Wool dyes

Contemporary wool dyeing and finishing

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Summary

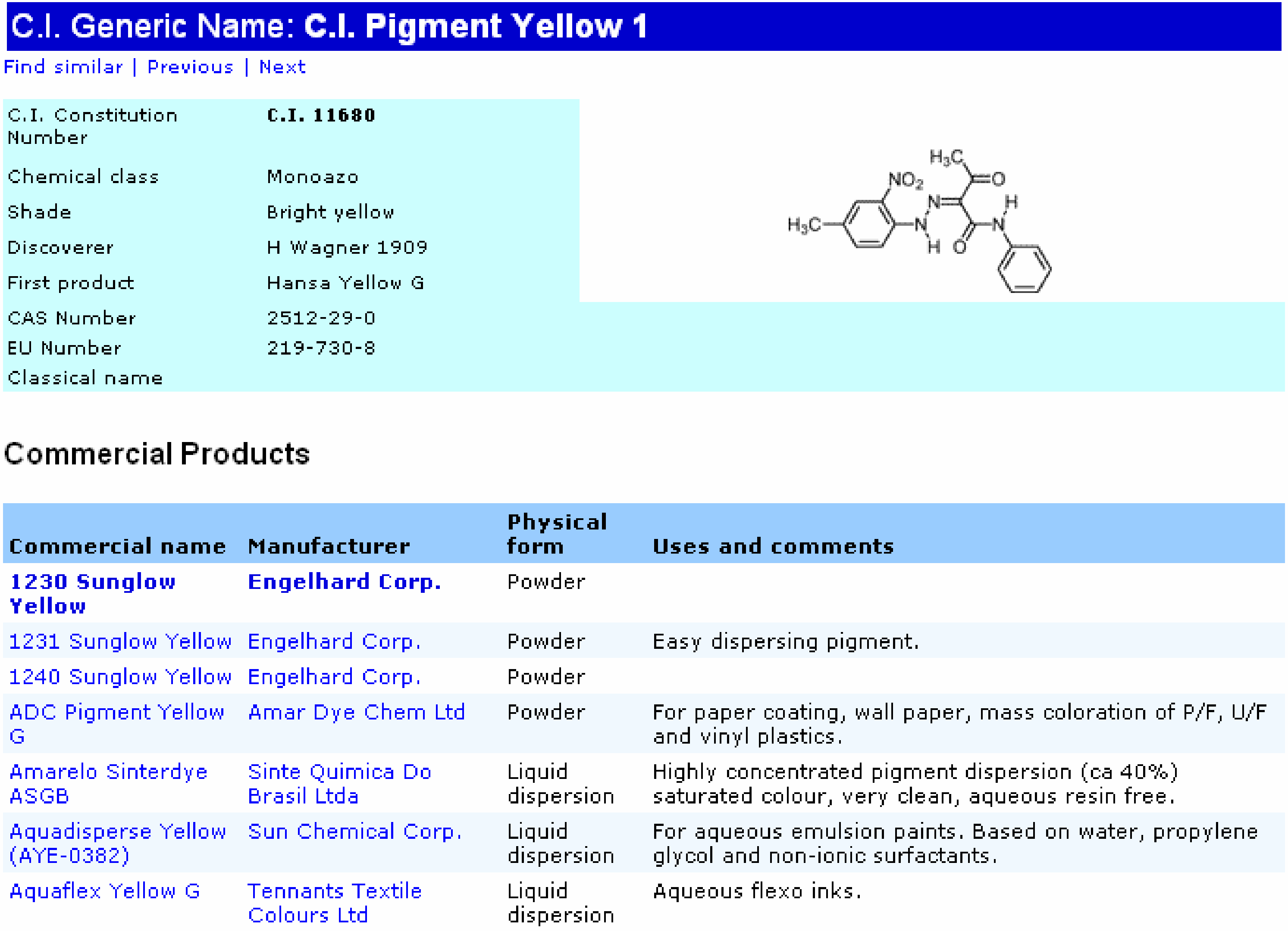
1. Introduction to dyes
2. Colour and chemical constitution
3. The different types of dyes used for wool

1. Introduction to dyes

Colour Index International

- **All known dyes and pigments are listed** according to Colour Index Generic Names and Colour Index Constitution Numbers.
- First published in 1925, fourth edition is now **online**.
- For each colourant, **manufacturers and distributors are listed** together with some technical details.
- **Structures** and of many colourants are given.
- Now **compiled by SDC and AATCC**.

A Colour Index page



C.I. Generic Name: C.I. Pigment Yellow 1

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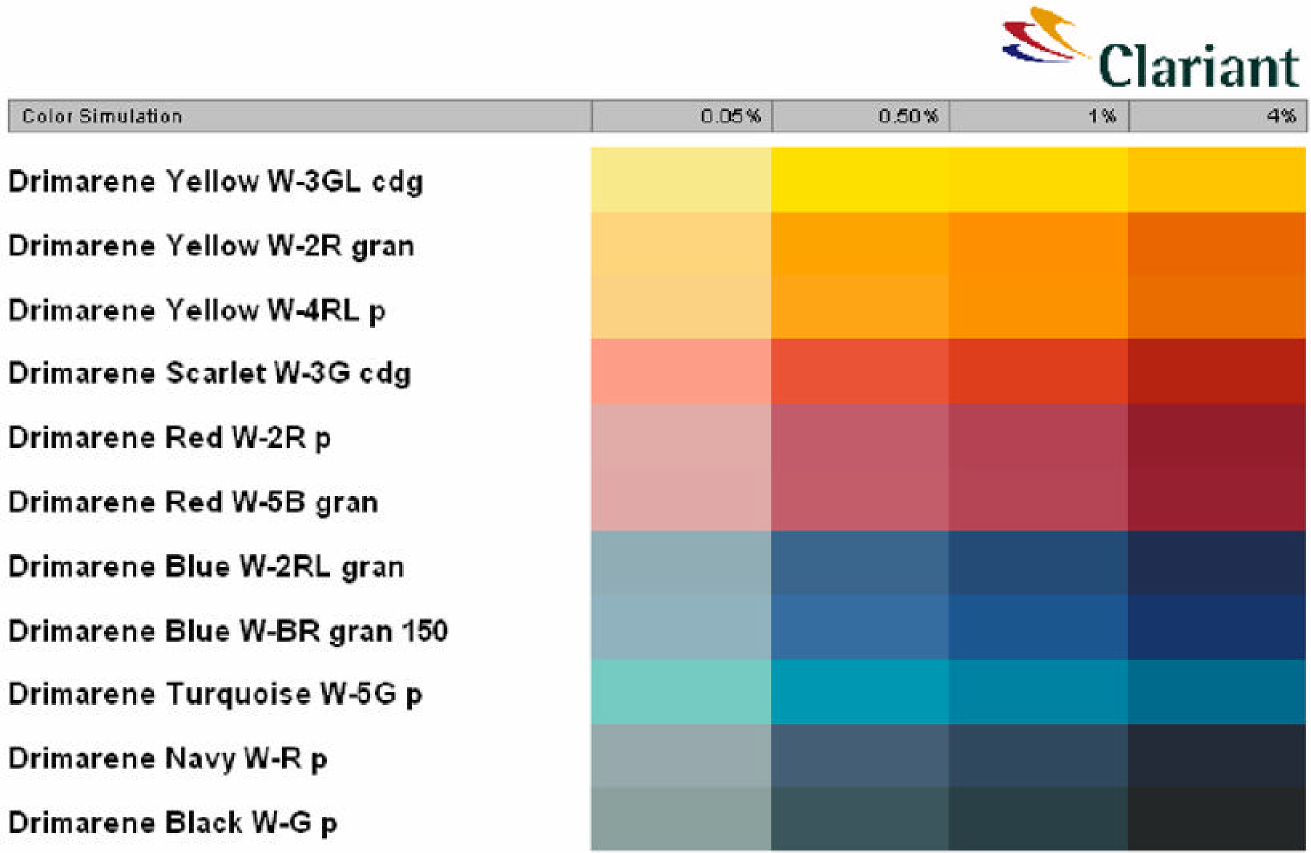
C.I. Constitution Number	**C.I. 11680**
Chemical class	Monoazo
Shade	Bright yellow
Discoverer	H Wagner 1909
First product	Hansa Yellow G
CAS Number	2512-29-0
EU Number	219-730-8
Classical name	

Commercial Products

Commercial name	Manufacturer	Physical form	Uses and comments
1230 Sunglow Yellow	**Engelhard Corp.**	Powder	
1231 Sunglow Yellow	Engelhard Corp.	Powder	Easy dispersing pigment.
1240 Sunglow Yellow	Engelhard Corp.	Powder	
ADC Pigment Yellow G	Amar Dye Chem Ltd	Powder	For paper coating, wall paper, mass coloration of P/F, U/F and vinyl plastics.
Amarelo Sinterdye ASGB	Sinte Quimica Do Brasil Ltda	Liquid dispersion	Highly concentrated pigment dispersion (ca 40%) saturated colour, very clean, aqueous resin free.
Aquadisperse Yellow (AYE-0382)	Sun Chemical Corp.	Liquid dispersion	For aqueous emulsion paints. Based on water, propylene glycol and non-ionic surfactants.
Aquaflex Yellow G	Tennants Textile Colours Ltd	Liquid dispersion	Aqueous flexo inks.

