



CHAPTER 5

NATURAL SPIRIT VARNISH RESINS

SHELLAC

ALTHOUGH shellac is not used in the varnish trade in such large quantities as other natural and synthetic resins it has attracted a considerable amount of interest. Much research and development work has been done.

Source.—Lac is the secretion of an insect, *Laccifer lacca*, which swarms on the twigs of special trees. A comprehensive list of host trees is given by Parry.¹

The insects extract sap from the twigs but its constitution and the nature of the process involved for the production of lac are not completely understood. Gibson² suggests that if the food for the lac insect could be produced synthetically, the insect could be cultivated under ideal conditions.

The greater part of the world's shellac supply comes from India. Assam, Burma, Indo-China and Siam supply smaller quantities. Attempts have been made to produce lac in Abyssinia. Two crops of lac are produced yearly. Climatic influences seem to alter the properties of the lac produced. In the areas west of Calcutta lac has a yellow or orange colour; in Assam it is pale red, and dark red in Siam.³ Other variations in properties may be due to the type of host tree, the time of the crop and the district, species of lac insect and method of cultivation. Shellac as used by the varnish trade may vary in properties for various reasons, including method of production and time of storage.

Production

Sticklac.—The incrustated twigs are scraped to remove the lac and this crude product is known as sticklac. The twigs may be scraped with knives, twisted by hand to remove the incrustation, or crushed in mills. Sticklac tends to become insoluble on ageing so that it is converted to seedlac rapidly. Parry⁴ notes that deterioration of sticklac may arise from the fermentation of sugars, animal debris or proteins, or from the evolution of ammonia.

Seedlac.—Seedlac is obtained from sticklac by crushing and separating the crushed product into wood splinters, dust and larger lac particles. Water-soluble impurities are removed by agitation in water, which serves also to remove dye, and the resultant product when dry becomes the seedlac of commerce. Lac is used in the form of seedlac in substantial quantities. Seedlac tends to polymerise on storage. Constancy of quality of finished shellac is achieved by blending different grades of seedlac before further processing.



Shellac.—Lac in the form of thin flakes is known as shellac. This may contain orpiment (arsenic trisulphide), the sole function of which is to mask the colour of the original shellac. It has been stated that its introduction is valueless and useless.⁵ Rosin may be added to shellac during manufacture up to 12 per cent. by weight. T.N. shellac contains up to 3 per cent of rosin.

Shellac is produced from seedlac by mixing it with rosin and/or orpiment if these adulterants are used at all, and the material transferred to calico bags and subjected to a cooking process. The filtered mass obtained, when plastic, is stretched into thin sheets from which common shellac flakes are derived.

Garnet lac.—Garnet lac is similar to shellac except that it is usually darker in colour, is free from wax, and appears on the market in thicker flakes ($\frac{1}{8}$ in.).

Button lac.—Button lac is manufactured by a similar method to that for shellac except that no stretching occurs and the molten lac is allowed to fall in small quantities on to flat surfaces.

Dewaxed Shellac.—Ordinary shellac contains about 3–5 per cent of wax. If shellac is dissolved in industrial alcohol the solution obtained is turbid, due to the wax which does not dissolve but remains in suspension. The wax may be allowed to settle or removed by filtration. Wax is removed from shellac by extraction with aromatic hydrocarbons such as benzene, toluene and xylene in the presence of water. The water is claimed to prevent polymerisation of the shellac.⁶ The wax may be precipitated from an alcoholic solution of shellac by the addition of water. The clear filtrate may be worked up for wax-free shellac. Another method is to dissolve the shellac in aqueous sodium carbonate, filter off the insoluble wax and liberate the wax-free shellac by addition of acid.

Dewaxed shellacs are obtainable by these means and yield thinner and more transparent solutions. Rosin and orpiment are absent. The advantages assigned to dewaxed shellacs over bleached shellacs are that they have better tensile strength and solubility.⁷

Bleached Shellac

Special pale grades of shellac are produced. These are known as bleached shellacs, obtained by chemical treatment, and as decolorised shellacs produced by special processes. The latter are claimed to be free from the defects of the chemically bleached product. It is further claimed that the decolorised shellacs retain all the properties of the original natural lac.

Lac is bleached by dissolving in a hot 2 per cent solution of sodium carbonate. Sodium hypochlorite is then added with constant stirring. The bleaching is a gradual process and the mixture is allowed to stand. The bleached shellac is then precipitated from solution by the addition of sulphuric acid. Excess acid is removed by washing and the plastic mass of shellac is converted into hanks. Chloride of lime and chlorine

are other bleaching agents used. Bleached shellac in the form of hanks contains a considerable amount of occluded water as well as wax. The water may amount to as much as 25–30 per cent. A so-called bone dry grade of bleached shellac is sold and this contains substantially less water, usually about 5–6 per cent.

