forms the chromates (K_2CrO_4) and the dichromates ($K_2Cr_2O_7$).

In a series of oxides, the one with most oxygen is the most acid: in the manganese series MnO is basic, Mn_2O_3 is indifferent, MnO_2 is weakly acid, MnO_3 (not isolated) is a fairly strong acid as it forms the manganates (K_2MnO_4) and Mn_2O_7 is a strong acid giving the permanganates ($KMnO_4$).

An acid oxide and a basic oxide can combine to give an *oxide salt*. For example, red lead has the following formula:

$$Pb_3O_4 \text{ or } 2PbO . PbO_2$$

The sulphides are also classed in groups similar to the oxides.

849. The chemical reaction

1. A chemical equation interprets the reaction schematically. Coefficients must be used for each substance so that the elements are balanced on each side. Taking the following reaction, the oxidation of ferrous chloride to ferric chloride by potassium permanganate in hydrochloric acid solution:

$$a\ KMnO_4 + b\ FeCl_2 + c\ HCl = d\ FeCl_3 + e\ KCl + f\ MnCl_2 + g\ H_2O.$$

To convert the 4 oxygen atoms of the permanganate to H_2O, 8HCl are necessary to provide the 8 H atoms, therefore $a = 1$, $c = 8$ and $g = 4$. Also Mn and K of the permanganate require 3Cl to give $MnCl_2$ and KCl. The 8 HCl used provide 8Cl leaving, by subtraction, 3Cl used for the $MnCl_2$ and KCl, 5 Cl being used to transform $5FeCl_2$ to $5FeCl_3$. This gives $e = 1$, $f = 1$, and $b = d = 5$. The reaction must therefore be written:

$$KMnO4 + 5FeCl_2 + 8HCl = 5FeCl_3 + KCl + MnCl_2 + 4H_2O.$$

The chemical reaction can be an *addition reaction*, a *displacement* reaction, or a *double decomposition* reaction.

In addition we have the simple scheme $A + B = AB$ as in the synthesis of ammonium chloride (conversely, it can be decomposition)

$$\underset{\text{Ammonia}}{NH_3} + \underset{\text{Hydrochloric acid}}{HCl} \rightarrow \underset{\text{Ammonium chloride}}{NH_4Cl}$$

In the displacement reaction, a group C replaces a group B:

$$AB + C \rightarrow AC + B$$

For example, hydriodic acid in solution is decomposed by aerial oxygen, liberating the iodine

$$\underset{\text{Hydriodic acid}}{2HI} + \underset{\text{Oxygen}}{O} \rightarrow \underset{\text{Water}}{H_2O} + \underset{\text{Iodine}}{I}$$

The decomposition of silver chloride by hydrobromic acid is a double decomposition reaction following the plan

$$AB + CD \rightarrow AD + BC$$

$$\underset{\text{Silver chloride}}{AgCl} + \underset{\text{Hydrobromic acid}}{HBr} \rightarrow \underset{\text{Silver bromide}}{AgBr} + \underset{\text{Hydrochloric acid}}{HCl}$$

In organic chemistry the *condensation* reaction is often used, where two simple molecules unite to form a heavier one, often eliminating a lighter one.

2. *Chemical affinity*. The chemical affinity of one substance for another is the ease with which the first reacts with the second. It is due to the tendency to form a stable electronic configuration by acquiring or donating electrons. This mechanism has already been described in connection with the inert elements, the ions and valency.

The molecules of a chemical system are not always in a state when they will react. Some of them appear to have greater energy: these are the *activated molecules*. The energy necessary for this activation can be provided by the reaction itself or by an external medium such as heat or light.

The activation is due to a change in the state of the electronic system. The instability can result from either a change in the spin of the electrons or by a change in their vibratory energies.

For one molecule to react with another, it must absorb energy. This heat is taken from that released by the reaction in the form of *heat of reaction* resulting from the displacement of the electrons from one atom to another and the movement of the atoms themselves.

The amount of heat released shows the variation in the total energy of the system. Part of this energy is used by the latter. The remaining free energy measures the external work which the reaction can provide, and is a characteristic of affinity. The released heat often differs very little from the free energy and can be used to forecast the possibility of a reaction. This is possible when the work is positive. For example, the heat of formation of silver chloride is 28,900 cals., whilst the mutual affinity of chlorine and silver is measured by 26,200 cals.

3. *Catalysis*. All chemical reactions take place at a certain individual velocity. But as it is difficult to forecast all the other factors which come in, one usually has to rely on empirical information to establish the rate of a reaction and the point of equilibrium. In general, a temperature increase raises the initial rate. This rate decreases as the equilibrium state is reached and the reaction finishes very slowly.

When a reaction is *reversible*, that is, when it can take place in either direction depending on the conditions, an equilibrium is established between the two opposite reactions.

Certain compounds called *catalysts* accelerate the reaction rate or even make them possible. The extent of their action is independent of their concentration, for traces of the catalyst are sometimes sufficient to bring about a reaction.

The mechanism of the catalysis phenomenon is still the subject of many hypotheses. For example, it has been supposed that the reacting molecule acquires additional energy which brings it to a critically active state. The catalyst can also function because of its great porosity which supplies a large area of contact in the cavities with a very small radius of curvature (inducing surface energy). This is the case with spongy platinum, alumina, porous pot, pumice stone and activated charcoal. Finally, there is the hypothesis that the catalyst forms an intermediate product which decomposes with regeneration following an endless chain reaction: this is the case with powdered metals such as reduced nickel, iron, copper, manganese, mercury salts, etc.

Catalysis is currently used in the preparation of inorganic, and particularly organic, compounds. We would mention the hydrogenation of the hydrocarbons and fatty products by gaseous hydrogen, the condensation of acetylene compounds and the manufacture of synthetic resins.

The catalyst can instigate a combination or decomposition equally well depending on the case: thus spongy platinum (porous substance) can bring about the combustion of a mixture of inflammable gas, hydrogen +oxygen for example, whilst it rapidly decomposes hydrogen peroxide H_2O_2 to water and oxygen. In both cases the most stable product, water, is the final product.

Chapter XLV

CONSTITUTION AND PROPERTIES OF ORGANIC COMPOUNDS

850. Organic radicals

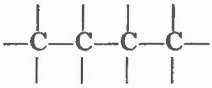
1. All organic compounds are derived from carbon. The carbon atom has the atomic number 6 and the atomic weight 12. This shows that the nucleus contains 12 neutrons and 6 positrons as 6 neutrons and 6 protons. The number of electrons is 6 divided into two shells: 4 electrons in the outer shell L.

Situated between two inert elements helium and neon (para. 841) whose electron systems are K : 2 and K : 2, L : 8, carbon can, by *gaining* 1–4 outer electrons approach the inert configuration of neon or by *losing* 1 to 4 outer electrons tend towards the helium system. It can therefore have 9 possible electrovalences of which the principal is *valency* 4. In the latter it is necessary to saturate the 4 valences by acquisition of 4 electrons from other elements, hydrogen for example.

2. *The tetravalency of carbon* is a fundamental concept in organic chemistry. However, in certain cases it appears to be divalent or trivalent.

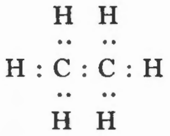
Carbon must therefore be generally combined with 4 atoms of a monovalent element—hydrogen, chlorine, bromine, iodine—to form a compound which will exist in the free state: one atom of carbon + 4 atoms of hydrogen forms a *saturated hydrocarbon*, methane CH_4, in which one or more of the hydrogens can be replaced by one or more atoms of a halogen (Fig. 141).

Several atoms of carbon united to each other by one valency form a *carbon chain with the structure*:



$$-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-$$

where the free valencies must be saturated by hydrogen (or any other monovalent electronegative element). Thus a series of saturated hydrocarbons homologous with methane are obtained CH_4, C_2H_6, C_3H_8, C_4H_{10}, etc., with the general formula $Cn\ H_{2n+2}$. Thus the developed formula for ethane C_2H_6 is represented by the structure



$$\begin{array}{ccccccc} & & H & & H & & \\ & & \cdot\cdot & & \cdot\cdot & & \\ H & : & C & : & C & : & H \\ & & \cdot\cdot & & \cdot\cdot & & \\ & & H & & H & & \end{array}$$

in which the dots are the common electrons, so that each carbon atom is surrounded by 8 electrons like the inert element, *neon*. One can also imagine each carbon atom as a sphere in which an imaginary tetrahedron is described: at the 4 apexes of the tetrahedron are the 4 pairs of electrons.

3. *Double bonds*. If two carbon atoms are mutually converted by two valencies instead of one there is a *double bond* of the form $: C = C :$. By saturating the remaining valencies, an *ethylene hydrocarbon* is obtained, ethylene having the formula

$CH_2 = CH_2$. The characteristic property of the double bond is the ability to combine with two atoms of hydrogen or chlorine to give a saturated hydrocarbon with single bonds. Also the strength of the links between two carbon atoms are so weak that the double bond can be completely ruptured by a strong oxidizing agent: two separate compounds are formed.

4. *Triple bonds.* Two carbon atoms joined by three valencies have a triple bond, a characteristic of the *acetylene hydrocarbons* $—C \equiv C—$. The simplest of these is acetylene $CH \equiv CH$.

5. *Radicals.* Any hydrocarbon in which one of the carbon atoms has a free valency cannot exist in the free state. But it can exist united with another group in the form of a *radical.* Thus the simplest of the radicals is the *methyl* radical CH_3—which is derived from methane CH_4 with one free valency. Ethane C_2H_6 gives the *ethyl* radical C_2H_5— or $CH_3—CH_2$—, which itself can be considered as a methyl radical CH_3— joined to a *methylene* radical $—CH_2—$ with *two* free valencies. Similarly the *allyl* or propenyl radical $CH_2{=}CH—CH_2$— corresponds to propylene $CH_2{=}{=}CH—CH_3$.

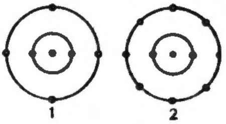


FIG. 141.

(1) Normal carbon with 4 free valencies.
(2) Carbon with 4 valencies saturated.

A radical can combine with a halogen (chlorine, bromine or iodine) to form a chloride, bromide or iodide of the radical: methyl chloride CH_3Cl, ethyl bromide $CH_3—CH_2—Br$, allyl iodide $CH_2{=}CH—CH_2—I$.

As a radical is, in practice, derived from the corresponding alcohol, it is called an *allyl radical,* generally designated by the letter R. As a halogen is designated by X an alkyl halide can be represented by RX.

851. Functions

A function features a number of properties possessed by a particular group called a *functional group* which is found in the same form in a large number of organic compounds. The functional group is generally associated with one or more radicals.

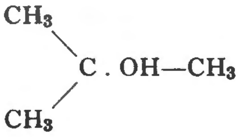
The most important of the functions are *alcohol, aldehyde, ketone, acid, amine, amide* and *nitrile.*

2. *Alcohol function.* This has a hydroxyl group OH linked to a radical $—CH_2—$, $>CH—$ or $>C—$ with the structures $—CH_2OH$, $—CHOH—$ or $>C\,.\,OH—$.

In the first case we have a *primary alcohol* such as ethyl alcohol $CH_3—CH_2—OH$ (or C_2H_5OH).

In the second case we have a *secondary alcohol* like isopropyl alcohol $CH_3—\,—CH\,.\,OH—CH_3$.

In the third, a tertiary alcohol like trimethyl carbinol (tert. butyl alcohol)



$$(CH_3)_2\,C\,.\,OH—CH_3$$

The alkyl radical includes all the chain except the hydroxyl OH. Thus the radical of $CH_3—CH_2—OH$ is ethyl $CH_3—CH_2—$. The radical of allyl alcohol $CH_2{=}CH—CH_2OH$ is allyl $CH_2{=}CH—CH_2—$.