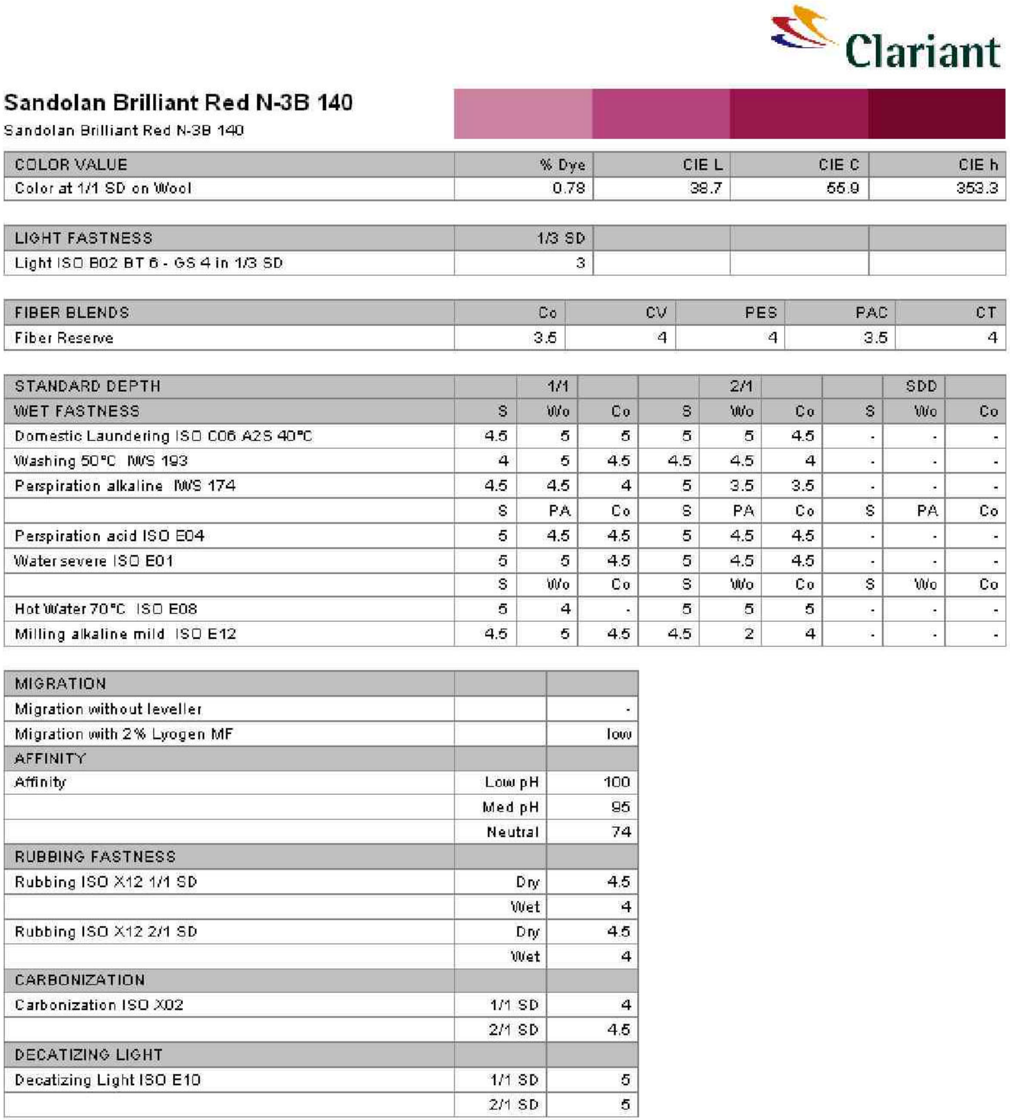
A pattern card for wool reactive dyes



Clariant

Color Simulation	0.05%	0.50%	1%	4%
Drimarene Yellow W-3GL cdg	🟨	🟨	🟨	🟨
Drimarene Yellow W-2R gran	🟧	🟧	🟧	🟧
Drimarene Yellow W-4RL p	🟧	🟧	🟧	🟧
Drimarene Scarlet W-3G cdg	🟥	🟥	🟥	🟥
Drimarene Red W-2R p	🟥	🟥	🟥	🟥
Drimarene Red W-5B gran	🟥	🟥	🟥	🟥
Drimarene Blue W-2RL gran	🟦	🟦	🟦	🟦
Drimarene Blue W-BR gran 150	🟦	🟦	🟦	🟦
Drimarene Turquoise W-5G p	🟦	🟦	🟦	🟦
Drimarene Navy W-R p	⬛	⬛	⬛	⬛
Drimarene Black W-G p	⬛	⬛	⬛	⬛

A manufacturer's pattern card



Clariant

Sandolan Brilliant Red N-3B 140

Sandolan Brilliant Red N-3B 140

COLOR VALUE	% Dye	CIE L	CIE C	CIE h
Color at 1/1 SD on Wool	0.78	38.7	55.9	353.3

LIGHT FASTNESS	1/3 SD			
Light ISO B02 BT 6 - GS 4 in 1/3 SD	3			

FIBER BLENDS	Co	CV	PES	PAC	CT
Fiber Reserve	3.5	4	4	3.5	4

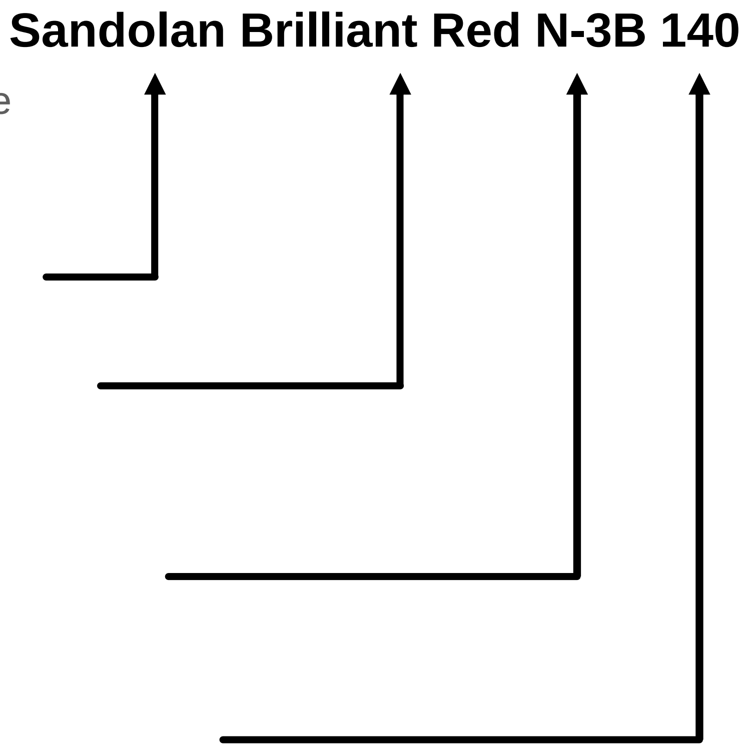
STANDARD DEPTH		1/1			2/1			SDD	
WET FASTNESS	S	Wo	Co	S	Wo	Co	S	Wo	Co
Domestic Laundering ISO C06 A2S 40°C	4.5	5	5	5	5	4.5	-	-	-
Washing 50°C IWS 193	4	5	4.5	4.5	4.5	4	-	-	-
Perspiration alkaline IWS 174	4.5	4.5	4	5	3.5	3.5	-	-	-
	S	PA	Co	S	PA	Co	S	PA	Co
Perspiration acid ISO E04	5	4.5	4.5	5	4.5	4.5	-	-	-
Water severe ISO E01	5	5	4.5	5	4.5	4.5	-	-	-
	S	Wo	Co	S	Wo	Co	S	Wo	Co
Hot Water 70°C ISO E08	5	4	-	5	5	5	-	-	-
Milling alkaline mild ISO E12	4.5	5	4.5	4.5	2	4	-	-	-

MIGRATION		
Migration without leveller		-
Migration with 2% Lyogen MF		low
AFFINITY		
Affinity	Low pH	100
	Med pH	95
	Neutral	74
RUBBING FASTNESS		
Rubbing ISO X12 1/1 SD	Dry	4.5
	Wet	4
Rubbing ISO X12 2/1 SD	Dry	4.5
	Wet	4
CARBONIZATION		
Carbonization ISO X02	1/1 SD	4
	2/1 SD	4.5
DECATIZING LIGHT		
Decatizing Light ISO E10	1/1 SD	5
	2/1 SD	5

Nomenclature of dyes

The name of each textile dye is made up of up to four parts:

- First, an **identifying name** is given by the maker. Dyes with similar characteristics, designed to be applied together have the same identifying name. Sometimes extra letters also are appended to the generic name.
- Then the general **hue** of the dye is usually described with a word. (Yellow, Red, Blue etc.)
- **Numbers and letters** following the hue word further differentiate the dye from others of similar hue by referring to the class and tone of the dye (eg. 3B is bluer than 2B).
- Finally a three digit number describes the **relative strength** of the dye relative to standard depth. (140 means 1.4 times the’strength of a ‘normal” dye for which a 1% dyeing produces a shade of 1:1 standard depth.)



Sandolan Brilliant Red N-3B 140

Limitations on dyes with similar CI names

- **Dyes with the same generic name** in the Colour Index resemble one another only to the extent that they **contain the same major coloured component** – according to a declaration by the manufacturer.
- In some cases, the **colour content may be as low as 10 to 15%** of the product by weight.
- **Equivalence of CI Generic Names does not imply any similarity of colour strength** or in the nature or amounts of other components present.
- **The active component of reactive dyes may vary** depending on how they are synthesised, isolated and stabilised. Varying amounts of hydrolysed dye may be present, leading to variations in fixation and fastness properties
- **Ecotoxicological data** are strictly applicable only to the specific dye formulation under test. Such data **are not transferable between products** sharing the same CI Generic Name.

Characteristics of dyes

Dyes should have the following **features**:

- **intense color** (molar absorptivity ε >10,000)
- **solubility** in water
- **substantivity** to the fibre
- **durability** to further treatments in production and normal use
- **safe**, easy to handle, and reasonably priced
- **bright shades are preferred for light to medium depths** (up to 3% o.w.f.), since duller shades can be made by mixing the brighter ones
- **dull shades are OK for heavy depths**, particularly if the cost is lower.

Operational requirements of dyes

Optimum reproducibility from a combination of dyes will only be obtained if they are:

1. **robust** - unaffected by slight changes in processing conditions (such as pH, liquor ratio, temperature and time)
2. **compatible** - function in combinations as if they were single dyes
3. **stable** - not degraded by contaminants in the water supply or substrate
4. **consistent** - insensitive to slight changes in substrate quality.