Selection of Shellac for Bleaching.—Great care must be exercised in choosing a shellac for bleaching. The best grades of seedlac for bleaching are derived from kusum and khair lacs. Lacs from ber and palos hosts are inferior. If the sticklac used as the starting material is stored under conditions such that it tends to “block,” it is less satisfactory for subsequent bleaching.⁸ Gardner, Koprowski and Murty emphasise the importance of collecting lac for the manufacture of shellac from the tree at correct times, and the necessity for short storage. It should not be left on the host tree after the young insects have swarmed, since polymerisation may occur. When sticklac or seedlac is stored changes occur as evidenced by alterations in both physical properties and chemical constitution. Fluidity of the melted lac decreases and the solubility in boiling acetone changes also.⁹

Amount of Bleach Liquor Required.—Gardner and Harris record that the amount of bleaching liquor necessary varies with the percentage of resin insoluble in hot acetone. When the amount insoluble in acetone is 15.7 per cent, 54 per cent excess of bleaching liquor is necessary. If the amount insoluble is not more than 4.8 per cent no excess is required.¹⁰ Murty records that the nitrogen content of shellac controls the amount of sodium hypochlorite necessary. The amount of hypochlorite also varies with the colour of the initial seedlac. A preliminary washing of crude shellac with a very dilute alkali solution reduces the amount of bleach liquor required. If orpiment is present the time for bleaching is prolonged and the amount of bleach liquor increased. The presence of rosin has no material effect.¹¹ Rapid bleaching tends to induce insolubility. After the hypochlorite has been used up further prolonged contact with the alkaline solution results in the colour returning to the shellac. Hydrochloric acid splits off and the unsaturation of the shellac increases. During the bleaching process the chlorine is believed to enter the shellac partly by substitution and partly by addition.¹² If old and polymerised seedlac is used as a starting material for bleached shellac, the product is more brittle than that from fresh seedlac and may need plasticising.

Other Methods of Production.—A bleached shellac in the form of needles, originating in Belgium, has been introduced, and is said to be prepared by a spinning process. Bleaching is obtained by the use of chlorine and chlorine compounds and any shellac is stated to be suitable for conversion to needles.¹³ Contradictory reports have been recorded on its stability. Its chief advantage is that it dissolves very rapidly in alcohol, due to its fine capillary structure. It contains less than 2 per cent moisture.¹⁴



Another method of bleaching shellac electrically has been described. A solution of shellac in a sodium carbonate-sodium hydroxide-sodium chloride solution is subjected to an alternating current for eight to sixteen hours.¹⁵

Hard Lac Resin.—Another specially manufactured form of shellac which has appeared in recent years is known as hard lac resin. It is sometimes described as pure lac resin.

Its preparation is based on the fact that the soft resin constituent of shellac can be removed by fractional solvent extraction.

The soft resin is soluble in ether and can be removed by extraction. Hard lac resin is insoluble in ether and constitutes about 75–80 per cent of the original shellac.¹⁶

A works process for the manufacture of hard lac resin has been evolved by the London Shellac Research Bureau.¹⁷ The best results were obtained by solvent extraction, and the solvents studied include naphtha, benzene, toluene and trichloroethylene.

Hard lac resin may be obtained also by dissolving shellac in alcohol to which chlorinated or aromatic hydrocarbons are added. Addition of water causes the precipitation of the hard resin, leaving wax and soft resin in solution.¹⁸ Two further methods of preparation are described by Venugopalan and Sen.¹⁹ Shellac or seedlac (40 pts.) is dissolved in acetone (60 pts.), 7–8 per cent of urea, calculated on the shellac is added and the whole left until gelation occurs. This usually happens within four days. The residue from the gel after acetone extraction is polymerised hard lac resin. After depolymerisation with boiling water it is dried under vacuum. Alternatively, a solution of shellac is prepared in acetone or in an acetone-benzene mixture and stirred at a low temperature (0°–5° C.) for thirty minutes until gelation occurs. The soft resin is separated from the hard resin by squeezing through muslin. According to Bhattacharya, hard lac resin can be obtained by means of aqueous sodium pyrophosphate. Its use is claimed to be cheaper than extraction with organic solvents.²⁰

Many claims have been made in favour of hard lac resin against ordinary shellacs. Hard lac resin is said to have better water resistance, polymerises more readily under heat, has better adhesion, flexibility, gloss, durability, scratch hardness; and better compatibility with drying oils, alkyds and nitrocellulose; almost complete elimination of solvent retention, superior heat resistance and a higher melting-point. Cold hardening of hard lac resin may be accomplished by the addition of urea. Some grades of hard lac resin available on the market need special treatment to obtain a solution in alcohol. Concentration of the lac seems to be fairly critical. It is recommended that a 30 per cent solution be prepared first and this is then thinned out with further alcohol. At concentrations of less than 15 per cent lac precipitation may occur. The addition of a few per cent of white spirit to an alcoholic solution of hard lac resin is said to yield harder films on drying.