The hydroxyl OH is replaceable by a halogen atom or an oxygen acid ion such as SO_4^{--} taking account of the valencies. For example, methyl alcohol CH_3OH, treated with hydrochloric acid is *esterified* to methyl chloride CH_3Cl. Propyl alcohol $CH_3—CH_2—CH_2—OH$ treated with sulphuric acid gives propyl sulphate:

$$2CH_3—CH_2—CH_2—OH + H_2SO_4 \rightarrow (CH_3—CH_2—CH_2)_2—SO_4 + 2H_2O$$

The *esters*, treated with caustic soda, regenerate the original alcohol: this reaction is termed saponification.

When two alkyl radicals are joined together via an atom of oxygen, the compound is an *ether*: ordinary ether is diethyl oxide $C_2H_5—O—C_2H_5$.

An organic compound can have several alcohol functions: *glycol* is a dihydric alcohol $CH_2OH—CH_2OH$; *glycerol* is a trihydric alcohol $CH_2OH—CH.OH—CH_2OH$ (twice primary and once secondary); *erythritol* is a tetrahydric alcohol $CH_2OH—CH.OH—CH.OH—CH_2OH$.

3. *Aldehyde function.* If the hydroxyl hydrogen and a second hydrogen from the $—CH_2—$ removed from a primary alcohol group $—CH_2OH$, the *aldehyde* group $—CH:O$ is obtained. The operation is carried out by oxidizing the corresponding alcohol, the two H uniting with the oxygen to give a molecule of water:

$$\underset{\text{Ethyl alcohol}}{CH_3—CH_2—OH} + O \rightarrow \underset{\substack{\text{Ethyl aldehyde}\\ \text{or acetaldehyde}}}{CH_3—CHO} + H_2O$$

With *sodium bisulphite* $NaHSO_3$ the aldehydes form crystalline compounds with the formula $R—CH.OH.SO_3Na$ which are decomposed by alkalis with regeneration of the aldehyde.

With *hydroxylamine* NH_2OH, an *aldoxime* is produced $R—CH:NOH$, and with *hydrazine* $NH_2—NH_2$, a *hydrazone* $R—CH:N.NH_2$.

The aldehydes are reducing agents.

4. *Ketone function.* The ketone function is to the secondary alcohol as the aldehyde to the primary alcohol. By dehydrogeneration of the group $—CH.OH—$ the characteristic $—C:O—$ group of the ketones is formed. The general formula is $R—C:O—R'$. Examples: ordinary acetone or dimethylketone $CH_3—CO—CH_3$ and methyl propyl ketone $CH_3—CO—C_3H_7$.

Hydroxylamine combines with ketones to produce the *ketoximes* $R—C:NOH—R'$, and hydrazine the *hydrazones* $R—C:N—NH—R'$. Sodium bisulphite forms crystalline compounds as with the aldehydes, $R—C.OH.SO_3Na—R'$.

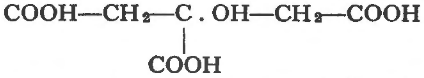
5. *Sugars.* The sugars are polyhydric alcohols which also contain an aldehyde or ketone function. Thus *arabinose* is a tetrahydric alcohol and an aldehyde; glucose is a pentahydric alcohol and an aldehyde $CH_2OH.(CH.OH)_4—CH:O$; laevulose is a pentahydric alcohol and ketone $CH_2OH(CH.OH)_3.CO.CH_2OH$.

The combination of glucose and laevulose with elimination of a molecule of water gives saccharose (or ordinary sugar). The union of n molecules of glucose gives the *polyglucosides* of which the starches, the dextrins, the cellulose and the gums are the best known representatives.

6. *Acid function.* By oxidizing the aldehyde group the *carboxylic acid* group $—C(OH):O$ is obtained; this is usually written *—COOH* or *—CO₂H*. An organic acid will therefore have the formula $R.CO.OH$. The first member of the series is *formic acid* $H.CO.OH$, whose salts are the formates; the second is *acetic acid* $CH_3—CO.OH$ corresponding to ethyl alcohol $CH_3—CH_2.OH$; it gives the acetates such as sodium acetate, $CH_3—CO.ONa.3H_2O$. The high molecular weight

compounds like stearic acid $C_{17}H_{35}—CO.OH$ combined with glycerol constitute the *fats*.

Among the diacids, the simplest is *oxalic acid* $COOH—COOH$, then malonic acid $CO.OH—CH_2—CO.OH$ which has been mentioned in connection with complex inorganic developers.

There are acids with multiple functions: *glycollic acid* $CH_2—OH—COOH$, a derivative of glycol, which is an acid and an alcohol at the same time. *Lactic acid* $CH_3—CHOH—COOH$ obtained by fermentation is a secondary alcohol and an acid. Tartaric acid has two alcohol and two acid functions: $COOH—CHOH—CHOH—COOH$. *Citric acid*  $COOH—CH_2—\underset{\displaystyle COOH}{\underset{|}{C}}.OH—CH_2—COOH$ has one alcohol and three acid functions. There are also the aldehyde acids like *glyoxylic acid* $COOH—CH:O$ and keto-acids like *pyruvic acid* $CH_3—CO—COOH$ and *acetone dicarboxylic acid* $COOH—CH_2—CO—CH_2—COOH$.

Heating organic acids with phosphorus pentachloride PCl_5 gives the acid chlorides: for example, acetic acid gives *acetyl chloride* $CH_3—CO.Cl$ in which the group $CH_3—CO—$ is the acid *acetyl radical* derived from $CH_3—CO.OH$. If the acetyl chloride is reacted with a further molecule of acetic acid, *acetic anhydride* $CH_3—CO—O—CO—CH_3$ is obtained. This is a general method for the preparation of the anhydrides of organic acids.

Reduction of the acids yields the aldehydes, then the corresponding alcohols.

7. *Amino function*. The amines are basic compounds resulting from the substitution of an alkyl radical R for a hydrogen atom of ammonia NH_3.

Their general formulas are:

$$RNH_2,\ R_2NH,\ R_3N,\ R_4NOH$$

Thus methylamine CH_3NH_2 is a *primary amine*. Diethylamine $(C_2H_5)_2NH$ is a *secondary amine*. Triethylamine $(C_2H_5)_3N$ is a *tertiary amine* and tetraethylammonium hydroxide $(C_2H_5)_4NOH$ is a quaternary amine.

If the amines are considered as derivatives of alcohols in which the OH has been replaced by NH_2, the *polyamines* correspond to the polyhydric alcohols: glycol $CH_2OH—CH_2OH$ gives ethylene diamine $NH_2.CH_2—CH_2.NH_2$.

Glycollic acid $CH_2OH—COOH$ gives an *amino acid*, glycine $NH_2.CH_2—COOH$, the first member of a series of important compounds leading to the proteins. The silver salt of glycine has the formula $NH_2.CH_2—CO.OAg$.

The amines are produced when ammonia is reacted with an alkyl iodide

$$\underset{\substack{\text{Ethyl}\\\text{iodide}}}{C_2H_5I} + \underset{\text{Ammonia}}{NH_3} \rightarrow \underset{\text{Ethylamine hydriodide}}{C_2H_5NH_2.HI}$$

8. *Amide function*. As the amines are derivatives of the alcohols, so the amides are derived from the acids by substituting the group NH_2 for the OH of the acid function.

$$\underset{\text{Acid}}{R—CO.OH} + \underset{\text{Ammonia}}{NH_3} \rightarrow \underset{\text{Amide}}{R—CO.NH_2} + \underset{\text{Water}}{H_2O}$$

Conversely, the amides can be considered as the result of substituting an acid radical $R.CO—$ for a hydrogen of NH_3. Thus we have the primary, secondary, and tertiary amides depending on whether 1, 2 or 3 hydrogen atoms have been replaced.

The primary amides are obtained by dehydrating the ammonium salts:

$$\underset{\substack{\text{Ammonium}\\\text{acetate}}}{CH_3—CO.ONH_4} \rightarrow \underset{\text{Acetamide}}{CH_3—CO.NH_2} + \underset{\text{Water}}{H_2O}$$

Similarly ammonium oxalate gives oxamide $(CO\,.\,NH_2)_2$.

If carbonic acid H_2CO_3 is considered as the equivalent OH—CO—OH, it is easy to see that —CO— is an acid radical, and that the two hydroxyls could be replaced by two NH_2. In fact the *carbonic diamide* thus formed is urea, NH_2—CO—NH_2, a weak base soluble in water. A *thiourea* NH_2—CS—NH_2 corresponds to urea, a *thiocyanic acid* CNSH to cyanic acid CNOH, and *thiols* R—SH correspond to the alcohols.

9. *Nitrile function.* If, in dehydrating an ammoniacal organic salt, two molecules of water instead of one are removed, the compound $R—C\equiv N$ is obtained in which the group $—C\equiv N$ is the *nitrile function.*

By heating an ammonium salt such as ammonium acetate, acetamide is formed, as we have seen, by loss of a molecule of water. By more vigorous dehydration, using phosphorous pentoxide, an acetonitrile results

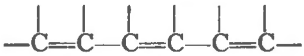
$$\begin{array}{ccccc} CH_3—CO\,.\,ONH_4 & \rightarrow & CH_3—C\equiv N & + & H_2O \\ \text{Ammonium} & & \text{Acetonitrile} & & \text{Water} \\ \text{acetate} & & & & \end{array}$$

A nitrile, treated with potash, regenerates the parent acid with loss of ammonia.

By reacting an alkyl iodide RI with silver cyanide AgCN, a *carbylamine* is obtained isomeric with a nitrile but not decomposed by potash, $R—N\equiv C$.

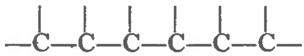
852. Cyclic compounds

The compounds of the cyclic series are based upon a fundamental hydrocarbon, *benzene* C_6H_6. Benzene is usually represented by a hexagonal 'nucleus' of 6 carbon atoms in a chain joined by alternate single and double bonds. Each carbon atom is placed at a peak of the hexagon. The remaining free valencies are saturated by hydrogen. Such an arrangement depends on the hypothesis that carbon is tetravalent.