Standardisation of dyes

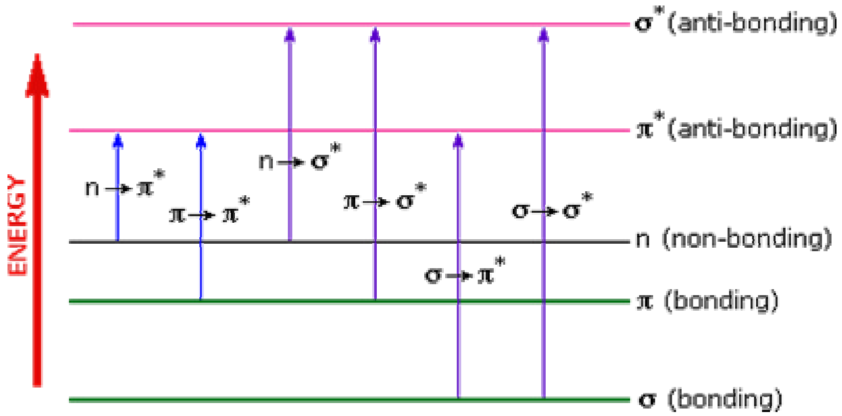
Quality assurance of deliveries of dyes to a mill must be carried out if reproducibility is to be assured.

- **Each dye lot should be checked** by: spectrophotometrical measurement and by carrying out a trial dyeing under standard conditions against a master batch.
- Dye makers can provide **certificates of conformity** to standard for individual batches or deliveries.
- Certification is an essential part of the **quality accreditation procedures** for the dye house (for example under ISO 9000).

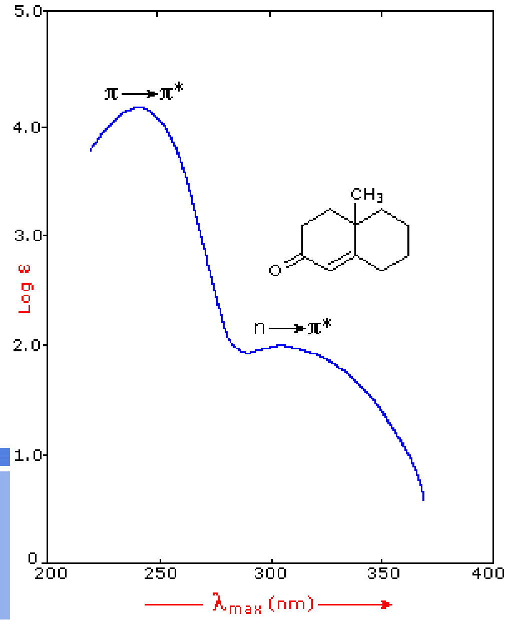
Without standardisation, shade reproducibility can not be guaranteed.

2. Colour and chemical constitution

Colour and chemical constitution



- Any substance that absorbs wavelengths in the visible region will appear coloured.
- Molecules absorb radiation of definitive wavelengths that cause some change within their electronic structure.
- The absorbed energy will cause particular electrons (p electrons) to move from their ground state orbitals to higher energy-level orbitals, located further away from the atomic nucleii. The absorbed energy is subsequently converted into heat-energy, and the electrons return to their normal state.
- The visible region of the spectrum 750-400 nm comprises photon energies of 36 to 72 kcal/mole.

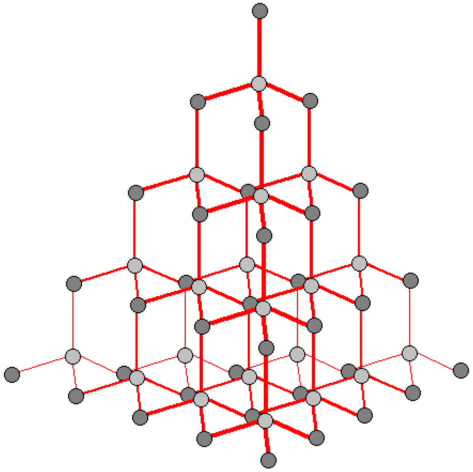


Colour and chemical constitution

- Electrons involved in **single bonds**: i.e. C-C and C-H, in saturated hydrocarbons, are held firmly between the atoms and **cannot be excited by visible light**. However, these bonds can absorb high energy radiation such as far U.V. ~130 nm.
- **Unsaturated hydrocarbons absorb radiations of longer wavelengths** (~180 nm and above) due to the p (pi) electrons of the double bonds which require less energy for excitation.
- **In order for a molecule to absorb visible light, it must have conjugated double bonds**, in which the p electrons are delocalised and can move between all the carbons (sp^2 carbons) of these systems. Delocalised electrons require less energy for excitation and can absorb visible radiation with a high intensity.

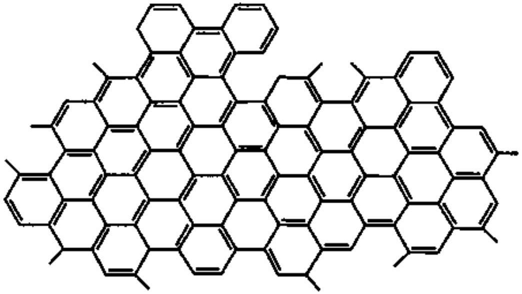
Colour of diamond

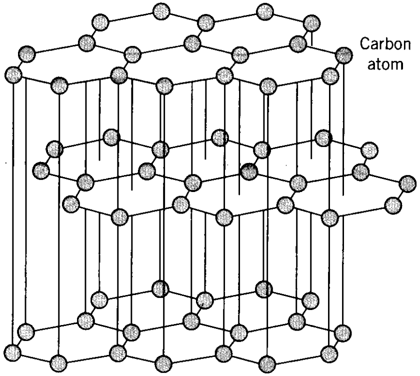
- To demonstrate the relation between visible light absorption and chemical constitution, it is interesting to compare the two allotropes of carbon: diamond, and graphite.
- While diamond is colorless and transfers (or reflects) all visible light, graphite absorbs the entire spectrum of visible light and therefore appears black. The reason for this is the difference in the way the carbon atoms are bonded to each other in these compounds.
- In diamond, all the carbon atoms are bonded to each other through single bonds (sp^3 hybridization) to form one gigantic crystal molecule. Therefore, diamond cannot absorb visible light and appears colorless.



The colour of graphite

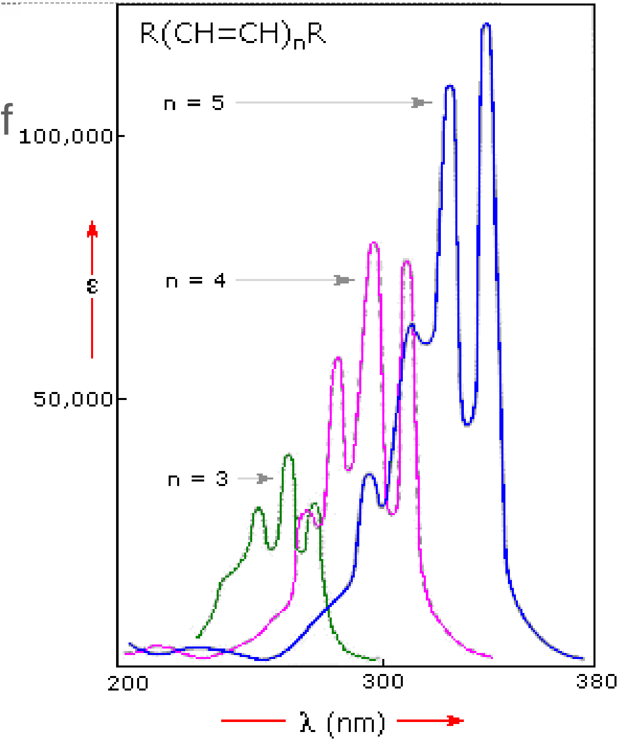
- Graphite, on the other hand, is made of sheets of huge planar molecules consisting of thousands of fused benzene rings
- Each of the carbons exhibits double bond characteristics (all carbons are with sp^2 hybridisation) and the whole macro-molecule contains thousands of conjugated double bonds. Accordingly, the p electrons are highly delocalised and require low energy to be excited, thus molecules of graphite absorb the whole visible spectrum. The delocalisation of the p electrons in graphite accounts also for its ability to conduct electricity through its mobile p electrons.

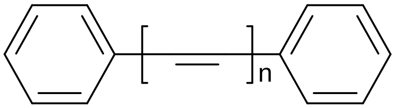




The effect of increasing conjugation on colour

- The effect of increasing the number of conjugated double bonds on the colour of the molecule is shown in the table.
- Every double bond added to the conjugation causes a shift in the absorption toward longer wavelengths.

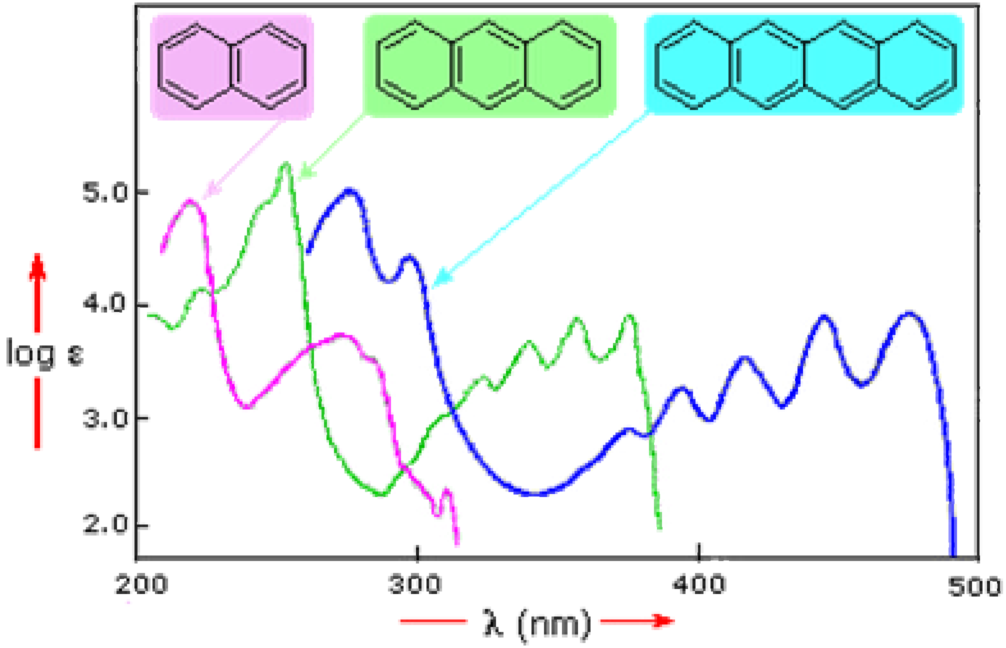




n	1	2	3	4	5	6	7	11	15
Colour	None	None	Pale yellow	Green - yellow	Orange	Brown - orange	Green - brown	Violet - black	Green - black

The effect of fused aromatic rings on colour

As the number of rings increases, the absorption bands shift to longer wavelengths.