Composition of Shellac

Chemical Constitution of Components.—A chemical examination of lac reveals the following components: extraneous matter comprising twigs, wood, bark, mineral dust, sand, pieces of charcoal, insect carcases, etc., lac dye and water soluble material, wax, soft lac resin (ether soluble), and hard lac resin (ether insoluble). Karim points out that the impermeability of plastic shellac to solvents makes separation of the components difficult.²¹

Other materials present in shellac which are added subsequently include orpiment (0.2–0.5 per cent) and rosin. Gardner and others have shown shellac to be a blend of constituents. Bhattacharya states that lac resin comprises, among other constituents, hydroxy acids, and of these two have been isolated. One is a trihydroxy palmitic acid (aleuritic acid) and the other is believed to be a dihydroxy hydroaromatic dibasic acid (shellolic acid). Other unidentified unsaturated acids are also present.²²

According to Parry, shellac contains about 30 per cent of aleuritic acid, 10 per cent of shellolic acid, and the remainder consists of colouring matter, etc.²³

The chemical constitutions of the components of shellac have been investigated by the following workers: Tochirch and Farner, Harries and Nagel, Endemann, Nagel, Ulzer and Defris, Indian Lac. Res. Inst., Nagel and Mertens,^{24, 25} Bhattacharya,²⁶ and Verman.²⁷

Modifications of Shellac

Modifications of shellac have been made. Shellac is heated at 180° with 3 to 4 per cent of sulphur. The product obtained is greenish in colour. It has better adhesion, elasticity, toughness and water resistance than the original shellac.²⁸ If sulphur chloride is added to a solution of shellac in carbon tetrachloride its water resistance is reduced.²⁹

The addition of a fractional percentage of concentrated hydrochloric acid to an alcoholic solution of shellac causes appreciable modification in properties. The film obtained dries more slowly, is matt and has poor adhesion under moist conditions. Corrosion of the container also occurs.³⁰

Dry zinc oxide (10–7 pts.) and dry shellac (10–13 pts.) are heated together at 120°–280° C. to yield a compound.³¹

A large amount of work has been conducted on the modification of shellac with urea or thiourea and it is believed that chemical combination occurs. The addition of small percentages of these substances to shellac solutions promotes substantial increases in viscosity on ageing. Shellac treated with 2 to 3 per cent of these substances shows an improvement in hardness, abrasion resistance, water resistance, elasticity and adhesion. The results obtained are not so marked with thiourea as with urea. The heating of shellac with urea or thiourea improves its heat



resistance.³² Etherification of shellac can be accomplished by interaction with mono or poly alcohols, of which ethylene glycol is typical. The reaction products yield tough flexible resins on heating.³³

Gidvani and Bhattacharya have reported the formation of an ether from shellac and ethylene glycol in which only one hydroxyl group of the glycol is involved. The remaining hydroxyl groups are reacted with drying oil fatty acids. Rubbery products are obtained on heating the resultant resins at 120°–135° C.³⁴

Esters can be produced from shellac by interaction of its hydroxyl groups with acids. Three of the hydroxyl groups react more readily than the other two. Resins which air dry or stove are obtained from the esters of high molecular weight unsaturated acids. If careful control is exercised, esterification of each of the five available hydroxyl groups can be accomplished separately. Bhattacharya and Gidvani have studied the esters of shellac, derived from the following acids: acetic, caprylic, stearic, lauric, oleic, rosin and linseed oil fatty acids. The progress of esterification is followed by determinations of acid and hydroxyl values.³⁵

When shellac has been etherified with ethylene glycol, esterification of the free hydroxyl groups can be brought about by means of unsaturated acids. A range of polymerisable resins is obtained.³³ The methyl and butyl esters of shellac are used in cellulose lacquers.³⁶ Esters have been prepared from shellac and rosin in the presence of castor oil or phenol.³⁷

A reaction occurs when shellac, fatty acids and glycerol are reacted together in the presence of a catalyst. Monoglycerides are formed initially and these react subsequently with the hydroxyl groups of the shellac. Under favourable conditions the carboxyl group of shellac reacts with monoglycerides.³⁸ Shellac in its various forms has been hydrogenated at ordinary temperatures using Raney nickel as catalyst.³⁹

Valuable products are claimed from the interaction of maleic acid and an alcoholic solution of shellac if refluxed.⁴⁰

One molecule of shellac is found to absorb six molecules of sulphur dioxide. The sulphited products are said to be commercially useful.⁴¹

Shellac Substitutes

From time to time shellac substitutes have appeared, but generally they do not possess the characteristic properties which one associates with shellac. Some substitutes are on a phenol formaldehyde basis. Schreiber and Noack claim that a shellac substitute is derived from linseed oil fatty acids and soft Manila resin acids. The acids are blended, oxidised by means of potassium permanganate and heated at 150° C. to yield an alcohol soluble resin of melting-point 90° C.⁴² Harries and Nagel have recorded experiments on the synthesis of shellac.⁴³ A shellac substitute is claimed by adding sodium carbonate in quantity just less than that necessary to neutralise the free acidity of Pontianac