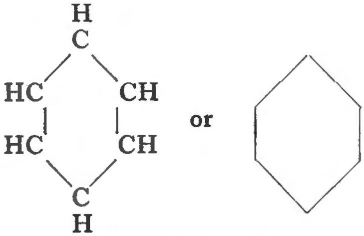
$$—\overset{|}{C}=\overset{|}{C}—\overset{|}{C}=\overset{|}{C}—\overset{|}{C}=\overset{|}{C}—$$

Now, we have good reason to believe that *carbon* with double (ethylene) links is not tetravalent, but *trivalent*, and that it can easily become tetravalent. Under these conditions, the carbon chain of benzene should actually be written

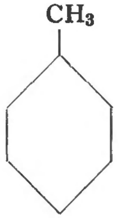


$$—\overset{|}{C}—\overset{|}{C}—\overset{|}{C}—\overset{|}{C}—\overset{|}{C}—\overset{|}{C}—$$

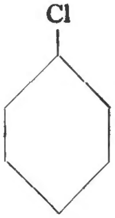
However, for reasons of convenience we retain in open chains the = notation as it shows the presence of trivalent carbon. The benzene hydrocarbons are, however, shown as follows:



Benzene C_6H_6

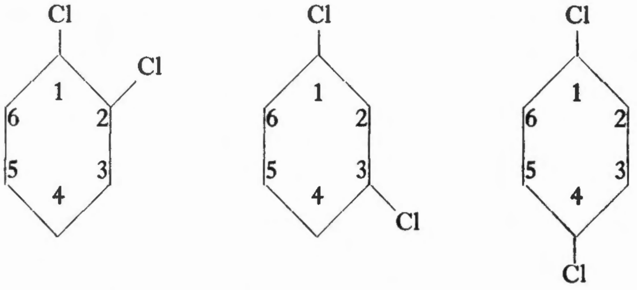


Toluine $CH_3C_6H_6$



Chlorobenzene C_6H_5CL

The representation of benzene by a hexagon enables the isomeric forms resulting from substitution to be readily shown. If the peaks are numbered 1–6, there are three disubstituted derivatives corresponding to the three possible relative positions. The three isomers are distinguished by the prefixes ortho-, meta-, and para- or by the corresponding numbers. For example, there are three dichloro derivatives

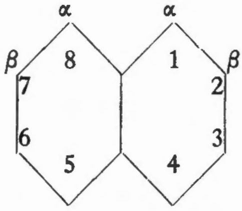


Ortho or 1 : 2 **Meta or 1 : 3** **Para or 1 : 4**

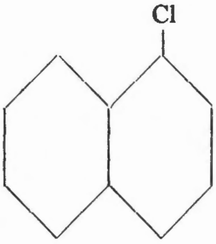
Dichlorobenzene

2. By replacing 2 or 3 hydrogen atoms of the methane molecule by benzene or *phenyl* radicals C_6H_5—, *diphenylmethane* $C_6H_5—CH_2—C_6H_5$ and *triphenylmethane* $(C_6H_5)_2{=}CH—C_6H_5$ are obtained.

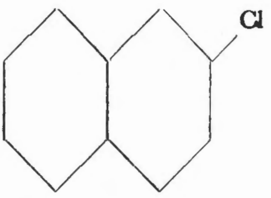
The action of heat on the benzene hydrocarbons results in compounds with multiple nuclei. That of *naphthalene* can be represented by the direct fusion of two benzene nuclei and *anthracene* by two benzene nuclei joined by two carbons:



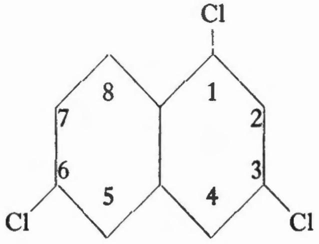
Naphthalene $C_{10}H_{10}$



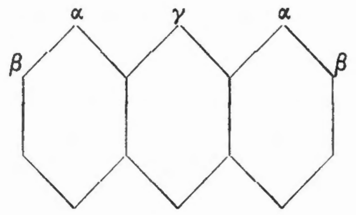
α-Chloronaphthalene



β-Chloronaphthalene



1-3-6-Trichloronaphthalene

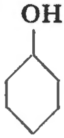


Anthracene $C_{14}H_{10}$

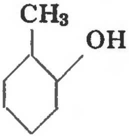
Naphthalene can have 10 disubstituted isomers, 14 trisubstituted, etc., which are shown by numbering. The monosubstituents can be in position α or β.

Very many substitution products are derived from the benzene hydrocarbons. When the substituent replaces a nuclear hydrogen, the compound has the special properties of the cyclic compounds. Treated with sulphuric acid, the benzene hydrocarbons give *sulphonic acids* such as $C_6H_5SO_3H$, $C_6H_3(SO_3H)_3$, etc. With naphthalene the naphthalene sulphonic acids are obtained.

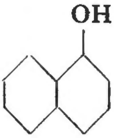
A sulphonated hydrocarbon, fused with a caustic alkali, produces a *phenol* in which an hydroxyl OH is directly attached to the nucleus.



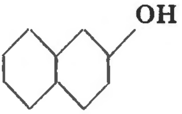
Phenol



O-cresol



α-naphthol



β-naphthol

The phenols behave as weak acids towards the alkalis by giving phenates like C_6H_5ONa.

When several hydroxyls are joined to the same nucleus, *polyphenols* result, diphenols or triphenols. These have been studied in a previous chapter: *pyrocatechin* or o-dihydroxybenzene $C_6H_4(OH)_2$, *resorcinol* or m-dihydroxybenzene, *hydroquinone* or p-dihydroxybenzene, *pyrogallol* or 1:2:3-trihydroxybenzene $C_6H_3(OH)_3$.

The substitution of a hydrogen atom by an acyclic functional group gives products having, to some extent, properties similar to those of the acyclic compounds. These include:

benzyl alcohol	$C_6H_5—CH_2OH$
benzaldehyde	$C_6H_5—CHO$
benzoic acid	$C_6H_5—COOH$
cinnamic acid	$C_6H_5—CH=CH—COOH$
phthalic acid	$C_6H_4(COOH)_2$
benzamide	$C_6H_5—CO.NH_2$
acetophenone	$C_6H_5—CO—CH_3$

A compound can have both cyclic and acyclic functions together: aldehyde and phenol for example as in salicylaldehyde $OH—C_6H_4—CHO$.

Sodium phenate treated with a current of carbon dioxide gives the sodium salt of a phenolic acid: salicylic acid $OH—C_6H_4—COOH$ and its isomer, p-hydroxybenzoic acid.

If methyl iodide is reacted with sodium phenate an *ether* is obtained $C_6H_5—O—CH_3$.

The oxygen of phenol can be replaced by sulphur by treatment with phosphorus sulphides. The resulting *thiophenol* has the formula C_6H_5SH. There are also *thionaphthols*, *selenophenols* C_6H_5SeH and selenonaphthols.

4. *Nitrogen derivatives.* The *aromatic amines* correspond to the alkyl amines, the NH_2 group being attached directly to the nucleus:

aniline	$C_6H_5NH_2$
o-toluidine	$CH_3—C_6H_4—NH_2$
ethylphenylamine	$C_6H_5.NH.C_2H_5$
dimethylaniline	$C_6H_5.N(CH_3)_2$

When two NH_2 groups are fused to the nucleus, a *phenylenediamine* results $NH_2.C_6H_4.NH_2$ of which there are 3 isomers. The phenylenediamines are very strong bases.

The aromatic amines are prepared by reduction of the *nitro compounds*. Thus nitrobenzene $C_6H_5NO_2$ (formed by the action of a mixture of nitric and sulphuric acids on benzene) is reduced by hydrogen (produced by the action of hydrochloric acid on iron filings) to aniline $C_6H_5NH_2$.

Similarly, the *nitrophenols* $OH—C_6H_4—NO_2$, are converted by reduction to the *aminophenols* which have basic properties from the amino group and acidic properties from the phenol: $OH—C_6H_4—NH_2$.

The amino hydrogen can be replaced by acid radicals, such as acetyl, to give the *anilides*:

$C_6H_5{-}NH_2$	$+$	$CH_3{-}CO\,.\,Cl$	$=$	$C_6H_5{-}NH\,.\,CO\,.\,CH_3$	$+$	HCl
Aniline		Acetyl chloride		Acetanilide		Hydrochloric acid

The aromatic amines can be sulphonated like benzene, to give *aminosulphonic acids*: example: sulphanilic acid $SO_3H{-}C_6H_4{-}NH_2$.

With fuming nitric acid the *nitroamines* like p-nitroaniline $NO_2{-}C_6H_4{-}NH_2$ are obtained, whilst nitrous acid, with tertiary amines, gives the *nitrosamines*, p-nitrosodimethyl aniline for example, with the formula $(CH_3)_2\,.\,N{-}C_6H_4{-}NO$.

When the O of the OH of an aminophenol such as $NH_2{-}C_6H_4{-}OH$ is replaced by sulphur or selenium an *aminothiophenol* $NH_2{-}C_6H_4{-}SH$ or an *aminoselenophenol* $NH_2{-}C_6H_4{-}SeH$ is produced.

5. The aromatic amines, treated with nitrous acid at low temperatures, produce the *diazo compounds*. The operation is called diazotization.

$C_6H_5{-}NH_2$	$+$	HNO^2	$+$	HCl	$\rightarrow$	$C_6H_5{-}N{=}NCl$	$+$	H_2O
Aniline		Nitrous acid		Hydrochloric acid		Benzene diazonium chloride		Water

The group —M═N— is characteristic.

A diazonium compound treated with a phenol or an amine produces an *azo compound*, hydroxy-azo or aminoazo.

$C_6H_5{-}N{=}NCl$	$+$	$C_2H_5\,.\,OH$	$\rightarrow$	$C_6H_5{-}N{=}N{-}C_6H_4\,.\,OH$	$+$	HCl
Benzene diazonium chloride		Phenol		Hydroxyazobenzene		

$C_6H_5{-}N{=}NCl$	$+$	$C_6H_5\,.\,NH_2$	$=$	$C_6H_5{-}N{=}N{-}C_6H_4\,.\,NH_2$	$+$	HCl
Benzene diazonium chloride		Aniline		Aminoazobenzene		

Heating the diazonium compounds in sulphuric acid solution produces the corresponding phenol.

By reducing benzene diazonium chloride with stannous chloride S_nCl_2, *phenylhydrazine* hydrochloride $C_6H_5{-}NH{-}NH_2\,.\,HCl$ is formed.

$C_6H_5{-}N{=}NCl$	$+$	$4HCl$	$+$	$2SnCl_2$	$=$	$2SnCl_4$	$+$	$C_6H_5{-}NH{-}NH_2\,.\,HCl$
Benzene diazonium chloride				Stannous chloride		Stannic chloride		Phenylhydrazine hydrochloride

The hydrochloride is decomposed with soda to liberate the phenylhydrazine which can be crystallized.

Phenylhydrazine $C_6H_5{-}NH{-}NH_2$ is a derivative of hydrazine $NH_2{-}NH_2$ by substitution of a phenyl radical for one of the hydrogens. It combines with aldehydes and ketones better than hydrazine to produce the characteristic slightly soluble *phenylhydrazones*: thus with acetaldehyde it gives the compound $C_6H_5{-}NH{-}N{=}CH{-}CH_3$.

Many phenylhydrazones are 'phototropic'.

COMPLEMENTARY NOTES

PART I

Chapter II

Note referring to paragraph

12 **Photosynthesis** of cyclopentadiene and pyrrolidine derivatives. Cf. O. Süss: *Zeits. Wiss. Phot.*, Dec. 1955, 476–517.

14 **Phototropy** of m-toluidine-salicylaldehyde: yellow in darkness, becomes orange-red when lighted. Cf. Lindemann: *Zeits. Wiss. Phot.*, Dec. 1955, 347–386.

Chapter II

16 **Fused silver bromide** is superficially oxidized into Ag_2O which is a sensitizer. Therefore, when making strips of monocrystalline AgBr, care must be taken to avoid the presence of air, during the melting operation. Superficial fog is destroyed by immersing each lamella in an aqueous solution of bromine. Cf. Clark and Mitchell: *Zl. Phot. Sci.*, Feb. 1956, 1–20, or a bromine sat. 10% KBr solution.

Sensitizing of monocrystalline strip is carried out by digestion in a 17-gelatine solution (inert or active) or a 0·01 mg/l thiosulphate (or other sensitizer) solution. Sensitized strip can be developed without exposing to light, using the technique of Hayn, Langhammer and Staude (*Int. Konf. Wiss. Phot. Köln*, 1956; and *Sc. Ind. Phot.*, Feb. 1957, 71): digest 4 hours, without stirring rinse with hot water and develop 30 seconds in an hydroquinone-sulphite developer. This is an easy method for testing gelatin and sensitizers.