Chemical structures of dye molecules

- Graebe and Liebermann (1868) were the first to observe that dye molecules contain conjugated double bonds in their structure.
- A few years later, O. N. Witt observed that dye molecules contain certain functional groups attached to the **conjugated double bonds**, which he called '**chromophores**', which intensified the absorption of visible light.
- Other functional groups attached to the conjugated double bonds, referred to as '**auxochromes**', were found to affect the absorption by shifting it usually toward longer wave lengths and increasing its intensity.
- The **combination of these three components** in a molecule are **responsible for its colour**, and together are called the '**chromogen**'. In modern terminology this is often also called the chromophore!
- Certain functional groups can significantly reduce the number of double bonds in the conjugated system required for intense absorptions of visible light.
- Accordingly, the **resulting dye-molecules are small enough to diffuse into fibres.**

Chromophores

These are functional groups that by themselves absorb visible or near U.V. radiation. They are unsaturated functional groups (except for: $-NR_3^+$) that act as electron acceptors (directing to meta positions in elecrophilic substitution reactions of the benzene ring). Examples of chromophores are:

$-N=N-$	**diazo group,**
$-NO_2$	**nitro group,**
$-C=O$	**carbonyl group,**
$-NR_3^+$	**alkyl ammonium group.**

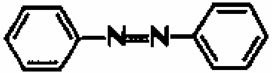
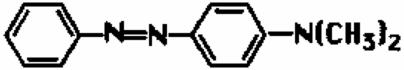
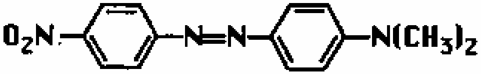
Auxochromes

- Auxochromes are saturated functional groups, with nonbonding electrons, on the atom attached to a conjugated system, and therefore can act as electron donors.
- These groups direct to ortho-para positions in elecrophilic substitution reactions of the benzene ring.
- Examples of auxochromes are:

$-NH_2$	**amino group,**
$-NHR$	**mono alkyl amino group,**
$-NR_2$	**dialkyl amino group,**
$-OH$	**hydroxy group,**
$-OR$	**ether group.**

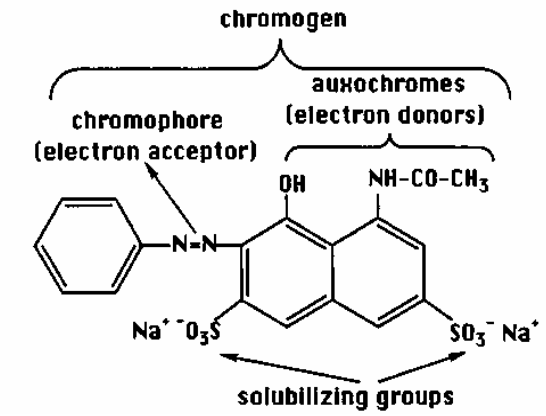
Absorption spectra of diazo compounds

- The affect of attaching an auxochrome to a conjugated double bond system containing a chromophore is shown below with azo-benzene.
- By adding the **dimethyl amino group** to azo benzine, the strong absorption bands shift to longer wavelengths and a more strongly coloured molecule is produced.
- When another chromophore, the **nitro group**, is added to the system a further shift to longer wavelengths with a further increase in absorption intensity is observed.

	λ max nm	ε max L mol^{-1} cm^{-1}
 Azo Benzene	330	17,000
 C.I. Solvent Yellow 2	408	27,500
 4-Nitro-4-dimethylamino-azobenzene	478	33,100

Other functional groups on dyes

Water soluble dyes have solubilising groups, usually sulfonic acid (-SO_3^- Na^+) groups.



C I Acid Red 1

Reactive dyes carry one or more reactive groups that allow the dye to covalently bond to suitable groups in fibres.

Still other dyes may have a **saturated hydrocarbon chain** attached to their structure to increase their hydrophobicity or molecular size, and thereby increase their affinity for different types of fibres.

Some common chromophores

Some common types of chromophores are listed in this table in order of increasing molar absorptivity and also in increasing brightness (sharpness of their absorption peaks).

The light-fastness of these dyes is in the reverse order of their e-values, except for the phthalocyanines.

Chromophore	**Molar Absorptivity (e)**
Anthraquinone	5,000-15,000
Azo	20,000-40-000
Cyanine	40,000-80,000
Triarylmethane	40,000-160,000
Phthalocyanine	~200,000

Summary of structural features of dye chromogens

- **Conjugated** systems

  -C=C-C=C- -C=N-C=N- phthalocyanine etc.

- **Chromophore** groups (electron withdrawing)

  -N=N-(azo types), -C=O (anthraquinone types),

  $-NR_3^+$ (triphenylmethane types)), $-NO_2$ etc.

- **Auxochrome** groups (electron donors) (ring substituents)

  $-NH_2$ -NHR $-NR_2$ -OH -OR etc.

- **Molecules should be planar.**

- **Solubilising** groups (soluble dyes only)

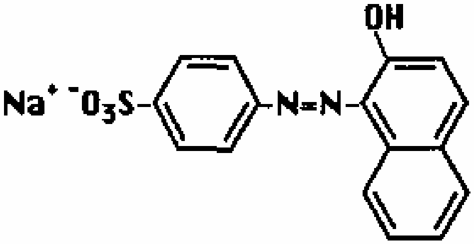
  - acid, direct, chrome, reactive etc. $-SO_3^-$

  - 2:1 premetallised $-SO_2CH_3$ $-SO_2NHCH_3$

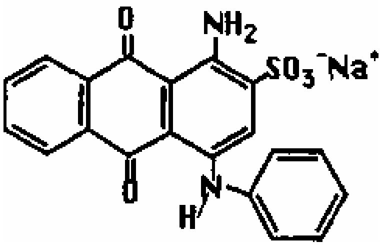
3. The different types of dyes used for wool

Acid dyes for wool

- Most acid dyes are sodium salts of organic sulphonic acids. They consist of an aromatic structure containing a **chromogen and at least one solubilising group**, almost always a sulphonic acid salt ($-SO_3^-Na^+$).
- About two thirds of the acid dyes contain **one or more di-azo groups**.
- Other acid dyes may be based on **anthraquinone, triaryl methane**, nitrophenyl amine, and other structures.
- Initially acid dyes were so called because an acid was required in their application. The term **'acid dyes'** is also consistent with their chemical structure since **they are salts of organic acids**. Often acid dyes are also referred to as **anionic** dyes.



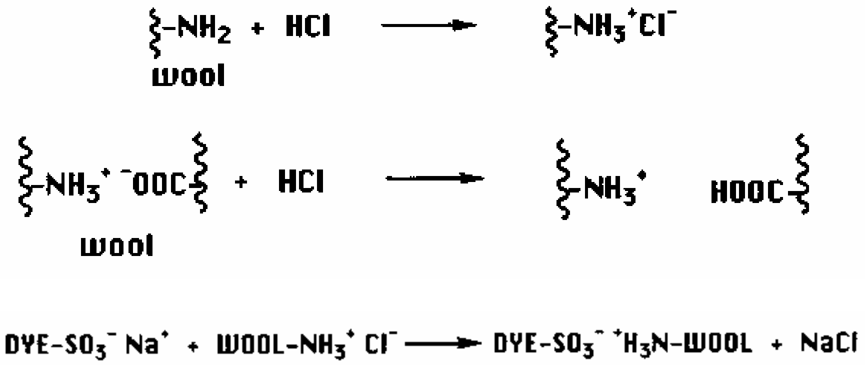
C.I. Acid Orange 7



C.I. Acid Blue 25

Mechanism of dyeing wool with acid dyes

- **Acid reacts with wool** to produce positively charged amino groups (-NH_3^+) on the fibres.
- The negatively charged coloured ions **(anions) on the dye are attracted** to the positively charged -NH_3^+ groups on the fibre.
- The more substantive **dye anion replaces the counter anion of the acid** (Cl^-, HSO_4^- CH_3COO^-, etc.), which has a very low affinity for the fibre**.**



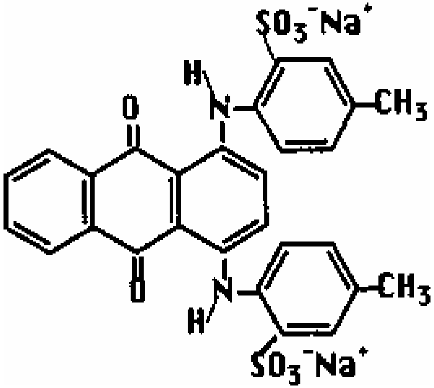
- **Sodium sulfate is used as a levelling agent** to slow down the rate of dyeing and enhance dye migration**.** Sulfate ions (SO_4^{2-}) compete with the dye anions (DYE-SO_3^-) for dye sites. The concentration of sulfate ions present far exceeds the concentration of dye ions, and since they are much smaller in size they will diffuse at a faster rate, and initially occupy all the dye sites available. The dye anions move at a much slower rate, and slowly replace the sulfate ions, resulting in a much more uniform dyeing.