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gum, dissolved in a solvent comprising equal parts of alcohol and toluene. A similar method is described whereby an alkali or alkaline earth compound with basic properties is added to a solution of Pontianac or soft Manila in a mixed solvent of ethyl alcohol and toluene. To 250 parts of resin, less than eight parts of alkaline compound are added.⁴⁴ Another shellac substitute is claimed in a fused blend of equal parts of rosin and accroides.⁴⁵

Analysis and Testing

The analysis and testing of shellac is important. From the varnish makers' point of view the following tests are necessary:—

Colour.—Colour of shellac should be determined by dissolving the shellac in industrial alcohol and comparing the colour of the solution obtained with that of a standard sample prepared similarly, or by filtering the solution to remove suspended matter. The clear filtrate obtained may be compared with a range of colour standards consisting of solutions of iodine in potassium iodide. Zoellner suggests that colours of shellac solutions can be matched against solutions of caramel containing precipitated chalk in suspension.⁴⁶

Rosin. Qualitative and Quantitative Analysis.—Since adulteration of shellac with rosin is always a possibility in view of the marked difference in price of these resins, the detection and estimation of rosin is important. Rosin in shellac may be determined qualitatively by application of the Halphen-Hicks test, although the test is unreliable for bleached shellacs.⁴⁷ The Liebermann-Storch test also gives satisfactory results for rosin in shellacs. Another method for the detection of rosin is by means of copper acetate. Parry describes the method whereby 1 gram of shellac is dissolved in 25 c.c. alcohol. The resin is obtained in a finely divided form by pouring the alcoholic solution into a large quantity of water which causes precipitation. The precipitate is dried and shaken with petroleum ether to extract the rosin. A 1 per cent aqueous solution of copper acetate is shaken with the petroleum ether extract. The presence of rosin is indicated by the development of a green colour in the petroleum extract.⁴⁸

Rosin may be estimated quantitatively by two methods: solvent extraction and iodine value determination. Both methods are open to criticism and the results obtained should be used with caution. Shellac in its original condition or even in the form of a fine powder is relatively impervious to the action of solvents and the rosin is not easily extracted. Further, there are always complications due to the fact that the solvent used to extract the rosin tends to dissolve out the shellac wax and other substances. The shellac is obtained in a favourable condition for extraction by dissolving it in aqueous sodium carbonate solution and removing the insoluble wax by filtration. The filtrate is acidified and the shellac precipitated in a finely divided condition for subsequent extraction.



The following extraction method is due to McIlhiney⁴⁹ :—

Two grams shellac are dissolved in 20 c.c. absolute alcohol by warming. After cooling, 200 c.c. of petroleum ether are added and the mixture vigorously shaken. 100 c.c. of water are added and the mixture again shaken. The mixture is filtered through 120 mesh wire gauze into a separating funnel. The petroleum extract is separated and washed once with 20 c.c. dilute alcohol (1 part alcohol, 5 parts water). The clear filtrate of the petroleum extract contains wax and rosin.

The rosin is removed by extraction with 25 c.c. N/5 alcoholic caustic soda. The lower layer is run into an evaporating basin.

A blank is prepared by titrating 25 c.c. N/5 alcoholic caustic soda with N/10 hydrochloric acid. The mixed solution is evaporated to constant weight. The alcoholic caustic soda solution containing rosin is titrated similarly with hydrochloric acid using phenol phthalein as indicator. The amount necessary for neutrality is noted and the amount of acid added is increased up to that used to neutralise 25 c.c. alcoholic caustic soda. The mixture is evaporated to constant weight as before and the difference between this weight and the blank weight gives the weight of rosin acids extracted. From the titrations and the weight of rosin extracted it is possible to deduce the acid value of the rosin acids. Since, according to McIlhiney, about 2 per cent of soluble acidic material is extracted from pure shellac and that extraction of rosin is completed only to the extent of 83 per cent, the figure obtained for the percentage of rosin present must be adjusted.

$100/83$ (per cent rosin acids — 2) = adjusted percentage of rosin. When very small percentages only of rosin are present, i.e. of the order of 2 per cent, the method has not sufficient accuracy.

The petroleum extract separated in the above method, as already indicated, contains shellac wax, together with a small percentage of soluble matter from the rosin. This is evaporated to constant weight to give the amount of wax present. A correction by deduction based on 10 per cent of the rosin present should be made for the other soluble matter present.

Rosin may be estimated also by an iodine absorption determination. The method is based on standards for the iodine absorptions of shellac and rosin and this may cause unsatisfactory results. Further, in deciding upon standards for shellac and rosin on which to base calculations, it is essential that the standards chosen are derived by the same method as that used for the actual iodine absorption determination of the shellac. To illustrate this, the iodine values for rosin and shellac based on the Wijs-Langmuir method are 228 and 18 respectively,⁵⁰ or for the Hubl method, 125 and 10 respectively. The presence of orpiment in shellac causes abnormally high iodine values. Parry and Ferguson confirm this both for Hubl or Wijs methods and state that high iodine values may lead to the erroneous conclusion of the presence of rosin.⁵¹

Solubility.—Solubility of shellac is a property which must be checked carefully since ageing produces insolubility. Shellac becomes insoluble



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in cold alcohol after two years' storage under Indian conditions.⁵² Submersion in water is claimed to regenerate solubility.