16 **Preparation of silver bromide crystals by steam injection** through a saturated solution of AgBr in KBr, during 30–40 mins. (cf. Sutherns: *Zl. Phot. Sci.*, 1956, 83–87). Diam.: 5–20 μ. *Specific surface* (determined by dye adsorption) is 850 cm²/g, against 2×10^5 cm²/g for AgBr sols. To *remove the fog* which is sometimes present, immerse the crystals in 10 times diluted sat. bromine water, then rinse 12 times 15 mins. in 0·001 N KBr.

Photographic emulsions behave like AgBr sols. but not like large crystals.

16 **Silver iodobromides**: See Chateau, Moncet and Pouradier: *Sc. Ind. Phot.*, Jan. 1957, 41.

18 **Optical absorption by AgBr and AgCl crystals:** One Å change brings a 2% variation of the absorption coefficient, and 1° C a 4% error. Cf. Moser and Urbach: *Phys. Rev.*, June 1956, 1519.

21 **Sensitivity specks**: Chibissor, Kirillov and Broun admitted that *sulphided* sensitivity specks are not formed of Ag_2S but rather of atomic silver: $Ag^+ + e$ (electron coming from a sulphur ion S^{--}) $\rightarrow$ Ag. (Cf. *Dokl. Akad. Nauk SSSR*, 1955, 1159, or *Sc. Ind. Phot.*, **27**, 270.) Hautot and Souvenier (*Sc. Ind. Phot.*, Feb. 1957, 57) opposed the fact that sensitivity specks obtained by sulphiding are less easily oxidizable than those obtained by reduction, and furthermore

they cannot be dispersed by infra-red rays, whilst reduction specks can be. The latter authors suggest the following formula: $Ag_n(S^-Ag^+)_n$.

22 **Mechanism of latent image formation:** According to Shamoskij, Dunina and Gosteva (*Zh. Eksper. Teor. Fiziki.*, April 1956, 640–648) AgBr photolysis does not free bromine atoms, but only positive holes which, when associated with vacant sites, form V centres. AgBr crystals, coloured in bromine vapour, had their conductivity measured, as a function of temperature and bromine pressure: it has been found that this conductivity varies, due to the positive holes migration, which would not be possible if bromine diffuses in the lattice.

26 **Latent image sub-specks:** Their existence was suggested by Eggert and Noddack in 1927 (*Naturwiss.*, **15**, 67). For a mathematical theory, see J. Stock: *Zl. Opt. Soc. Amer.*, Jan. 1956, 17–21.

27 **Latent image oxidation:** A 0·2% *chromic acid* solution is sufficient to dissolve the superficial latent image. The action starts quickly then slows down after a few minutes. With solutions containing 1% chromic acid, the internal image begins to be oxidized. The oxidant is more active when 0·1–1% potassium bromide is added. A preliminary washing decreases its efficiency (R. Debot).

31 **Auxiliary illumination:** The density resulting from two successive illuminations can be forecast (cf. Frieser and Eggers: *Mitteil. Forshungslabo Agfa, Severkusen-München*, 1955, 76–94, and *Sc. Ind. Phot.*, 1956, 275). The sensitivity is increased by:

(*a*) *Pre-illumination*: high intensity and short duration.
(*b*) *Post-illumination*: low intensity and long duration.

The increase of sensitivity is noticeable chiefly with slow emulsions and short developments. When the post-illumination is the result of a short-duration exposure, the density decreases first (desensitization, observed on Kodalith by Maurer and Yule: *Sc. Ind. Phot.*, 1952, 394). See also de Paul and Vigon: *Anal. R. Soc. Españ. Fis. y Quim.*, Dec. 1955, 257–274.

31b **Direct measurement of the latent image density** with extra-sensitive photometers, see Van Kreveld and Jurriens: *Sc. Ind. Phot.*, **8**, 197; and Nail, Moser and Urbach: *Jl. Opt. Soc. Amer.*, March 1956, 218–222.

Chapter V

37 **Theory of development:** The *adsorption of quinone* by the exposed AgBr is confirmed by Brauer and Staude (*Intern. Konf. Wiss. Phot. Köln*, 1956; *Sc. Ind. Phot.*, Jan. 1957, 29). The quinone is reduced into *semi-quinone*, by the electrons of the F centres which form (according to these writers) the latent image (Brauer, Staude and Langhammer: *Naturwiss*, Sept. 1956, 419).

40 **Developers without sulphite:** They can be stabilized with *ascorbic acid.*

Chapter VI

47 **Sulphite and bisulphite:** Their solutions are not stable: they are oxidized into sulphate, bisulphate and pyrosulphate. For analytical tests, follow the techniques used for developers, para. 127. See A.S.A. standards, para. 137.

65 **Warm tones** given by *silver chloride* emulsions are caused by developed *branchy* silver grains (cf. Koerber: *Intern. Konf. Wiss. Phot. Köln*, 1956).

Bluish black tones are due to *compact* silver grains. This is produced by ageing, excessive gelatine hardening, absence of bromide in the developer or benzotriazol addition.

Silver bromide gives compact silver grains. When potassium iodide is added to the developer, the grains become branchy and the tone warmer.

With no colloid, all silver halides tend to produce warm tones.

Chapter VIII

84 **Jet (or spray) developing:** See Turner and Jensen: *Jl. Soc. Mot. Pic. Tel. Eng.* Feb. 1956, 92–96. For colour films, a nitrogen atmosphere is necessary to avoid strong oxidation of the developer.

Chapter IX

116 **Pyrazolidones** (developers): 3-pyrazolidones have been obtained by catalytic dehydration, in acid medium, of a hydrazide substituted with an aromatic or heterocyclic group. Cf. Reynolds, Tinker (and Kodak): F.P. 1,114,874 (1955), U.S. prior. 3-8-53.

Agfa (F.P. 1,120,915—1955) uses 1-*aryl*-3-*aminopyrazolines* having in 4- of the aryl nucleus an OH or NHR group. Example: 1-(4-ethylaminophenyl)-3-aminopyrazoline.

Chapter XI

143 **Anhydrous thiosulphate** can be prepared by adding an organic liquid to the aqueous solution, which makes the thiosulphate crystallize anhydrous (Kendall, Axford and Dimsdale (Ilford): B.P. 737,295—1953).

150 **Washing accelerators:** Washing is more efficient when neutral salts are added to the water. The best is to immerse the fixed image 2 mins. in a 2% *sodium sulphite* solution, then wash 5 mins. With good agitation, 30 secs. immersion and 2 mins. washing are sufficient for a 'microfile'. The images are quite stable. Calcium sulphite precipitate can be avoided by a sequestering agent. The method is convenient for papers, except those with heavy support. Cf. Henn and Crabtree: *Jl. Soc. Mot. Pic. Tel. Eng.*, 1956, 378, and King and Crabtree: *Phot. Engng.* and *Sc. Ind. Phot.* (Nov. 1956, 445).

150 **Alumino-organic mud:** It is produced when films are washed after an *alum hardening-fixing bath*. The gelatinous mud is formed of alumina precipitated with the organic matter of the water, and contains iron oxide. *Boric acid* can be used to delay the precipitation. The cleaning of the tanks is difficult: they must be scrubbed frequently. To avoid any deposit on the film, it is recommended to project water on the two sides. Spots are removed with a pad dampened with 5% sodium carbonate. Cf. Hughes, Henn and Crabtree: *Phot. Sci. Techn.*, Aug. 1956, 107–112.

Chapter XII

162b **Dichromate reversal baths:** They sometimes stain the layer, if the first developer contains hypo. The latter is adsorbed by the silver image, then decomposed by the dichromate. This does not happen when the hypo is replaced by potassium thiocyanate. Cf. Levenson and Sharpe: *Jl. Phot. Sci.*, Aug. 1956, 89.

Chapter XIV

209 **Remarks on Schwarzschild's coefficient:** J. Stock: *Jl. Opt. Soc. Amer.*, Jan. 1956, 17–21.

211 **Study of the Villard Effect:** H. Arens: *Zeits. Wiss. Phot.*, Dec. 1955, 392–405.

Chapter XV

224–225 New densitometers:

Kodak (W. H. Carnahan): reflection densitometer; records automatically the sensitometric curve. Cf. *Phot. Engng.*, Dec. 1955, 237–243.

Ilford (Hercock and Sheldrick): transmission automatic densitometer. Cf. *Jl. Phot. Sci.*, Oct. 1956, 113–115.

Fuji (Tajima and Ouye): transmission and reflection automatic recording densitometers. Cf. *Bull. Soc. Sci. Phot. Japan*, Dec. 1955, 35–41 (in English).

233 Interferential resolving power meter: Bruscagnioli (*Sc. Ind. Phot.*, **7**, 241) used a converging group of rectilinear fringes produced by a Young interferometer having hyperbolic slits. In L. Falla system (*Sc. Ind. Phot.*, March 1956, 167–182) a group of parallel fringes is formed by interference with the monochromatic light of the virtual image given by a mirror parallel to the slit (Wolfe and Eisen: *Sc. Ind. Phot.*, **21**, 313). Mercury 5641 Å line and a 15 μ slit are used for resolving powers less than 250 lines/mm. A 40–70 μ slit is sufficient for low resolving powers.

Chapter XVI

244 Isohelia: System of interpretation of a normal continuous tone image, by only three or four densities (cf. W. Romer: *Sc. Ind. Phot.*, **5**, 46 and **9**, 337). Several negatives of the same subject are successively printed, in register, with different exposure times, on a high contrast emulsion.

Yule and Maurer use only one negative: after a short exposure, for the highlights, on Kodalith film, a second, longer, exposure is given, through a coloured screen (white, grey and black are thus obtained). Cf. *Penrose Annual*, 1956, 119.

PART II

Chapter XVII

261 Gelatine constituents:

Arginine determination: cf. J. W. Janus: *Nature*, March 1956, 529.

Hydroxyproline colorimetric determination: cf. Miyada and Tappel: *Anal. Chem.*, May 1956, 909.

Tyrosine, tryptophan and methionine termination: Genevoix and Baraud: *Chim. Anal.*, March 1956, 87–91.

When treated with nitrous acid, gelatine becomes coloured (Steigmann). This is probably due to tyrosine. Mineral impurities have a great influence on the reaction (Venet and Pouradier: *Sc. Ind. Phot.*, Nov. 1956, 418).

Fluorescence microdetermination of tryptophan: cf. Miller, Johnson and Miller: *Anal. Chem.*, May 1956, 884.

Microdetermination of aminoacids and peptides in the form of copper complexes. Cf. Cherkin, Wolkowitz and Dunn: *Anal. Chem.*, May 1956, 895.

Selective acetylation of the hydroxyl group of gelatin by acetic anhydride and trifluoracetic acid: Bello and Vinograd: *J.A.C.S.*, 1956, 1369.

Infra-red spectra of proteins: Hecht and Wood: *Proc. Roy. Soc.*, April 1956, 174–188.

Natural aminoacids: H. Musso: *Angew. Chem.*, May 1956, 313–323.

268–299 Sulphiding sensitizers: Active sulphur content in gelatin can be suggested by turbidity tests with the Ammann-Brass method. 0·5 and 5% gelatin solutions are used comparatively: when the 5% test gives higher turbidity than the 0·5% test, the gelatin contains active sulphur (*Zeits. Wiss. Phot.*, Dec. 1955, 173–197).

Thiosulphate and other similar sulphur compounds appear in gelatin, during manufacture, by the action of lime on cystine: a sulphide is formed first, it is then oxidized into thiosulphate (Steigmann, Wood) (Pouradier and Venet: *Sc. Ind. Phot.*, Aug. 1956, 297).

Polarography. 25 g gelatin is extracted at 0°C with 200 cc water. The solution is vacuum concentrated to 10 cc and examined. According to G. Russel (Ilford), polarograms of thiosulphate sensitized gelatins are similar to those of natural active gelatins (*Nature*, Aug. 1956, 280).