Acid milling dyes

- The bonds that are formed between wool and acid dyes with low relative molecular masses are not strong enough to withstand multiple launderings. This **limited wet fastness** is even more pronounced where milling (felting) operations follow dyeing. (In the milling process wool fabrics are felted by mechanically pulling and beating them in presence of a strong soap solution.)
- **The need for acid dyes that would not bleed during the milling** process resulted in the introduction of **the acid milling and super milling dyes**.
- These dyes consist of larger molecules which are capable of forming more **second order bonds (hydrogen, Van der Waals and hydrophobic bonds).** Though the increased molecular size results in improved wet fastness, these dyes are less soluble in water and diffuse more slowly inside fibres.

Acid milling dyes

- These dyes are made of **larger molecules** than those of the acid levelling dyes, and require only **a weak acid (e.g. acetic acid) for exhaustion** (C.I. application method #2, pH of dye-bath: 3.5-5.5). The behavior of the acid milling dyes during dyeing and in normal use is between that of the acid levelling dyes and the neutral dyeing acid dyes. An example of an acid milling dye is:

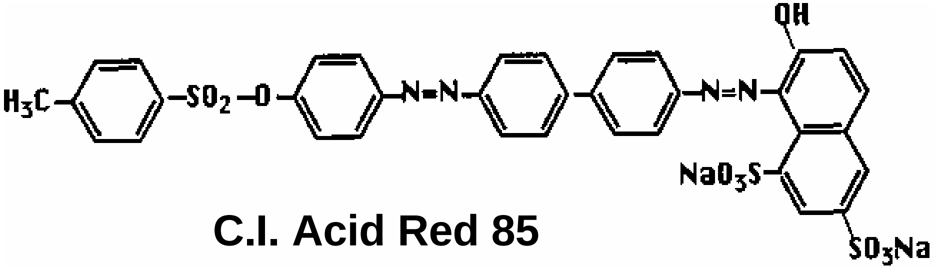


C.I. Acid Green 25

- The acid milling dyes have the advantage of being **applied at a pH close to the iso-electric point of wool (pH 4.5).**

Neutral dyeing acid dyes

- These dyes also are called Super Milling dyes, usually have the highest molecular weights, and therefore have very good wash-fastness.
- As their name implies, the neutral dyeing acid **dyes are applied at a pH close to neutral** (C.I. Dyeing method #1, pH of dye-bath: 5.5-7). They **are not very soluble in water, exhibit a high substantivity, and therefore do not migrate easily**. Because of their **poor levelling properties** the dyes are applied under controlled exhaustion. The **dye-bath temperature is raised slowly**, in particular during temperature ranges where a small change in temperature brings about a great increase in the rate of dyeing.



C.I. Acid Red 85

Properties of acid dyes

Acid Dye	Acid Leveling	Acid Milling	Neutral Dyeing
Type of Acid	strong (2-4% H_2SO_4) C.I. method #3 (pH<3.5)	weak (2-4% CH_3COOH) C.I. method #2 (pH 3.5-5.5)	ammonium salts ($(NH_4)_2SO_4$) C.I. method #1 (pH 5.5-7)
Solubility	high		low
Substantivity	low		high
Rate of Exhaustion	slow		fast
Dyeing Time	relatively short		longer time
Wet-Fastness	fair		very good
Color-range	wide range with bright colors		moderate brightness
Molecular Structure	relatively small size		larger size

Neutral dyeing acid dyes

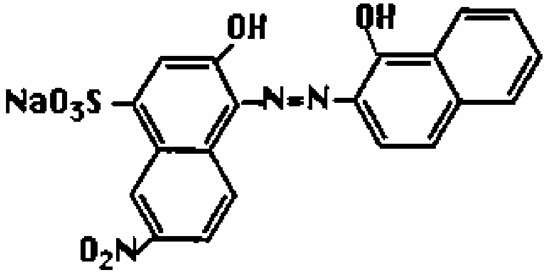
- The **addition of an acid, even a weak acid, may force these dyes to strike fast** and/or precipitate out of the dye-bath. **Therefore dyeing is performed in almost a neutral bath with the use of ammonium salts such as ammonium sulfate or ammonium acetate**. At the boil, some ammonia comes off and a small amount of acid is liberated slowly:

  $$(NH_4)_2S0_4 \Rightarrow 2NH_3 \Uparrow + H_2SO_4.$$

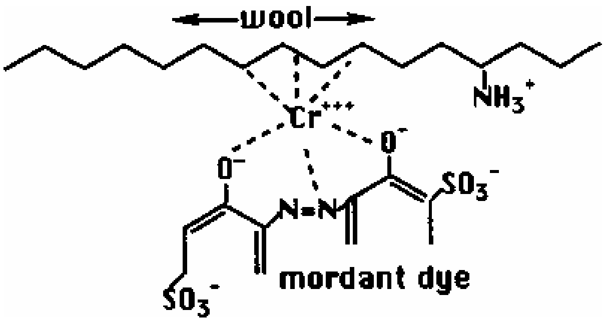
  This will provide but a small amount of acid, enough to promote proper exhaustion.
- Usually **sodium sulfate is not used with these dyes**. Being an electrolyte it may actually **increase the rate of dyeing or force these dyes to precipitate**.
- Most of the neutral dyeing acid dyes have **dull shades**. **Their larger molecules contain more chromophores, auxochromes, and conjugated double bonds,** resulting in increased absorption of visible light along the visible range of the electromagnetic spectrum.
- To overcome the effect of dulling caused by increasing molecular weight, other **dyes have been developed (e.g. Polar dyes by Ciba, and Carbolan dyes by I.C.I.) in which their molecular size is increased by saturated alkyl groups that do not affect the colour**.

Chrome dyes

- These dyes, also called mordant dyes, have been used on protein fibres where **maximum wet-fastness** is required. The chrome dyes have chemical structures similar to acid dyes, but they are capable of forming stable complexes with chromium ions (Cr^{+++}).
- The **typical feature** in this structure is the **two hydroxyl groups in ortho positions** to the azo group. Chrome dyes can be applied separately or together with a chromium salt.
- **The end result of the dyeing process is the formation of 1:1 or 2:1 chromium complexes inside the fibre**.
- Because these complexes form large molecules *in situ* within the fibres they can be difficult to remove and exhibit **good wet fastness properties.**
- The need to use chromium salts for complex formation leads to **problems of heavy metals in the effluent** from the dyeing process.



C.I. Mordant Black 11



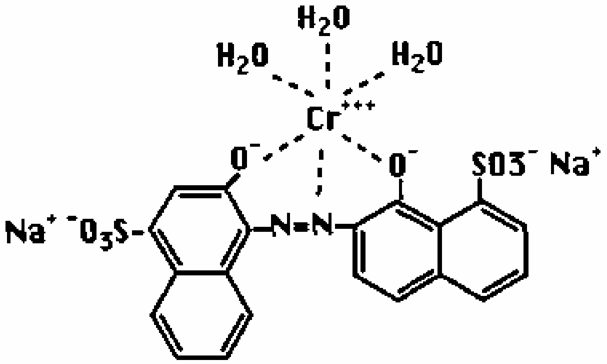
1.1 Dye-mordant-fibre complex

1:1 Premetallised dyes

These dyes usually contain a Cr^{3+} ion (some contain a cobalt ion) bonded to one dye molecule by ionic and coordinate bonds.

Though the Cr^{3+} ion carries three positive charges**, the net charge of the coloured ion is negative**. Therefore, **these dyes can behave as acid dyes**.

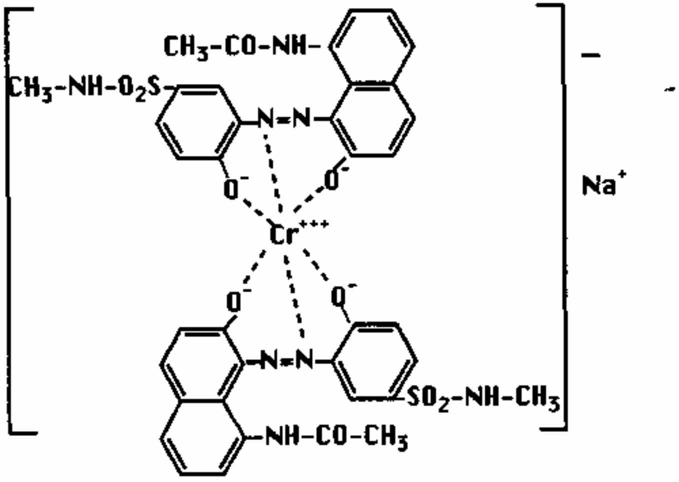
- The dyes are easy to dissolve, have good levelling properties at the boil and can be used for piece dyeing.
- The dyes bond to the fibres not only by ionic and second order bonds, as do regular acid dyes, but also by coordinate bonds through the Cr^{3+} ion. Consequently they exhibit **good wash-fastness**, the light-fastness of the dyes is also improved by the presence of the metal ion.
- The dyes are **available in a wide range of colours** of **moderate brightness**.
- Their **main disadvantage** is that they require approximately **8% of H_2SO_4** (pH 2) for exhaustion. This **strong acidity causes damage to the wool**. Therefore, fabric has to be checked in advance to see whether it is strong enough to be dyed by this method.