The percentage of shellac insoluble in cold 95 per cent alcohol after one hour's mechanical agitation is a good indication of the quality of the shellac. Refluxing will cause old shellac to dissolve into solution. Total impurities in shellac (dirt, etc.) may be regarded as the percentage material insoluble in boiling alcohol.

Orpiment. Qualitative and Quantitative Analysis.—If orpiment is present in shellac this may be detected qualitatively by dissolving the shellac in alcohol and allowing the solution to settle. The orpiment will settle out as a yellow precipitate. Alternatively, arsenic may be detected by the usual chemical means.

The arsenic in shellac may be determined quantitatively by a method due to Langmuir and White.⁵³ The organic matter in shellac is decomposed by boiling 2 g. with 15 g. of potassium sulphate and 50 c.c. of concentrated sulphuric acid. Arsenic sulphide is precipitated by passing hydrogen sulphide through a dilute acid solution. The precipitate is removed, dissolved in ammonium carbonate and reprecipitated by re-acidifying. Finally, it is dried and weighed.

Water Estimation.—The determination of water in shellac, especially in bleached shellac, which is liable to contain large amounts, is very important, although the best procedure to adopt constitutes a difficult problem. Shellac contains both free and combined moisture, and the difficulty is to devise a method which will give accurate results for either type of moisture. Temperatures in excess of 100° C. tend to drive off combined moisture, whilst free water is held so tenaciously that low temperatures may fail to dislodge it.⁵⁴ Conditions for moisture determination may vary from drying at ordinary temperatures by means of some dehydrating agent to drying at temperatures as high as 120° C. Probably the most satisfactory method for routine testing of bleached shellacs is to dry them in powdered form at 40° C. for a specified time, for example, for four to six hours, and to compare the result with some fixed standard obtained under the same conditions.

Assessment of Bleachability of Shellac.—Although the bleaching properties of a shellac are not the immediate concern of the varnish maker, a few notes on the subject may provide him with knowledge useful in assessing the value of a given bleached shellac. The bleachability of shellac may be obtained by determining the quantity of hypochlorite solution necessary to yield a certain standard of colour. A large shellac manufacturing concern has suggested an alternative method which is claimed to be more satisfactory in practice.⁵⁵ The time required to absorb a given amount of hypochlorite is taken as a guide to the amount of hypochlorite necessary. The shellac for test should be ground to 10 mesh gauge; very fine or very large particles must be avoided. 30 g. shellac or seedlac are dissolved at 65° C. in sixty minutes in 150 c.c. of a 2 per cent. sodium carbonate solution. The solution is



filtered through 100 mesh gauge, the insoluble material washed with water and the washings added to the filtrate. The insoluble material can be dried, if desired, to constant weight.

The filtrate is maintained at 40° C. in a water bath, with constant stirring, during the addition of the hypochlorite solution. Fifty c.c. of sodium hypochlorite solution (3 per cent. available chlorine) are added, and the time noted for complete absorption as detected by starch iodide paper. The volume of subsequent additions is controlled by the time occupied by the first absorption. The following data is given :—

<i>Time of absorption.</i>	<i>Less than 30 mins.</i>	<i>30–60 mins.</i>	<i>60–90 mins.</i>	<i>More than 90 mins.</i>
Next addition	20 c.c.	10 c.c.	5 c.c.	Nil.

The time for absorption is again noted and further additions are made on the same basis. The bleached shellac is precipitated from the cold alkaline solution by means of a slight excess of acid (10 per cent sulphuric acid). The precipitated lac is washed free from acid, dried at 40° C., and can be dissolved to yield a 10 per cent solution in alcohol from which colour can be assessed.

Langmuir ⁵⁶ has recorded that the presence of rosin in shellac increases the quantity of hypochlorite required for bleaching and yields products of inferior colour. The presence of orpiment in shellac during bleaching also necessitates the addition of extra hypochlorite, and Aldis has suggested that the shellac used should be free of this adulterant.⁵⁷

Detection.—Shellac can be detected readily in lacquers or varnishes by the characteristic smell it provides when films containing it are gently warmed. Bhattacharya and Verman have suggested its ready dispersability in sulphurous acid as a means of distinguishing it from other resins.⁵⁸ According to Thakur and Aldis a shellac having a refractive index outside the range 1.516 to 1.519 at 23° C. \pm 3° must be regarded as abnormal. Curing of shellac for three hours at 105°–110° C. causes no alteration in refractive index.⁵⁹ A method for the quantitative separation of shellac acids has been worked out by Schaeffer and Gardner.⁶⁰

Properties

Physical Constants.—Shellac has the following constants: melting-point 75°–85° C.; specific gravity 1.15–1.20; iodine value 13–17 (Wijs); and acid value 60–70.⁶¹

Solubility.—Its ready solubility in alcohol and its hardness, toughness and adhesion makes it a valuable component in quick-drying lacquers for many purposes. Shellac dissolves not only in a wide range of alcohols but also in ethyl ethers of ethylene and diethylene glycols, diethylene glycol, acetic, formic, propionic, butyric and lactic acids, diacetone alcohol, acetaldehyde, aniline and pyridine.