Chromatography shows, however, that thiosulphate is only a small part of the sulphur compounds of gelatin.

Silver bromide adsorbs some of the gelatin constituents selectively, chiefly those having imino or mercapto groups. Krummenerl noted that active gelatins are adsorbed 4 times more than inert ones, but that thiosulphate addition does not have any influence. Washing the gelatin increases the adsorption. The same writer found, by electrodialysis then chromatography, three anionic and two cationic sulphur compounds in gelatin, and which seem to be constituted by combinations of aminoacids such as cystine and cysteine, with neutral salts (thiosulphate and polythionate). The aminoacid function of these compounds can be evidenced by reacting with ninhydrine. Cf. *Intern. Konf. Wiss. Phot. Köln*, 1956; *Sc. Ind. Phot.*, 1957, 45. The maximum quantity of thiosulphate which can be adsorbed by AgBr having $10^3 cm^2/g$ specific surface, is 3×10^{-7} mol/g (Chateau and Pouradier: *Sc. Ind. Phot.*, Dec. 1956, 465). The thiosulphate ions, which are remote from one another, are decomposed into sulphide:

$S_2O_3^{--} + Ag^+ \text{ (crystal)} \rightarrow AgS_2O_3^-$

$AgS_2O_3^- + Ag^+ \text{ (sol.)} + H_2O \rightarrow Ag_2S + SO_4H_2$

The reaction is favoured by high pH and low soluble bromide content.

Chapter XVIII

284 Emulsion making, with ion exchangers: Porter (Kodak): F.P. 1,114,264 (1951); U.S. prior. 7-4-50, fixed silver on an ion exchanger which, in turn, was treated with a gelatin solution containing halides. Ag^+ was displaced by the latter.

286 Silver halide complexes: The equilibrium constants have been calculated by Klein (Agfa): *Phot. Korr.*, Sept. 1956, 139–148. Application to emulsion precipitation.

289 Physical ripening: See a mathematical work by C. S. Lyalikov: *Zeits. Wiss. Phot.*, Dec. 1955, 151–172. The ripening speed of ammoniacal emulsion is determined chiefly by $Ag(NH_3)_2^+$ ions.

294 Chemical ripening: It begins during the physical ripening and, according to Chibissor and coll., this plays an important part (*Zh. Fiz. Khim.* **1953**, 866–877). The influence of photolytic silver formed before chemical ripening had been pointed out by Ratner and Lyalikov.

295 Reducing sensitizers: *Hexamethylenetetramine*, suggested by Steigmann, was sold, in 1940, as a reducing agent for emulsion ripening, under the name of *Digensit* by PAC Chemicals.

Reducing sensitizer for emulsions is usually *stannous chloride*, but *imino-aminomethane-sulphinic acid* has also been used.

298 Emulsion speed increase (40–110%) by addition of small amounts of *phytic acid* (mesoinositol hexaphosphate) has been claimed (Moesson—Du Pont—U.S.P. 2,757,088 (1956)).

301 Gold, platinum and palladium sensitization: 50 g silver bromide, without gelatin or other binder, can be sensitized by the following amounts of precious metal salts (Faelens: *Sc. Ind. Phot.*, Feb. 1957, 68):

$AuCl_4H$	2 cc	0·03% Au. sol.
$Au(SCN)_2K$	6 cc	0·03% Au. sol.
$PtCl_4K_2$	3 cc	0·02% Pt. sol.
$PdCl_4(NH_4)_2$	3 cc	0·003% Pd. sol.

In the presence of gelatin, greater amounts of sensitizers are necessary due to the stable combination metal + gelatin. With polyvinylalcohol, the combination is less stable.

Gold centres formed on the AgBr crystals can be detected by *electron diffraction* (cf. Yamada and coll.: *Bull. Soc. Sci. Phot. Japan*, Dec. 1955, 1–6 (in German)).

308 Emulsion analysis with radioactive isotopes: For details, see a work by Zellez-Plasencia: *Sc. Ind. Phot.*, Sept. 1956, 337–345.

333 Autopositive paper*:* Agfa *Directoflex* paper is fogged during making. When exposed to yellow light >500 mμ it gives direct positives by Herschell effect. Speed: 3·4 times less sensitive than Copyrapid paper. Its very thin transparent support allows back exposures.

338 Polyvinylalcohol emulsions*:* Polyvinylalcohol (PV4) is a much stronger retarder than gelatin. When partially acetylated, it behaves more like gelatin (cf. Hoskins and Mitsuhashi: *Konishiroku Rev.*, March 1956, 26–38; *Sc. Ind. Phot.*, Sept. 1956, 360).

AgBr-PVA emulsions are 30 times less sensitive than the corresponding gelatin ammoniacal emulsions. They can be sensitized with gold. The following formula was worked out by Narath and Gernest (*Zeits. Wiss. Phot.*, Dec. 1955, 225–239):

A 45°C	Ammonium bromide	12·2 g	B	Silver nitrate	20 g
	Potassium iodide, 10% sol.	2·5 cc		Water, dist.	160 cc
	Polyviol W.48/02, 5% sol.	230 cc		Ammonia	32 cc

Add B to A (45°C) with stirring. Pour 320 cc 10% APV solution and 30 cc water. Ripen 30 mins. Then jellify with:

D	α-naphthol	3·5 g	E	Acetic acid	20 cc
	Ethanol	50 cc		Water	5 cc

Shred and wash 115 mins. Melt the noodles (300 g), add 20 cc 10% PVA, 1 cc 2% KBr, 1 cc 0·1% nitrobenzimidazol nitrate, and ripen 30 min., 50°C. Cool to 40° and add 7·5 cc 50% glycerine and 15 cc 2% α-naphthol alcoholic solution. Coat 5 cc for 10 sq. in., and dry at 30°C after setting.

Develop 3 mins. and 30 secs. and fix in an acid bath; wash 15 mins. Drying at 60°C gives more speed and contrast.

Gold sensitization (for 20 g $AgNO_3$):

(*a*) During precipitation: 1 g potassium thiocyanate and 0·6 g potassium chloroaurate ($KAuCl_4$) give ×3 increased sensitivity for 0·08 fog. If the gold salt is added before α-naphthol, the sensitivity increase is ×6 and fog 0·24. Too much acetic acid decreases the sensitivity.

(*b*) Before after-ripening: 0·05 g KSCN and 0·002 g $KAuCl_4$. Sensitivity ×4; fog 0·09.

0·250 g sulphite added to the thiocyanate lowers the fog to 0·04 without influencing the speed.

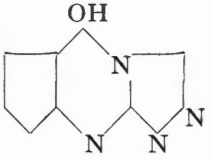
When KSCN is omitted, the α-naphthol present plays the same action towards the gold salt.

349 **Stabilizers:** Adsorption by the silver halides is not an indication of effectiveness: triazaindolizines and benzotriazol-sulphonic acid, although powerful stabilizers, are adsorbed very little (cf. Birr: *Zeits. Wiss. Phot.*, Dec. 1955, 101–124 and 124–138).

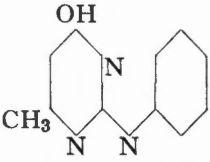
It must be noted that *a stabilizer is not necessarily an anti-foggant* and vice-versa. The anti-fogging action depends on the adsorption. Example: nitrobenzimidazol and triazaindolizines, with 5- position heavy alkyl groups, are good anti-foggants.

350 **Azaindolizines:** Syntheses of 17 azaindolizines, by Murofushi and coll.: *Bull. Sci. Phot. Japan*, Dec. 1955, 23–28 (in English). Added amount: 10^{-5} to 10^{-2} mol per $AgNO_3$ mol. The best *stabilizers* are the 5-methyl-7-hydroxy-2:3:4-triazaindolizine, the 5-methyl-6-ethyl-7-hydroxy-2:3:4-triazaindolizine, the 5-phenyl-7-hydroxy-2:3:4-triazaindolizine, and chiefly the 5-methyl-7-ethoxy-2:3:4-triazaindolizine (8×10^{-3} mol/$AgNO_3$ mol). When the 7-hydroxy group is substituted by other groups not containing hydrogen, the stabilizing effect is much reduced.

As *anti-foggants* in developing baths, the best azaindolizines are:



and



355 **Hardening agents:** 1:4-dihydroxymethyl-2:5-diketopiperazine, claimed to be a hardening agent, by a U.S. patent, proved to fog and desensitize the emulsions. Tejima and coll. (*Int. Konf. Wiss. Phot. Köln*, 1956) prefer to use *hydroxymethylbenzimidazol* and hydroxymethylphthalimide: 150 mg/100 cc 10% gelatin emulsion increases the melting point to 42°C, then 60°C after some days. Preparation: action of formaldehyde on imino groups of known anti-foggants.

Other work on 26 compounds, by Yamaguchi and Aoki: *Konishiroku Rev.*, March 1956, 1–8.

359 **Emulsion coating**: Calculation of the thickness of the coated emulsion, from Schwedoff and Bingham equation, cf. Deryagin and Levi: *Otdel. Zekhn. Nauk.*, 1955, **9**, 43–52.

Chapter XXII

365 **UV films:** One grain layer coating can be obtained by the technique of Audran Rock and Gougeon (F.P. 1,112,681; *Sc. Ind. Phot.*, Nov. 1956, 433): centrifuging the emulsion on a film support attached to a rotating cylinder, then transferring on another support, under pressure.

Chapter XXIII

370 **Solarization by X-rays:** Reciprocity law failure and intermittency effect have been observed by Ehrlich: *Jl. Opt. Soc. Amer.*, Oct. 1956, 801.

371 **X-ray film speed:** ASA Standards pH2-8-56 (industrial) and pH 2-9-56 (medical).

No screen: speed is the reciprocal number of the roentgens necessary to give a density of 1·5 for industrial films and 1 for medical films.

With screen: Speed is the reciprocal of the illumination in ergs/cm^2 of a blue light similar to that of tungstate (industrial plus) or of a green light (medical films). The blue light can be reproduced by a 2660°K lamp and Wratten filter No. 39, and the green light by a Corning filter 4-64.

The required contrast is represented by the gamma of the line joining two points of given densities:

0·5 and 2·5 for industrial plus
0·2 and 2 for medical plus.

Exposure: 0·25 sec. for one side coated films, and 0·1 sec. for double coated films.

375 **Radioactive drawings** with *inks containing radioisotopes* can give a great number of photographic prints. They have been perfected by H. Wheeler, of Louisiana Univ.

379 **Autoradiography:** Perfect contact between the emulsion and the histological preparation is essential for a high resolving power. *Liquid emulsion* can be applied by immersion or with a brush.

Histological stains such as azocarmin G and aniline blue, or phosphomolybdic acid, strongly desensitize the emulsion (cf. Mlle Olivereau: *Bull. Micro. Appl.*, July 1956, 100–104).

Coloured images. When radioactive elements (35S, 14C, 45Ca, 131I, 32P) are used, they can be differentiated by superimposed emulsions for colour. Conventional coloured images are obtained (cf. Buckaloo and Cohn: *Science*, Feb. 1956, 333).