C.I. Acid Blue 158 (1:1 metal complex)

2:1 Premetallised dyes

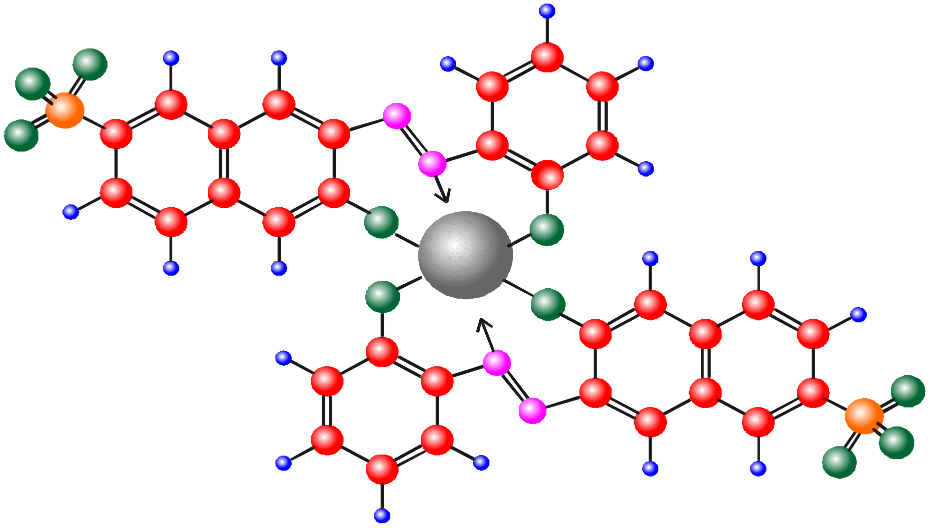
- These dyes were known for many years, but because of their high substantivity for wool could not be dyed level until special levelling agents were discovered.
- These dyes are 2:1 complexes of chromium and cobalt.
- They are solubilised with sulphone methyl groups and carry a negative charge.
- The dyes have **very good wash-fastness and light-fastness**.
- When using several different dyes in the same bath **they tend to exhaust at the same rate**, and to the same extent.
- The main disadvantages are the **lack of bright shades, and poor migration**.



C.I. Acid Black 60 (2:1 metal complex)

2:1 Premetallised dyes

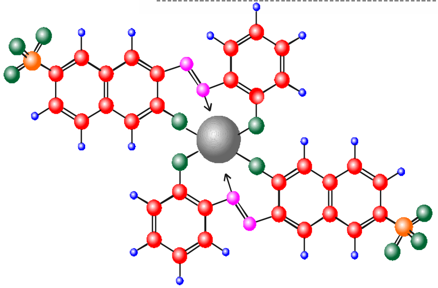
- Because of their large molecular size, these dyes behave similarly to the neutral dyeing acid dyes.
- Their application procedures are practically the same as those used for the neutral dyeing acid dyes (C.I. method #1, pH 5.5-7).



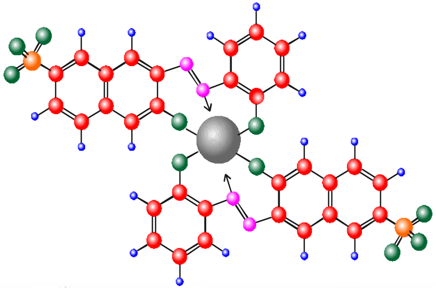
Sulphonated 2:1 metallised dyes

- Another group of acid dyes closely related to the 2:1 metallised dyes are the **sulphonated 2:1 metallised dyes**.
- These dyes, offered by several dye manufacturers (e.g. the Lanaset dyes of Ciba-Geigy and the Lanasyn S dyes of Sandoz) are made **by substitution of sulphonic acid groups on 2:1 metallised dyes**.
- The main advantage of **these dyes is that they are applied at a pH of 4.5-5**, near the iso-electric point of wool; otherwise they behave similarly to the 2:1 metallised dyes, both during application and in normal use.

The future for metal-containing dyes



- They have been very important for wool (economical).
- They are being replaced with metal-free types (particularly reactives) to reduce metal content of effluents.
- Chromium may not be as serious an environmental hazard as it has been portrayed by some.
- Current methods for reducing metals in effluent may be satisfactory.

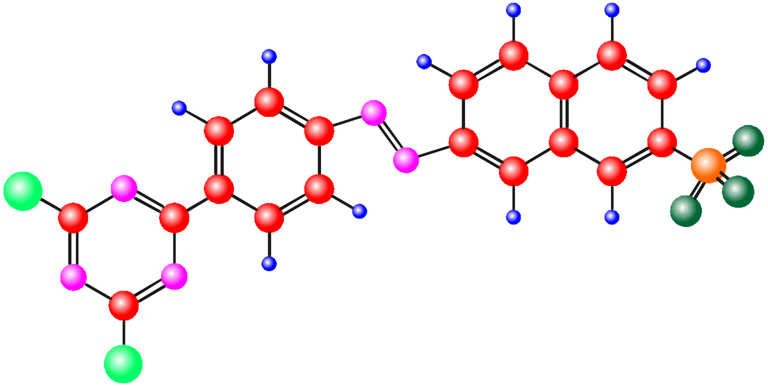


Reactive dyes

Reactive dyes link covalently to textile fibres, and in this respect differ from all other types of dye. The resultant **covalent bonds are much stronger than other binding forces**, such as electrostatic, non-polar, van der Waals and hydrogen bond interactions.

Bond type	Relative strength
Covalent	30
Ionic	7
Hydrogen	3
Van Der Waal's	1
Hydrophobic	1

Consequently, **reactive dyes produce dyeings of exceptionally good durability (fastness) to laundering and other wet treatments**. Reactive dyes are now available for **cellulosic, protein and polyamide fibre**s.



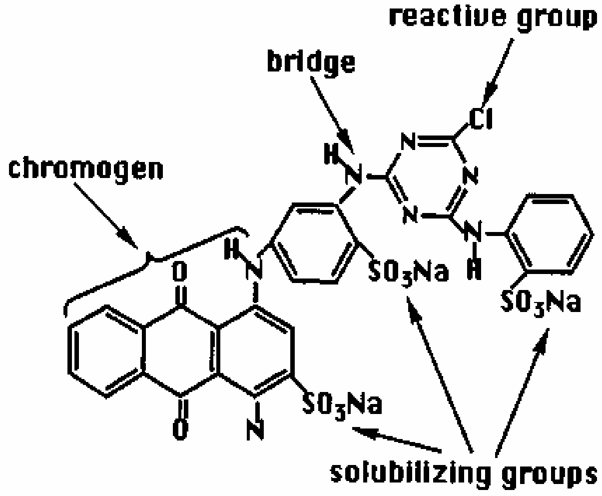
Chemical structure of a reactive dye

- The chemical structure of a reactive dye consists typically of a sulphonated acid dye of the monoazo, anthraquinonoid, 1:1 or 1:2 metal complex or phthalocyanine type, to which is attached one or more groups through which reaction with appropriate residues in the fibre can take place.
- Reactive dyes are **water-soluble anionic dyes.**
- The **reactive group is usually attached to the chromophore molecule via a bridging group:**

Chromophore — Bridging group — Reactive group

An example of a reactive dye

- The conjugated double bond system of the chromogen is discontinued at the bridge (-NH-).
- The reactive group itself, or any change that takes place at the site of the reactive group, will not have any effect on the colour of the dye. i.e the colour does not change when the dye reacts with the fibre.



C.I. Reactive Blue 5 (monochlorotriazinyl)

Characteristics of reactive dyes

- There are many variations in the types of reactive groups employed. Factors such as level of **reactivity, stability to hydrolysis, stability of the dye-fibre bond and cost and ease of manufacture all must be taken into account**.
- Because **reactive dyes can also react with water** as well as with fibres, hydrolysis is an inevitable problem in application of these dyes. Their **reaction with water is somewhat slower than with -OH groups in cellulose or with amino or thiol groups in wool**.
- The general order of reactivity is:

wool-thiol > wool-amino = polyamide amino > HO-cellulose > water

Types of reactive dyes for wool

Reactive groups in the commonly used, commercially available reactive dyes **are of two types**:

- groups that react by nucleophilic substitution reactions, and
- groups that react by the Michael addition reaction.

Nucleophilic substitution reactions

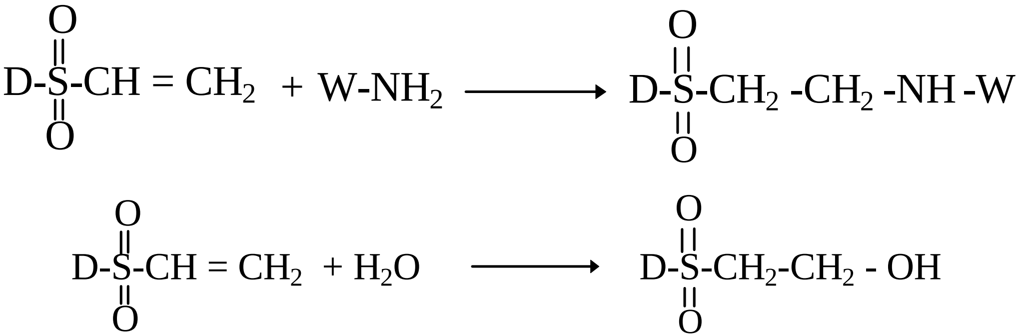
- These reactions can be best described as **the attraction of an electron-deficient carbon atom for the free lone pair of electrons on the nucleophile**.
- Usually this **reactive centre on the carbon atom is activated** by electron-withdrawing groups adjacent to it, usually $>SO_2$ or $>C=O$.
- The **reactive carbon atom is also attached to a leaving group**, usually a halogen, sulpho or quaternary nitrogen.
- **Reactive dyes with halogen groups can be considered to react with nucleophiles exclusively by this type of mechanism**. The reactive dyes that combine with wool and cotton following this reaction mechanism are Procion, Cibacron, Drimalan and Levafix E.
- Such a system may be described by the reaction of a chloroacetyl dye with free amino groups in wool (W):

$$\text{D-CO-CH}_2\text{ - Cl} \quad + \quad \text{W-NH}_2 \quad \longrightarrow \quad \text{D-CO-CH}_2\text{-NH-W} \quad + \quad \text{HCl}$$

$$\text{D-CO-CH}_2\text{ - Cl} \quad + \quad \text{H}_2\text{O} \quad \longrightarrow \quad \text{D-CO-CH}_2\text{-OH} \quad + \quad \text{HCl}$$

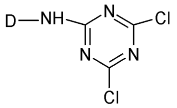
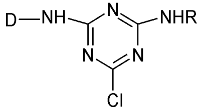
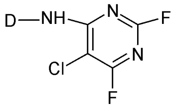
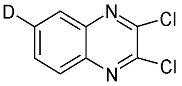
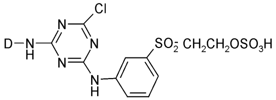
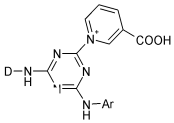
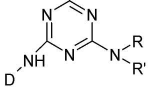
Michael addition reaction