Shellac is insoluble or only partly soluble in most esters, or ketones, and insoluble in glycols, glycerols, aromatic and aliphatic hydrocarbons,



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carbon disulphide, turpentine and chlorinated hydrocarbons. Shellac is soluble in aqueous alkaline solutions comprising sodium borate, sodium carbonate, sodium hydroxide, mono and triethanolamine, potassium hydroxide and ammonia. Aqueous solutions of shellac can be prepared in sodium carbonate or borate solutions or in ammonia, containing 15 per cent of shellac. Although initially the solutions may be viscous, there is a tendency to lose viscosity on ageing.⁶² The alkalies react with the acids in shellac to form sodium, potassium or ammonium salts.

When wax is present in shellac this remains undissolved both in alcoholic and aqueous alkaline solutions.

Plasticisers.—The following plasticisers have been suggested for use with shellac to improve flexibility; tricresyl phosphate, triphenyl phosphate, tributyl phosphate, tritolyl phosphate, sextol phthalate, heavy pine oil, lac wax, diethyl and cyclohexyl phthalates, elemi, Venice turpentine, and castor oil. Verman and Bhattacharya recommend sextol phthalate as a very good plasticiser for shellac.⁶³ The effect of plasticisation has been studied by the same workers who have recorded these conclusions. The addition of plasticisers to films on copper increases adhesion and flexibility but reduces scratch hardness. If the films are stoved scratch hardness increases. Films on tin behave differently in that plasticisation hardly affects scratch hardness. An increase in hardness of films whether stoved or air dried is observed when the plasticiser is increased from 5 to 10 per cent. Lac wax may act as a plasticiser, and its addition improves flexibility and scratch hardness. Verman makes the interesting suggestion that the modulus of elasticity calculated from velocity of sound measurements would assist in the elucidation of plasticisation problems.

Deterioration on Storage.—Shellac should be stored under cool conditions. As indicated already long storage induces polymerisation and insolubility.

Thermosetting Properties.—When shellac is heated it melts but under prolonged heating thermosetting occurs. Thermosetting or curing is believed to be due to lactone or anhydride formation.⁶⁴ The thermosetting process can be accelerated by the addition of zinc chloride, aluminium chloride, oxalic acid, hexamine or urea, especially at lower temperatures.

Thermosetting is retarded by alkalies and solvents, or if the escape of water is prevented. Ammonia is an alkali, however, which has an accelerating effect. Ranganathan and Aldis have suggested a simple method for the determination of curing time. Molten shellac is heated at a fixed temperature until a glass rod when twisted in the mass, twists in the opposite direction when released. The time taken to assume this condition is noted. Figures given show that shellac requires 227 minutes to cure at 120° C. and only 6.5 minutes at 250° C.

Depolymerisation of Shellac.—Polymerised shellac can be depolymerised by heating with water in an autoclave at 5–20 kg. per sq. cm.



pressure for 10–120 minutes. Iodine and acid values increase on depolymerisation whilst the part insoluble in alcohol decreases from 60.6 to 0.5 per cent.⁶⁵ Two parts of polymerised shellac are soluble in three parts of phenol. Aliphatic acids such as oleic acid are also suggested as solvents.⁶⁶

The addition of 5 per cent of strong acid to a solvent provides a mixture capable of dissolving polymerised shellac.⁶⁷

Darkening of Shellac on Storage.—Shellac under certain conditions tends to darken on storage, due to interaction with the metal of the containers. This aspect has been studied by Bhattacharya and Verman, and Gardner and Levy.⁶⁸

The latter investigators demonstrated that the worst darkening occurred with tin, with iron next, and with zinc having the least effect.

The presence of oxalic acid inhibits this discoloration, and earthenware or glass jars are frequently used, instead of metal ones. Sometimes when lacquers formulated on bleached shellacs are applied to oak, darkening may occur. This is attributed by Anderson to the interaction between iron in the shellac and tannin in the wood. Oxalic acid is claimed to prevent this also.⁶⁹ Temperature is another contributory cause for the darkening of bleached shellac and the most critical range is recorded as 100°–110° F.⁴⁶