381 **Nuclear emulsions:** Ilford C-2 emulsion contains per cm^3: 3·536 g silver halides, 0·527 g gelatin and 0·117 g glycerin. When immersed in a solution, the glycerin diffuses in the bath. This must be compensated to prevent any contraction of the dry gelatin, by a glycerin treatment. (Cf. Catala and Casanova: *Anal. R. Soc. Españ. Fis y Quim.*, Aug. 1956, 155–172.) Barkes and Young found the following glycerin solutions suitable related to the water content of the dry emulsion, for different RH:

RH %	35	50	60	70	82
Water/cc emulsion	0·097	0·108	0·134	0·160	0·209
Glycerin/100 cc sol.	10·66	10·56	10·32	10·09	9·68

383 **Differentiation of nuclear tracks:** The background can be reduced by the Herschell Effect: expose to the infra-red radiations of a 300 W lamp through a filter before developing. A redistribution of the latent image occurs. With RG.7 and RG.10 Schott filters, and 3 mins. exposure for Ilford C.2 emulsion or 10 mins. for Ilford G.5, at 10 cm from a Mazda 375 W lamp, α tracks become visible on a γ background (Jarczyk and Lewandowski: *Acta Phys. Polon.*, 1956, 143; Cüer, *Sc. Ind. Phot.*, **21**, 161).

An efficient method of track differentiation is *physical development* (see Curtis and Osborne: *Sc. Ind. Phot.*, **21**, 198). Longchamp, Gegauff and Cüer use the Rzymkowski quinhydrone developer (para. 71–73) (*Sc. Ind. Phot.*, Oct. 1956, 398).

Chapter XXIV

385 **Daguerreotype:** Very high resolving power has been obtained with Daguerreotypes on *silvered glass*, since 1901. Holweck tried to use it for electronic micrography, and Poppe made a recent important study (*Phot. Sc. Techn.*, May 1956, 75–79). Exposure in sunlight is 45–90 secs. at f/4·5.

391 **Actinometers:** Rogers (*Chem. and Ind.*, June 1956, 572) used *uranyl oxalate*, but *potassium ferrioxalate* seems to be much more sensitive (Hatchard and Parker: *Proc. Roy. Soc.*, June 1956, 518–536).

404 **Sensitized aluminium:** In the *Seofoto* process, 1935, of Siemens and Halske, the aluminium plates, oxidized in oxalic or chromic acid (more porous), were sensitized by alternate immersions in sat. NaCl+KBr sol. and 10% $AgNO_3$. Development in acid bath. The plates did not keep.

In the *Alphot* process, the pores of the oxide are filled with an organic reducer, then treated with an ammoniacal silver nitrate solution which gives colloidal silver. The plates are sensitized, just before use, in three successive baths.

(*a*) Permanganate + sodium chloride→silver chloride and oxidized residual organic reducer.

(*b*) Oxalic acid→reduces MnO_2.

(*c*) Potassium bromide + ferricyanide + dichromate→silver bromide (in part).

Development in alkaline bath and anti-foggant. Gold toning gives warm brown tones. Thickness 10–15 μ. D: 1·2–1·4—γ: 1·1–1·23. Resolving power: 170 lines (Cf. Meyer: *Bild. u. Ton*, Jan. 1956, 2.)

406 **Diffusion-transfer:** Images are generally yellowish-brown. Average diameter 60 mμ. *Neutral tones* can be obtained by adding of nitrogen or sulphur compound, such as *mercaptotetrazole*, or substitution of gelatin by another colloid. The mercaptoderivatives slow down the transfer of the silver complexes and their reduction (with local supersaturation). The spherical shape of the grains and their dimensions remain the same, but X-ray diffraction shows different lattice structures. The primary crystallites of black grains are smaller. This confirms Jelley's hypothesis: two grains of the same shape and dimension can have different optical properties. (Cf. Cassiers (Gevaert): *Sc. Ind. Phot.*, Jan. 1957, 36 and *Int. Konf. Wiss. Phot. Köln.*, 1956).

408 **Xerography:** Xero X plates consist of aluminium coated with vitreous selenium. ASA index: 2. Spectral sensitivity up to 570; max. 350 mμ.

Panchromatic plates, 10 times more sensitive, are being studied.

The plates are charged to 600 V, with 6 kV.

408b **Electrofax:** Preparation of the ZnO sensitized paper. Cf. H. G. Greig: F.P. 1,125,235 (1955), U.S. prior., 2-6-54.

410 **Photosensitive glasses:** Forty-one formulas of photosensitive glasses, by F. Reinhart: *Glas-Email-Keramo Techn.*, May 1956, 153–156.

Chapter XXV

412 **Nylon fibre paper** is not absorbant, and very resistant. It is dimensionally stable. Made by Roegal Paper Corp., New York.

436 **Polystyrol films:** *Gevaert Litholine ortho* emulsion for graphic arts is coated on polystyrol film, which has greater dimensional stability than triacetate.

	Length	*Width*
Triacetate after treatment	0·03%	0·04%
Polystyrol, „ „	0·01%	0·01%

442 **Static discharges on film:**

Measurement of the surface resistivity of films: two polished stainless steel electrodes 10 cm long and 1 cm apart, are pressed against the film which is placed on polystyrol plate. The surface resistivity is measured with a tube voltmeter. $10^{10}\Omega$ are normally sufficient.

Rubbing test with a nylon pad driven by a motor. The film is then developed, to count the discharge marks, light or dense.

Discharges production speed. Use the apparatus designed by A. S. Cross (*Sc. Ind. Phot.*, 1954, 371).

Static charge indicator. A system used by Larson and Nitke (Ansco) comprises an antenna, a transistor and a receiver—total weight 500 g. (*Intern. Konf. Wiss. Phot. Köln*, 1956.)

PART III

Chapter XXVI

453–478 **Studio lighting** for wide screen pictures. Lighting for Eastman Color films theoretically is 6000 lux at f/3·5; in fact 10,000 lux are needed. 10 kW 3350°K tungsten lamps age very rapidly: they lose 1°K per hour and 11°K per volt decrease. Tungsten lamps can now be replaced by 3200°K arcs associated with UV filters (Morgan Crucible Co.).

458 **Low tension discharge lamps, xenon filled:** The light efficiency increases with the tube diameter, up to 5 mm for 50 W/s, and with the gas pressure. Low tension, xenon-filled lamps are now available with 150 V battery. The lamps, fed by an electrolytic condenser, give a longer duration flash (2·6 ms) than those fed by an electrostatic condenser at higher voltage.

Tubes in synthetic sapphire, more transparent to UV, have been used by the Bell Telph. Laboratories.

Chapter XXVII

492 **Trichromatic inks** according to the *British Standards* Institution:

Half-tone: BS-1480 (1949)—3 or 4 inks
Off-set: BS-2650 (1955)—5 inks

one transparent yellow and one opaque yellow.

495 **Lenticular films** are used for recording colour television programmes. Cf. Evans and Smith: *Jl. Soc. Mot. Pic. Tel. Eng.*, July 1956, 65–72.

Chapter XXVIII

508 **Reciprocity Law failure of colour films:** When the exposure time is too short or too long, reversal films show differences, mostly in the magenta, then the cyan. The failure is greater with long exposures; the contrary for negative films. With reversal films, the reciprocity law failures appear during the first development, when the solvent acts on the internal image of the AgBr grains.

$$\text{Long exposures: } \begin{cases}\text{the light greys turn yellowish;}\\ \text{The dark greys turn bluish.}\end{cases}$$

$$\text{Short exposures: } \begin{cases}\text{The light greys turn bluish;}\\ \text{The dark greys turn yellowish.}\end{cases}$$

Cf. R. von Wartburg: *Zeits. Elektrochem.*, Aug. 1956, 487–500.

511 **Influence of colour formers on gelatin viscosity:** Coupling compounds, when added to an emulsion, increase the gelatin viscosity. After a maximum, there is a decrease and a new increase. Highly concentrated gelatin solutions show the greatest viscosity increase. The phenomenon is caused by the adsorption of the coupler on the hydrophilic groups of the polypeptide chain of the colloid, through hydrogen bonds or salification. The viscosity increase is

counteracted, to some extent, by a lesser contraction of the peptide chain. Cf. Evva and Berty: *Koll. Zeits.*, Oct. 1956, 10–16.

515–545 **Ansco Color printing:** The separation positives now obtained from negative 844, are printed on duplicate negative 846, then on positive 848. The three primary positive images have the following gammas: cyan 2·4, magenta 2·5, yellow 3·2. Cf. Schadlick: *Jl. Soc. Mot. Pic. Tel. Eng.*, July 1956, 375.

Copying by means of a mixture of three monochromatic lights seems to give better results than by means of filtered light.

516b **Colour prints:** Printing positive colour photographs is hazardous on a commercial scale. It is difficult to control the contrast and the average density of all the prints, and to avoid any red or blue cast. Abrasion may be caused by steel rollers. Silver deposits on immersed rollers, and Prussian blue forms in the bleaching bath. Cf. Pavelle and Varden: *Phot. Sc. Techn.*, Aug. 1956, 97–100.

Estimate of a developing and printing installation for 35 mm photo film and 100,000 prints yearly, see O. M. Kadstrup (Kodak): *Phot. Sc. Techn.*, Aug. 1956, 86–90.

Chapter XXIX

526 **Contrast increase:** A new Gevaert film, *Correctone*, has two superimposed emulsions with different contrasts and colour sensitivities. A first exposure is given in white light; then a second one, in yellow light, increases the contrast in the highlights.

530b **Gevaert recording densitometer for colour films:** A. Thiels: *Intern. Konf. Wiss. Phot. Köln*, 1956; *Sc. Ind. Phot.*, Feb. 1957, 76.

The incident light reaches a photomultiplier, alternatively, by two different ways, by means of a rotating mirror (50 c/s). One of the light beams goes through the test strip and a compensating wedge moved by a motor, so that the sum of the two densities remains constant and equal to the density of a second adjustable photometric wedge placed in the path of the second light beam. Three coloured wedges, cyan, magenta and yellow, allow equivalent density measurements to be made. Automatic readings of a sensitometric strip take 80 secs.

530d **Kodak reflection densitometer for colour prints:** P. B. Watt: *Jl. Phot. Sci.*, Oct. 1956, 116–120; *Sc. Ind. Phot.*, Jan. 1957, 32. The reflected light (at 45°) is collected all around the incident beam, by a photocell connected to an amplifier and a galvanometer. The reflection is elliptical, and the light modulated by a rotating disc at 100 c/s. Three sets of three-coloured filters are used for the measurements. The sensitometric strip is held by a vacuum system.

532 **Post-illumination of Agfacolor films:** The three superimposed emulsions react differently. Therefore, the colour of the light must be adjusted. Gain: 20–30% in speed. The auxiliary illumination depends on the time of the first exposure. Also it varies with each batch of film. This is true for all other makes of colour films.

Chapter XXX

534 **Theory of colour development:** Besides the classic theory explained para. 534, it is believed that in very alkaline media, or with phenols, the *quinone-diimine* is formed (instead of the semi-quinone-imine) which can react directly with the coupler and form a dye.

See: Vittum and Weissberger: *Sc. Ind. Phot.*, Feb. 1954, 63–65; *R.P.S. Centenary Conf.*, 1913.

Eggers and Frieser: *Zeits. Elektrochem.*, June 1956, 372–376.

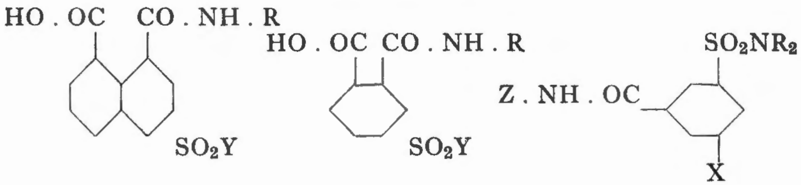
Brune and Kronacher: *Zeits. Wiss. Phot.*, Dec. 1955, 78–95. The semi-quinone-imine has been prepared by reacting p-amino-diethylaniline and bromine (drop by drop), cooling and stirring vigorously. The brominated semi-quinone-imine is obtained. It is washed with anhydrous ether.