- The general reaction of **dyes** containing polarised**, unsaturated carbon-carbon double bonds** with nucleophiles can be considered to be a 1, 2-trans-addition.
- The **double bond is activated** by the presence of an adjacent electron-withdrawing substituent such as a **carbonyl or sulphonyl** group.
- The reaction of a vinyl sulphone dye with an amino group in the wool may be represented as follows:



$$D\text{-}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}\text{-}CH = CH_2 + W\text{-}NH_2 \longrightarrow D\text{-}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}\text{-}CH_2\text{-}CH_2\text{-}NH\text{-}W$$

$$D\text{-}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}\text{-}CH = CH_2 + H_2O \longrightarrow D\text{-}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}\text{-}CH_2\text{-}CH_2\text{ - }OH$$

Structure	Reactive group	Trade name	Manufacturer	Used for
$D\text{-}SO_2CH = CH_2$	vinyl sulphone	Remazol/ Remalan	Hoechst	cellulose wool
$D\text{-}SO_2CH_2CH_2OSO_3H$	b-sulphatoethyl sulphone	Remazol/ Remalan	Hoechst	cellulose wool
$D\text{-}NHCOCH_2Cl$	chloroacetamide	Cibalan Brilliant	Ciba	wool
	dichlorotriazine	Procion MX	ICI	cellulose
	monochlorotriazine	Procion H Cibacron	ICI Ciba	cellulose cellulose
$D\text{-}NHCOCH= CH_2$	acrylamido	Procilan	ICI	wool
$D\text{-}NHCOCH(Br) = CH_2$	a-bromoacrylamido	Lanasol	Ciba	wool
$D\text{-}SO_2CH_2CH_2N(CH_3)\text{-}CH_2CH_2OSO_3H$	N-methyltaurine-ethyl sulphone	Hostalan	Hoechst	wool
	5-chloro-2,4-difluoropyrimidyl	Drimalan/ Verofix	Clariant	wool
	dichloroquinoxaline	Levafix E	Bayer	cellulose
	bifunctional	Sumifix Supra	NSK	cellulose
	bifunctional	Kayacelon React	KYK	cellulose
 modified vinyl sulphone	bifunctional	Cibacron C	Ciba	cellulose

Requirements of commercial reactive dyes

The common types of reactive dyes and their structures are summarised in the table. All reactive systems generally must satisfy the following criteria:

- **a high degree of dye-fibre covalent bonding** should be achieved at the end of the dyeing process. A clearing treatment may still be required to remove any unfixed or hydrolysed dye and give the maximum possible wet fastness
- the **rates of adsorption and diffusion are greater than the rate of reaction**; otherwise the dyeing will be uneven
- a dye that is too highly reactive will react rapidly with the fibre even at low temperatures, reducing the possibility for dye levelling or migration. Conversely, a dye that has too low a reactivity will require extended dyeing times at the boil to ensure adequate covalent bonding for optimum wet fastness.

Differences between reactive dyes for cotton and wool

- In contrast to cellulose, **dye-fibre bond stabilities in wool do not govern wet-fastness properties**. It has been shown that the rate of splitting of these bonds is much lower than the degradation of wool.
- **It is much more difficult to remove unfixed dye from wool than from cotton**. As a rule **on wool, at least 90% per cent of the dye on the fibre should be fixed by covalent bonds** if the wet-fastness properties are to be as high as possible.
- Not all cotton reactive dyes are suitable for wool because of poor substantivity and reactivity that is too high or too low. Careful selection of cotton reactive dyes is possible. Lanasol dyes contain a special type of reactive group more appropriate for wool.

Dyeing wool with reactive dyes

- While reactive dyeing of cellulosic fibres is very popular, the use of reactive dyes for **wool** has grown comparatively slowly, mainly owing to the difficulty of obtaining level dyeings and, at the same time, high levels of covalent fixation of the dye.

- Considerable **improvements** have now been achieved in the following ways:
  - use of dyes with **more than one reactive moity**
  - employment of **special levelling agents** auxiliary products
  - improved **understanding of the effect of pH and temperature** in obtaining optimised migration and reaction
  - **improvements in machinery design** and operation to promote level uptake of dye in the early stages of dyeing.

Reactive dyeing conditions for wool

- Owing to the sensitivity of wool to alkali, the reactive dyeing of wool has to be **performed in the pH range 4-6.** This is possible because many dyes react readily with **amino groups in wool even under slightly acid conditions**.
- Application methods are designed so that **diffusion precedes fixation,** by **control of the temperature and pH**. This maximises the possibility of dye reaction with the fibre and avoids wasteful hydrolysis outside the fibre.
- Dyeings on wool generally possess:
  - **good fastness to light**, typically (ISO BO1) 5-6 to 6 1/1 SD, 4-5 to 5 1/12 SD (by the manufacturer using appropriate chromophores)
  - **excellent fastness to washing**, typically (1/1 SD) 5 (ISO CO3 and ISO CO6/B2)
  - excellent fastness to **wet treatments**, eg. alkaline perspiration 5 and alkaline milling 4-5.

Batchwise dyeing of wool with reactive dyes

- Reactive dyes are usually applied to wool by **exhaustion methods at pH 4.5-6.5.** At lower pH values, dyeing may be unlevel owing to a high rate of dye uptake, while at higher pH, exhaustion is low. The particular pH employed depends on the depth of shade, being commonly in the **range pH 5.5-6 for pale depths and pH 5.0-5.5 for full depths**.
- The dyebath temperature is raised slowly and generally involves two stages:
  - **low temperature (40-70°C) exhaustion at pH 5-6**, following by,
  - **diffusion and fixation**, most commonly at 100°C.
- Some dyeing methods include **a hold period at 60-70°C** to promote even dye uptake. The period of time at the boil depends on depth of shade, deep shades necessitating longer dyeing times to achieve maximum dye-fibre fixation.

Aftertreatment of reactive dyeings

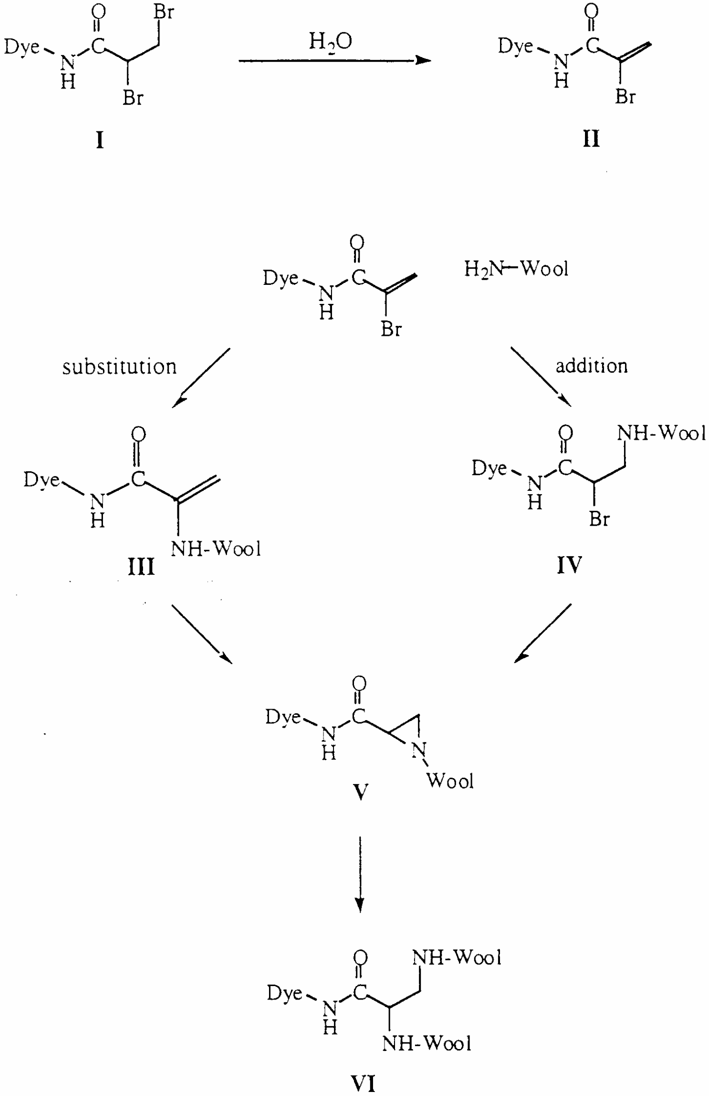
- **To develop maximum wet and washing fastness properties, dyeings often require an alkaline after-treatment**, commonly by **using ammonia or hexamine at pH 8-8.5 for 15-20 min at 80°C**, to remove unfixed and hydrolysed dye. Alternative methods of aftertreatment include the use of hexamine at the boil, which enables more efficient removal of unfixed dye at pH 6.5 with reduced fibre damage. Also sodium sulphide was found to be more effective than ammonia.
- Recent studies have demonstrated **that reactive dyes exert a fibre-protective effect** during dyeing, possibly by the blocking of the thiol/disulphide interchange reaction.

Lanasol dyes – bifunctional reactivity

Lanasol dyes (Ciba) contain chromophores with a mixture of dibromoacrylamide (I) and α-bromoacrylamide (II) reactive groups.

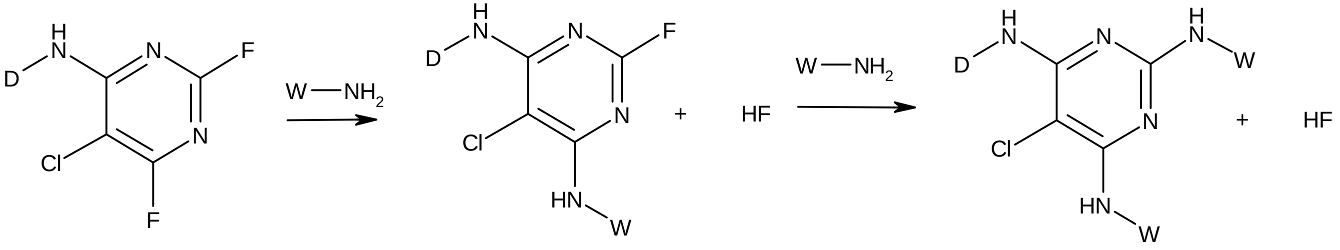
The dibromoacrylamido group hydrolyses to the α-bromoacrylamido group in the dyebath before it reacts with wool. Either an substitution reaction (III) or an addition reaction (IV) is possible with wool sulphydryl (-SH) groups (also called thiol groups) or amino groups (-NH2).