Variation of Drying Time with Age.—The drying time of bleached shellac solutions changes on ageing and this phenomenon has been studied by Zoellner. The drying time is increased more if exposed to diffused light than if stored in darkness. The presence of iron aids in the temporary maintenance of drying properties. Zoellner has devised a method of testing whereby it is possible to predict the drying time of bleached shellac solutions. The reagent used is a solution of thymol blue in aqueous potassium hydroxide. A few drops of shellac solution are added to this reagent and distinctive colours or precipitates are produced. If the precipitate is yellow this corresponds with a drying time of one hour; an ivory precipitate in a chrome yellow solution corresponds with a drying time of two to three hours; a flesh-coloured precipitate in an orange-red solution corresponds with a time of eighteen hours.⁷⁰

Change of Acidity of Bleached Shellacs on Ageing.—Solutions of bleached shellac tend to lose their acidity on ageing. The important factor appears to be time of storage, although light exerts some influence. Some free acid may be involved in reaction with the metal of the container but reduction of acidity occurs even in the absence of metal.⁷¹

Deterioration of Bleached Shellac.—Because of the comparatively rapid deterioration of bleached shellac it is used as soon as possible after manufacture. It may be stored under water to prevent deterioration and maintain solubility.

It has been established that the method of manufacture of bleached shellac controls to a substantial degree its keeping properties. Watson



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and Mulany have given a process whereby shellac is derived which is said to be stable for long periods of time without loss of alcohol solubility. A minimum amount of hypochlorite is used, e.g. one part of bleaching powder to every 6.5 parts of shellac. After precipitation of the bleached product from the alkaline solution by acidification, the excess chlorine is removed from the shellac by shaking with one part of 10 per cent sodium thiosulphate. The product is washed free of soluble matter and dried at ordinary temperatures.⁷² Murty, also, has made a comprehensive study of the factors during manufacture which influence the stability of the bleached shellac. His conclusions are not always in agreement with those of other workers, for he states that free chlorine has no effect on the keeping properties. The factors enumerated as follows are said to diminish stability on ageing: too little sodium carbonate in the initial shellac solution, treatment of the lac with mineral acids before dissolving in alkaline solution, rapid addition of hypochlorite, and absolute neutralisation to produce precipitation. Precipitation of shellac by means of an organic acid like acetic acid is preferable to the use of strong mineral acids.⁷³

Solvent Retention.—Shellac films show pronounced solvent retention properties. Lubke has reported that alcohol is present in a film of 0.1 mm. thickness, after a year. Nagel and Baumann have confirmed this tendency to alcohol retention.⁷⁴

Water Resistance.—The water resistance of shellac is not of a high order and many attempts have been made to eliminate this defect. The poor water resistance of shellac is attributed to the presence of soft lac resin or the ether soluble part of the resin. Its removal resulting in the production of hard lac resin provides a resin with improved water resistance. The absorption of water by a shellac film causes the film to whiten or bloom. Gardner and Kappenberg have studied the water absorption of shellac films with the following results. When a shellac film is exposed to a moist atmosphere it absorbs moisture rapidly at first, but then slowly loses weight until equilibrium is attained. The reduction in absorption is believed to be due to swelling of the film.⁷⁵ Indiscriminate addition of plasticiser to shellac does not necessarily improve its water resistance. In fact, according to Rangaswami and Aldis the reverse may be the case. The addition of tricresyl phosphate causes an increase in the water absorption.⁷⁶ Blooming of shellac films is prevented if they are stoved at 60°–140° C. for one to two hours.⁷⁷

Incorporation of Shellac in Drying Oils

Although shellac is used primarily in spirit varnishes, much attention has been devoted to its incorporation in drying oils. Considerable difficulty is encountered when attempts are made to dissolve shellac directly into drying oils. Temperatures of the order of 380° C. are necessary for the dissolution of shellac in linseed oil, according to Hadert, but the mix must be cooled rapidly to avoid gelling. Many solubilising



agents have been suggested to facilitate solution at lower temperatures ; they include rosin, rosin ester, tritoyl and triphenyl phosphates ; oxides and carbonates of barium and magnesium and carbonates of sodium and potassium ; stearic acid, litharge, and triacetin.⁷⁸ Pre-esterification of shellac with monoglycerides produces oil solubility.⁷⁹ A similar process can be used for solubilising accroides.

Fielder records the manufacture of varnishes by dissolving shellac in linseed oil monoglycerides. Alternatively, the shellac may be heated with a mixture of glycerol and high molecular weight unsaturated fatty acids. Fielder believes that the reactions involved include etherification, esterification and polymerisation.⁸⁰

In the experience of the author litharge is one of the best and most convenient of the solubilising agents suggested. The method of incorporation is to dissolve the litharge, previously ground finely in a little of the drying oil, in the drying oil at 240° C. with constant stirring. The temperature of the leaded oil is then maintained at 220°–240° C. and the shellac, broken small, is added in small quantities at a time with constant stirring. Overheating is avoided and as soon as the shellac has dissolved the mixture is cooled and thinned. In a varnish of this type it is an advantage to use thinners with strong solvent power. Thus a mixture of white spirit and naphtha may be used, and it is sometimes convenient to include a percentage of butyl alcohol also. Shellac-drying oil compositions show a tendency to instability on storage. Aldis has incorporated castor oil with shellac at 270° C. If glycol is present the temperature of incorporation may be reduced.⁸¹ By adding a shellac which has become insoluble in alcohol to 1½ parts of rosin at 270° C. a product is obtained which is soluble both in drying oils and aromatic hydrocarbons.⁸² Bhattacharya has discussed the subject of oil solubility of shellac fully in a recent paper.⁸³