When the silver bromide amount in the emulsion layer is small, the speed of the emulsion decreases and granulation increases. Vittum and Weissberger *prevent high contrasts* with normally rich emulsions, without reducing the AgBr amount, by adding, to the usual coupler, a second coupler which gives a soluble dye. Examples: sulphonated naphthols and citrazinic acid derivatives (*Intern. Konf. Wiss. Phot. Köln*, 1956; *Sc. Ind. Phot.*, Jan. 1957, 37).

534 **Metol + colour developers:** Colour development is activated by metol. See Van Veelen (Gevaert): *Sc. Ind. Phot.*, Feb. 1957, 83; *Int. Konf. Wiss. Köln*, 1956.

536 **Colour formers (couplers):** See the following patents:

Kodak: F.P. 1,111,514 (1955), U.S. prior. 23-1-52.
1,111,827 (1955), U.S. prior. 23-3-53.



539 **Other colour developing systems:**

E. Azine dyes. Schmidt (XII Congrès Intern. de Chimie pure et appliquée) found that when the developer, or the coupler, has a supplementary amino group, a second bond appears between the developer and the coupler, which produces a stable azine nucleus. Azine dyes have pure colours and can be used with reversal films (Ansco). 1:2:4-triaminobenzene is a suitable developer.

G. Acetylated anthraquinone couples with the quinone-imine derived from a developer, to form quinone-imine blue oxidizable into a yellow dye, by potassium dichromate (Schmidt).

H. Pyrimidine derivative. Following experiments by Wilmanns, Fricke and Birr with 2:5-diaminopyrimidine as a black and white developer, Saunders (Kodak) tried 4-substituted 5-amino-2-dimethylaminopyrimidines for colour development: these compounds proved to be poor developers (*J.C.S.*, Aug. 1956, 3, 232).

I. Hydrazine developers. Oxidized hydrazine derivative can combine with couplers to produce azo dyes. W. A. Schmidt and J. A. Spring discovered the β-*arylsulphonylhydrazines* which are oxidized into diazosulphones, before coupling with methylene compounds. Huenig used *hydrazones* derived from carbonyl derivatives of heterocyclic bases. These hydrazones are also oxidized into diazo compounds. The dyes thus obtained have very pure colours, due to their polar structure.

J. We have seen already that hydrazones can be good couplers. Marriage used hydrazine derivatives, with dioxynaphthalene as a developer. *Indazolones* have been suggested as couplers by Jennen and by Wooley: the latter used indazolones substituted in the 2-position (see para. 538).

Cf. Schmidt (Ansco): *Intern. Konf. Wiss. Phot. Köln*, 1956.

544 **Agfacolor** (*Zeits. Wiss. Phot.*, Dec. 1955, 96–107).

	Negative	Positive
Sensitivity maxima	440 $m\mu$	440 $m\mu$
	525 $m\mu$	525 $m\mu$
	700 $m\mu$	640 $m\mu$

Agfacolour ZN 35 mm: for making negatives from original reversal positives.

545 **Printon Ansochrome:** New opaque positive film, with increased cyan and yellow contrasts, and less fog. Treatment at 68°F: development 15 mins; bleaching 6 mins.; fixing 5 mins. Cf. *Phot. Sci. Techn.*, May 1956, 53, and Aug. 1956, 113.

546 **Gevacolor:** New *negative film No.* 652—32 ASA—6000 lux at f/4—resolving power 58 lines/mm.

*Positive T*952. The yellow filter is superfluous, due to the use of silver chloride emulsions which are not sensitive to blue. The top emulsion is sensitized to green, so the resolving power of the copies is increased: 40–45 lines instead of 30. $\gamma_N \times \gamma_p = 2$.

550 **Ektachrome:** The use of couplers more soluble in the dispersed semi-solid binder made it possible to reduce the thickness of the layers, in the new 35 mm Ektachrome. The anti-halation layer is placed under the emulsions and is protected by a gelatin coating. Sets of 20 sensitometric strips kept at —20°C (—4°F), and a developed one, are furnished by the maker.

The first developing time is very critical: 10 minutes at 24°C, with an error smaller than – 15 secs. Longer times give a purplish-blue cast and less density. Shorter times produce a yellowish-green cast and more density. (Cf. Millikan and Groet: *Phot. Sci. Techn.*, May 1956, 60–64.

550 **Eastman Color developers:** Soluble bromide can be removed by anion exchangers such as Amberlite IRA-400 (Röhm and Haas): 1 dm^3 for 50 L. The normal amount of NaBr is 0·25 g/L. The exchanger is regenerated with sodium sulphate. (Cf. Priesthoff and Stott: *Jl. Soc. Mot. Pic. Tel. Eng.*, 1956, 478–484.)

551 **Kodachrome:** 16 mm Internegative 7270, corrected by coloured coupler masks, is used for printing commercial copies. A soluble purple dye, in the emulsion, limits light scattering. The copies are made on Eastman Color print film 7382. The amount of light necessary for the printing of an original commercial Kodachrome, on that Internegative, is 25–50 times greater than the amount of light required for Kodachrome duplicating. (Cf. *Jl. Soc. Mot. Pic. Tel. Eng.*, April 1956, 426.)

Chapter XXXI

591 **Dyco Color** (Louisville, U.S.A.). Three-colour positives are made by three successive printings followed, each time, by colour development, with subsequent rehalogenation.

Chapter XXXII

612–614 **Photomechanical reproduction:** The synthesis of colours by the screen processes is generally supposed to be additive in the light areas and subtractive in the dark or strongly coloured areas. In fact, there is a mixture of the two. Therefore, masks for photomechanical processes cannot be identical to those for ordinary colour work. The correction of the highlight contrast is always detrimental to the colour balance. The optimum gamma of a mask should increase with density, in *photogravure*, and decrease, in *half-tone*. (Cf. Clapper and Yule: *VII Annual Meeting Techn. Ass. Graphic Arts*, Boston 1955, 1–14.)

Chapter XXXIII

626 **Dye Transfer:** The presence of a pH buffer has an influence on dye diffusion into gelatin layers:

(*a*) The dye concentration decreases in depth from the contact surface to the bottom.

(*b*) All the elementary concentrations increase with time, but the layers near the contact surface become richer.

(*c*) The increase of dye concentration is slower in the presence of a buffer.

Cf. Pontius, Kaplan and Husney. *Jl. Chem. Phys.*, Jan. 1950, 9–12.

Chapter XXXIV

633 **Decolorizable dyes:** Tests with 16 decolorizable dyes, see K. McKlaren (I.C.I.): *Jl. Soc. Dyers and Colourists*, March 1956, 86–99.

649b **Photosensitive polyvinyl chloride** (activated by *chlorinated paraffin*) is decomposed by ultra-violet light into *HCl* and other compounds. HCl is fixed by alumina $Al_2O_3 \rightarrow AlCl_3$. The plastic material is then heated: the aluminium chloride catalyzes the transformation of an incorporated base such as *naphthaquinone* (see para. 648) which changes into a brown image. T = 135–170°C. Chlorinated paraquinone can be the HCl generator and the colour former, at the same time. *Calimar*, a plastic photosensitive material, made by Ferro Chemical Co. (Ohio), has the above composition.

EQUIVALENTS OF METRIC, BRITISH AND U.S. WEIGHTS AND MEASURES

Mass

Metric weights: 1 kilogram (kg) = 1000 grams (g) = 1,000,000 milligrams (mg).

1 gram = 0·5643 dram = 0·035274 ounce avdp.
=15·432 grains = 0·6430 pennyweight
= 0·03215 ounce (troy)
1 kilogram = 2·20462 pounds avdp. = 2·6792 troy pounds.

Avoirdupois weight: 1 pound (lb.) = 16 ounces (oz.). 1 ounce = 16 drams (dr.).

1 dram = 1·772 grams
1 ounce = 28·250 grams = 437·5 grains
1 pound = 453·593 grams = 1·21528 troy pounds.

Capacity—liquid measure

Metric: 1 litre (l) = 1000 millilitres (ml) or cubic centimetres (cc).
1 litre = 7·042 gills = 1·7598 pints = 0·8804 quarts = 0·2200 gallon (imperial).
1 litre = 2·1134 pints = 1·0567 quarts = 0·26418 gallon (U.S.).
1 cc = 0·27052 fluid dram (U.S.) = 0·0338 fluid ounce (U.S.).

Imperial: 1 gallon (gal.) = 4 quarts (qt.); 1 quart = 2 pints (pt.); 1 pint = 4 gills.

1 gill = 0·1420 litre
1 pint = 0·5679 litre
1 quart = 1·1359 litres
1 gallon = 4·5435 litres = 1·20095 U.S. gallons.

U.S.: 1 fluid ounce (fl. oz.) = 8 fluid drams (fl. dr.); 1 fluid pint (fl. pt.) = 16 fluid ounces.

1 fluid dram = 3·6966 cc (cubic centimetres)
1 fluid ounce = 29·573 cc
1 fluid pint = 0·47317 litre
1 fluid quart = 0·94633 litre
1 gallon = 3·7853 litres = 0·83267 Imperial gallon.

Length

Metric: 1 metre (m) = 100 centimetres (cm) = 1000 millimetres (mm).

1 centimetre = 0·3937 inch
1 metre = 3·2808 feet = 1·0936 yards.

Imperial and U.S.: 1 yard (yd.) = 3 feet (ft.); 1 foot = 12 inches (in.).

1 inch = 0·02540 metre = 2·540 centimetres
1 foot = 0·30479 metre
1 yard = 0·91440 metre.

Area

Metric: 1 sq. metre (m^2) = 100 sq. decimetres (dm^2); 1 sq. decimetre = 100 sq. centimetres (cm^2).

1 sq. centimetre = 0·1550 sq. inch = 0·001065 sq. foot
1 sq. metre = 10·764 sq. feet = 1·1959 sq. yards.

Imperial and U.S.: 1 sq. yard (sq. yd.) = 9 sq. feet (sq. ft.); 1 sq. foot = 144 sq. inches (sq. in.).

1 sq. inch = 6·452 sq. centimetres
1 sq. foot = 9·290 sq. decimetres
1 sq. yard = 0·8361 sq. metre.

Volume

Metric: 1 cubic metre (m^3) = 1000 cubic decimetres (dm^3); 1 cubic decimetre = 1000 cubic centimetres (cm^3 or cc) = 1 litre.

1 cubic centimetre = 0·06102 cubic inch
1 cubic decimetre = 0·03531 cubic foot
1 cubic metre = 35·313 cubic feet

Imperial and U.S.: 1 cubic yard (cu. yd.) = 27 cubic feet (cu. ft.); 1 cubic foot = 1728 cubic inches (cu. in.).

1 cubic inch = 16·387 cubic centimetres
1 cubic foot = 28·317 cubic decimetres
1 cubic yard = 0·7645 cubic metre.

BIBLIOGRAPHIC ABBREVIATIONS

Ann. or *Ann. d. Chemie*	=	*Justus Liebig Annalen der Chemie*, Leipzig.
Ann. Phys.	=	*Annales de Physique*, Paris
Atti Accad. Lincei	=	*Atti della Accademia dei Lincei*, Roma.
Ber.	=	*Berichte der Deutschen Chemiken Gesellschaft*, Berlin.
Bild u. Ton	=	*Bild und Ton*, Berlin.
Brit. Jl. Appl. Physics	=	*British Journal of Applied Physics*, London.
Brit. Jl. Phot.	=	*British Journal of Photography*, London.
Brit. Kinema	=	*British -Kinematography*, London.
Bull. Soc.	=	*Bulletin de la Société Chimique de France*, Paris.
Canad. Jl. Phys.	=	*Canadian Journal of Physics*, Ottawa.
Chem. Abstr.	=	*Chemical Abstracts*, Easton (Pa.), U.S.A.
Chem. Ztg.	=	*Chemiker Zeitung*, Cothen.
Chimie et Ind.	=	*Chimie et Industrie*, Paris.
C.R. or *Compt. Rend. Ac. Sc. Paris*	=	*Comptes Rendus de l'Academie des Sciences*, Paris.
Helv. Chim. Acta	=	*Helvetica Chimica Acta*, Basel.
Helv. Phys. Acta.	=	*Helvetica Physica Acta*, Basel.
Ind. and Eng. Chem.	=	*Industrial and Engineering Chemistry*, Easton (Pa.), U.S.A.
J.A.C.S. or *Jl. Amer. Chem. Soc.*	=	*Journal of the American Chemical Society*, Easton (Pa.), U.S.A.