In each case, the product of the addition or substitution reaction is the same and it contains an aziridine ring (V). This product can then react with another group in wool to crosslink two wool polymer molecules (VI).



More bi-functional reactive dyes

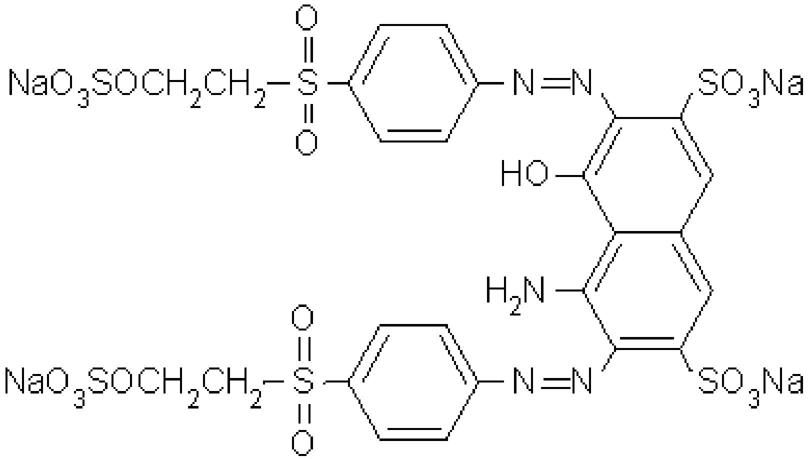
Verofix and Drimalan dyes contain the chloro difluoro pyrimidyl reactive group. The two fluorine atoms can take part in substitution reactions.



This leads to dyeings of higher fastness - even though one group may be hydrolysed, the other may still react with the fibre.

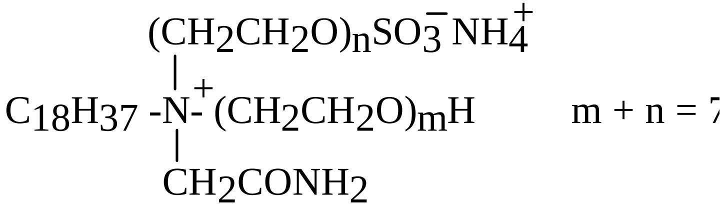
C. I. Reactive Black 5

- This dye has two reactive groups.
- The wet fastness of this dye is increased by the presence of two separate reactive groups in the molecule.
- Even though one group may be hydrolysed the other may still react with the fibre.



Auxiliary agents used for the reactive dyeing of wool

- Reactive dyes for wool would not have been commercially successful without parallel developments in auxiliary products.
- With **appropriate auxiliaries, dyeing can be less skittery**, and the concept of trichromatic mixture shade dyeing can be realised.
- All manufacturers of reactive dyes for wool offer amphoteric or weakly cationic auxiliary products that promote dye uptake at low temperatures.
- The well-known auxiliary **Albegal B** was introduced by Ciba-Geigy at the same time as the launching of the Lanasol dyes. Christoe and Datyner have assigned the structure shown below to Albegal B.



$$\begin{array}{c} (CH_2CH_2O)_nSO_3^-\,NH_4^+ \\ | \\ C_{18}H_{37}-\overset{+}{N}-(CH_2CH_2O)_mH \qquad m+n=7 \\ | \\ CH_2CONH_2 \end{array}$$

Auxiliary products for use with reactive dyes

This table lists the common auxiliaries for reactive dyeing of wool.

By promoting rapid and even dye uptake at low temperature they increase the amount of dye fixed on the wool fibre.

Range of dyes	Auxiliary product
Drimalan F (S)	Lyogen FN
Lanasol (CGY)	Albegal B
Hostalan (HOE)	Eganol GES
Verofix (BAY)	Avolan REN

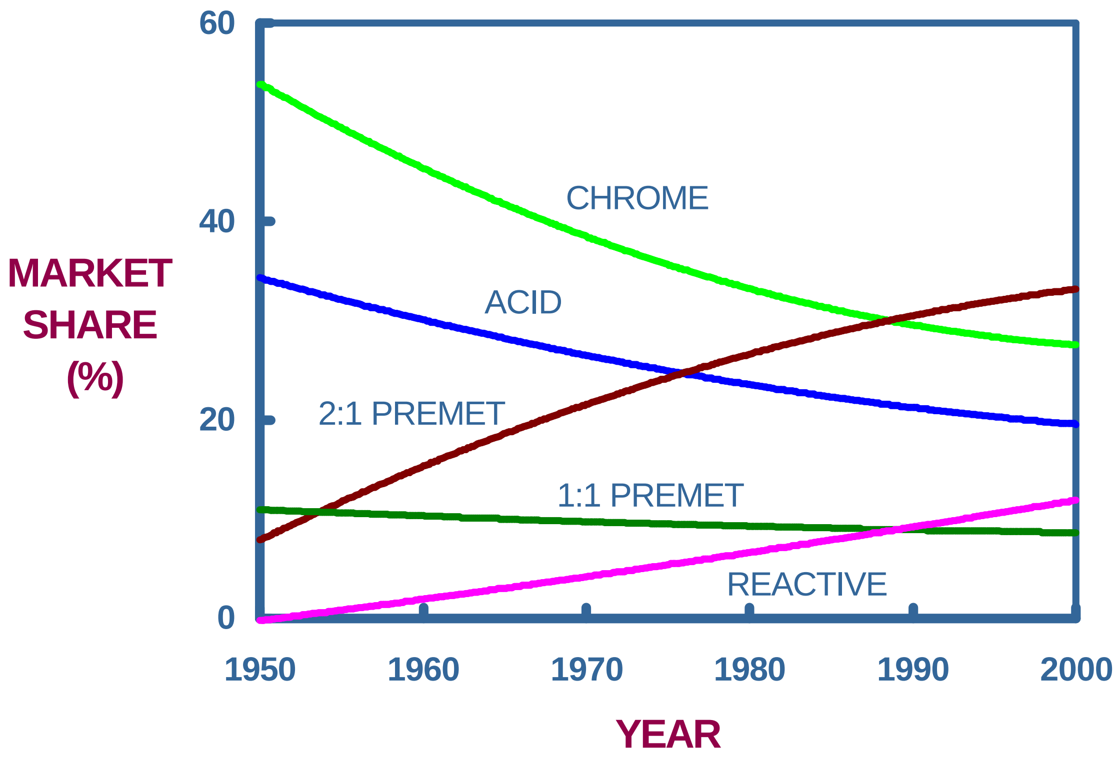
Lanaset dyes

- These are an example of the ‘systems’ approach to dyeing.
- Lanaset dyes include two entirely different classes of dye;
  - some are fibre reactive dyes and
  - others are 1:2 premetalized acid dyes.
- They all can be dyed under similar conditions, all may be intermixed freely and all have similar fastness properties.
- As far as the dyer is concerned, the chemical identity of any dyes is of little concern.
- We will see this type of methodology becoming more common in future.

Sandolan MF dyes

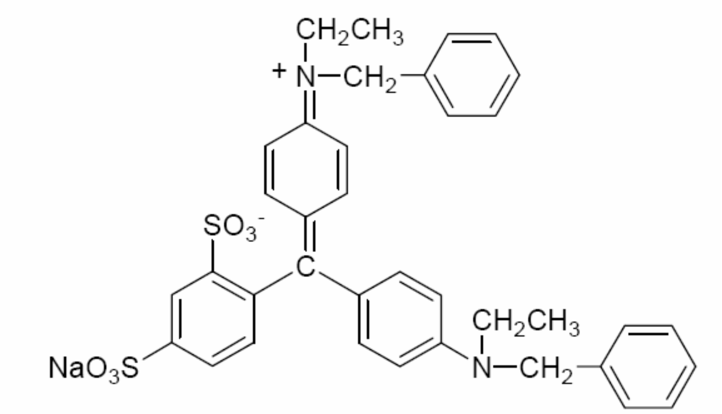
- MF stands for metal free.
- The dyes are of the milling type and are applied at pH 4-6 with minimum damage to the wool.
- The dyes have good compatibility between different members of the range for rate of dyeing and migration.
- The standard trichromatic combination recommended by Sandoz is:
    - Sandolan Golden Yellow MF-RL
    - Sandolan Red MF-2BL
    - Sandolan Blue MF-GL
- The recommended dyeing method is robust, with:
    - high exhaustion
    - good coverage of tippy wool
    - relative insensitivity to the pH and temperature of application.
- The dyes have good wet fastness suitable for carpets.
- Applicable to wool/nylon blends.

Changes in consumption of wool dyes

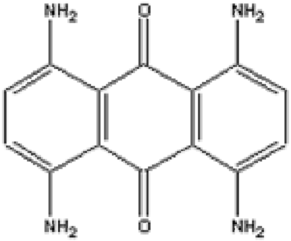


Some common types of dyes not used on wool

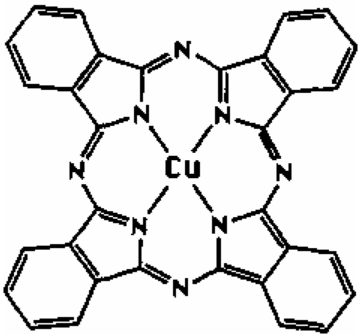
Triarylmethane
C I Acid Blue 7
poor lightfastness



Anthraquinone
C I Disperse Blue 1
low RMM



Cu-phthalocyanine,
C I Pigment Blue 15
not soluble in water



Bis-azo
C I Direct Red 81
RMM too high