Jl. Appl. Phys. = *Journal of Applied Physics*, Lancaster (Pa.), U.S.A.
Jl. Chem. Phys. = *Journal of Chemical Physics*, Lancaster (Pa.), U.S.A.
J.C.S. or *Jl. Chem. Soc.* = *Journal of the Chemical Society*, London.
Jl. Chim. Phys. = *Journal de Chimie Physique*, Paris.
Jl. Frankl. Inst. = *Journal of the Franklin Institute*, Philadelphia (U.S.A.).
J.O.S.A. or *Jl. Opt. Soc. Amer.* = *Journal of the Optical Society of America*, Lancaster (Pa.), U.S.A.
Jl. Phot. Sci. = *Journal of Photographic Science*, London.
Jl. Phys. = *Journal de Physique et le Radium*, Paris.
Jl. Phys. Chem. = *Journal of Physical and Colloid Chemistry*, Baltimore.
Jl. f. Prakt. Chem. = *Journal für Praktische Chemie*, Leipzig.
Jl. Res. Bur. Standards = Journal of Research, Bureau of Standards, Wash.
Jl. Sci. Instrum. = *Journal of Scientific Instruments*, London.
Jl. Soc. Chem. Ind. = *Journal of the Society of Chemical Industry*, London.
Jl. Soc. Mot. Pict. Tel. Eng. or *J.S.M.P.T.E.* = *Journal of the Society of Motion Picture and Television Engineers*, Easton (Pa.), U.S.A.
Jl. Soc. Sci. Phot. Japan = *Journal of the Society of Scientific Photography of Japan*, Tokyo.
Kino-Technik = *Kino-Technik*, Berlin.
Kodak Abstr. = *Abstract Bulletin, Kodak Research Laboratory*, Rochester, U.S.A.
Koll. Zeits. = *Kolloid Zeitschrift*, Frankfurt a/M.
Nature = *Nature*, London.
Non destr. Testing = *Non-destructive Testing*, Skiokie (Ill.), U.S.A.
Nuovo Cim. = *Nuovo Cimiento*, Firenze.
Phil. Mag. = *Philosophical Magazine*, London.
Phot. Engng. = *Photographic Engineering*, Washington.
Phot. Ind. = *Die Photographische Industrie*, Berlin.
Phot. Jl. = *Photographic Journal* (actuallement *Jl. Phot. Sci.*).
Phot. Korr. = *Photographische Korrespondenz*, Vienne.
Phot. Sci. Techn. = *Photographic Science and Technique*, Philadelphia.
Phys. Rev. = *Physical Review*, Lancaster (Pa.), U.S.A.
Phys. Zeits. = *Physikalische Zeitschrift*, Leipzig.
Proc. Roy. Soc. = *Proceedings of the Royal Society*, London.
Process Engr. Month. = *Process Engravers' Monthly*, London.
Radiology = *Radiology*, Springfield (Ill.), U.S.A.
Rev. Opt. = *Revue d'Optique theorique et instrumentale*, Paris.
Rev. Sci. Instrum. = *Review of Scientific Instruments*, Lancaster (Pa.), U.S.A.
Sc. et Ind. Phot. = *Science et Industries Photographiques*, Paris.
Trans. Farad. Soc. = *Transactions of the Faraday Society*, London.
Zeits. Anal. Chem. = *Zeitschrift für Analytische Chemie*, Wissbaden.
Zeits. Angew. Chemie = *Zeitschrift für Angewandte Chemie*, Heidelberg.
Zeits. Anorg. Chemie = *Zeitschrift für Anorganische Chemie*, Hamburg.
Zeits. Elektrochem. = *Zeitschrift für Elektrochemie*, Weinheim.
Zeits. Physik. = *Zeitschrift für Physik*, Berlin.
Zeits. Wiss. Phot. = *Zeitschrift für Wissenschaftlische Photographie*, Leipzig.

THERMOMETER EQUIVALENTS

To convert Centigrade into Fahrenheit degrees, multiply by $\frac{9}{5}$ and add 32.
To convert Fahrenheit into Centigrade degrees, subtract 32, and multiply by $\frac{5}{9}$.

C	F	C	F	C	F	C	F
—40	—40	23	73·4	63	145·4	110	230
—35	—31	24	75·2	64	147·2	115	239
—30	—22	25	77	65	149	120	248
—25	—13	26	78·8	66	150·8	125	257
—20	— 4	27	80·6	67	152·6	130	266
—17·8	0	28	82·4	68	154·4	135	275
—15	+ 5	29	84·2	69	156·2	140	284
—10	14	30	86	70	158	145	293
— 9	15·8	31	87·8	71	159·8	150	302
— 8	17·6	32	89·6	72	161·6	155	311
— 7	19·4	33	91·4	73	163·4	160	320
— 6	21·2	34	93·2	74	165·2	165	329
— 5	23	35	95	75	167	170	338
— 4	24·8	36	96·8	76	168·8	175	347
— 3	26·6	37	98·6	77	170·6	180	356
— 2	28·4	38	100·4	78	172·4	185	365
— 1	30·2	39	102·2	79	174·2	190	374
0	32	40	104	80	176	195	383
+1	33·8	41	105·8	81	177·8	200	392
2	35·6	42	107·6	82	179·6	205	401
3	37·4	43	109·4	83	181·4	210	410
4	39·2	44	111·2	84	183·2	215	419
5	41	45	113	85	185	220	428
6	42·8	46	114·8	86	186·8	225	437
7	44·6	47	116·6	87	188·6	230	446
8	46·4	48	118·4	88	190·4	235	455
9	48·2	49	120·2	89	192·2	240	464
10	50	50	122	90	194	245	473
11	51·8	51	123·8	91	195·8	250	482
12	53·6	52	125·6	92	197·6	255	491
13	55·4	53	127·4	93	199·4	260	500
14	57·2	54	129·2	94	201·2	265	509
15	59	55	131	95	203	270	518
16	60·8	56	132·8	96	204·8	275	527
17	62·6	57	134·6	97	206·6	280	536
18	64·4	58	136·4	98	208·4	285	545
19	66·2	59	138·2	99	210·2	290	554
20	68	60	140	100	212	295	563
21	69·8	61	141·8	105	221	300	572
22	71·6	62	143·6				

INDEX

FOUNTAIN PHOTOBOOKS

PHOTOFACTS

1. The Camera	2/6
2. Focusing	2/6
3. Exposing	2/6
4. Colour Filters	2/6
5. Composing the Picture	2/6
6. Outdoor Portraiture	2/6
7. Landscape Photography	2/6
8. Seaside Photography	2/6
10. Developing the Film	2/6
11. Contact Printing	2/6
12. Enlarging	2/6
13. Developing the Print	2/6
14. Holiday Photography	2/6
15. Outdoor Lighting Effects	2/6
16. Lantern Slides and Transparencies	2/6
17. Artificial Lighting	2/6
18. Flash Photography	2/6
19. Portraits Indoors	2/6
20. Action Photography	2/6
21. Exposure Meters	2/6
23. Negative Faults	2/6
24. Print Faults	2/6
25. Photographing Architecture	2/6
26. Photography at Night	2/6
27. Still Life Photography	2/6
28. Animal Photography	2/6
29. Electrical Facts	2/6
30. Chemicals in Photography	2/6
31. Toning the Print	2/6
32. The Exhibition Print	2/6
33. All the Year Round	2/6
34. Buildings	2/6
35. Weddings	2/6
36. Photographic Competitions	2/6
37. Without Sunshine	2/6
38. Close-up Photography	2/6
39. Black-and-White Prints from Colour	2/6
40. Humorous Photographs	2/6

SPECIAL TECHNIQUES

Applied Microscopy	21/-
Art of Photographic Salesmanship	8/6
Colouring, Tinting and Toning Photographs	10/6
Camera Movements	15/-
Composition for Photographers	21/-
Creative Table Top Photography	35/-
Document Copying and Reproduction Processes	52/6
Entomological Photography in Practice	32/6
Linhof Practice	63/-
Modern Enlarging Technique	15/-
Pearlman on Print Quality	12/6
Professional Methods for Amateur Photographers	25/-
Flash Photography	10/6
Photo Composition	35/-
Press Photography	52/6
Zoological Photography	52/6

COLOUR

Taking Colour Photographs	12/6
Colour Before the Camera	7/6
Colour Separation Negatives	7/6
Colour Pictorial Photography	7/6
Colour Portraiture	7/6
My Experiences in Colour Photography	50/-
Photography in Colour with Kodak films	15/-
Photographing Colour with Walther Benser	42/-
Pilkington on Colour Photography	48/-
Reproduction of Colour	63/-
Sharp's Colour Chart and Grey Scale	19/6

PORTRAITURE

Donovan on Child Portraiture	21/-
Photographic Make-up	18/6
Portrait Manual	45/-

CREATIVE PHOTOGRAPHY

Erith on Pictorial Photography	32/6
Modern Control in Photography	32/6

GENERAL SUBJECTS

Basic Photographic Chemistry	15/-
Boys' Book of Photography	10/6
Build Your Own Enlarger	9/6
Build Your Own Stereo Equipment	10/6
Complete Photobook	10/6
Exposure Manual	45/-
Gevaert Manual of Photography	25/-
Handbook of Amateur Photography	90/-
Hints, Tips and Gadgets for Amateur Photographers	9/6
How to Photograph Boats	7/6
How to Photograph Trains	7/6
How to use your Camera	12/6
International Photos	72/-
Photographers' Data Book	9/6
Photographic Exhibition Reference Book	4/6
Properties of Photographic Materials	35/-
Science of Photography	38/6

CINEMATOGRAPHY

Cine Data Book	25/-
Cine-Film Projection	15/6
G. B.-Bell & Howell 8 mm. Cine Manual	32/6
Film Strip Projection	8/6
Handbook of Amateur Cinematography Vol. I and II	27/6 (each)
Introduction to Cine	12/6
Movie Making for Everyone	10/6
Principles of Cinematography	63/-
Special Effects in Cinematography	22/6

CINEFACTS

Filming Indoors	2/6
Home Movie Shows	2/6
Making a Story Film	2/6
Cine Stereo for Amateurs	2/6
Tricks with Movies	2/6
Processing Amateur Movies	2/6
The Animated Cartoon	2/6
Adding Sound to Movies	2/6
Filming in Colour	2/6
Finishing the Film	2/6

MINIATURE PHOTOGRAPHY

The Living Leica	32/6
Contaflex Manual	35/-
Photography with a Leica	10/6
35 mm. Photography with an Exakta	25/-
Rollei Handbook	15/-
Rollei Manual	45/-
Exakta Handbook	15/-
Jouhar on 35mm. Picture Making	30/-
Retina Manual	45/-
Retina Handbook	15/-
Leica in Professional Practice	50/-

Send 3 x 3d. Stamps for *Complete Photobook Catalogue*

FOUNTAIN PRESS · 46/47 CHANCERY LANE . LONDON W.C.2