Uses

Shellac is a raw material with valuable properties which meet the requirements of many industries. A comprehensive list of its uses would include the manufacture of french and white polishes, foil lacquers, lacquers for wood and metal, media for white road paints and anti-fouling paints, hat stiffening lacquers, cellulose lacquers, good quality sealing waxes, gramophone records, water varnishes for leather and paper, varnishes for rubber, media for mirror backing paints, adhesives and cements for wood, paper and metal ; lacquers for cans, painting compounds for oil tanks, gaskets, etc. ; sealing primers, seaming solutions for cans, glazing of confectionery, lacquers for playing cards, and lacquers for shells, fuses and detonators to many government specifications.

One of the most important consumers of shellac is the electrical industry. Shellac has good insulating properties, and is not susceptible to tracking. Pure shellacs only should be used in insulating compositions



and they should be free of orpiment and rosin. Shellacs are used in the production of moulded electrical components; in mica dust, for wire enamels, for laminated paper tubes, and for impregnating and finishing varnishes for coils, cotton and paper.

The soft lac resin produced in the manufacture of hard lac resin can be used in varnishes. This is rendered possible by condensing it with aniline and formaldehyde, phenol and formaldehyde, or with acetone and phosphoric acid.⁸⁴

A method of hot spraying of shellac has been devised.⁸⁵

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SANDARAC

Sandarac is an exudation of coniferae which occur in North and South Africa and Australia. The tree yielding sandarac is found also in North America. Other sources of the resin are Tasmania and the West Indies. North African sandarac is called Mogador sandarac. Sandarac is also known as pine resin or gum juniper. The exudation



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of the resin may be hastened by incision. The resin appears on the market in the form of drops or tears which have a pale yellow colour. It may be contaminated with dust and dirt but the resin commands a high price and normally it is almost free of dirt.

According to Balzer the resin is composed almost entirely of a mixture of two carboxylic acids, namely sandaracolic and callitrolic acids.¹ Sandarac has an acid value of 140 approximately.

Sandarac should be examined for initial colour, colour in solution, clarity of solution, viscosity of solution, and percentage of insoluble matter.

Sandarac is a harder resin than mastic and powders fairly easily. It has a characteristic smell and a melting-point of 150° C. It yields brittle films and like other spirit soluble resins, such as Manila, it needs plasticising. Barry and Dunster suggest camphor, Venice turpentine, and elemi as suitable plasticisers.²

It is soluble in alcohols, turpentine, ether, and acetone, and partly soluble in chloroform, carbon disulphide, white spirit and petroleum ether. It is insoluble in benzol and esters.

Its uses include the manufacture of paper varnishes used for labels, maps, etc.; varnishes for bookbinders, lacquers for leather and metal, blackboard varnishes and negative varnishes.

MASTIC

Mastic comes from Greece, the Grecian Islands especially Chios, North Africa and Central Asia. It is an exudation caused by incision and is available in the form of pale yellow tears.

It is a softer resin than sandarac, having a melting-point of 105° C. approximately. It has a tendency to brittleness. Its acid value is about 50-55. Mastic is said to be more durable than damar.

Mastic is soluble in turpentine, chloroform, acetone, alcohols, carbon disulphide, esters and aromatic hydrocarbons. The solubility in petroleum hydrocarbons varies with the type of resin. The solubility is given in literature as soluble, partly soluble or insoluble in petroleum hydrocarbons.

Mastic is the basic constituent of varnishes for pictures, maps and of artists' paint media.

Blends of mastic may be made with damar or sandarac.

ACCROIDES

Gum accroides is known by many different names, including acaroid resin, grass tree gum, yacca gum, black boy gum, and xanthorrhoea resin.

Two varieties of the resin are known; yellow and the red variety. The yellow variety is sometimes described as Botany Bay gum, and the red as red gum accroides.



The resin is obtained from *Xanthorrhoea Australis*, *X. hastilis*, *X. arborea*, *X. quadrangularis*, *X. Drummondii*, and *X. Preisii*. The places of origin include Australia, New South Wales, Tasmania and Kangaroo Island.

The resin is obtained as an exudation. Semi-fossilised resin is also found sometimes.

Accroides as it reaches the consumer is usually in a very dirty condition. It contains dirt and substantial quantities of wood, bark, etc. This may constitute as much as 10 per cent of the total weight of the resin.

The red resin consists chiefly of the erythroresinotannol ester of paracoumaric acid. Small amounts of paracoumaric acid and paraoxybenzaldehyde are also present.³ Yellow accroides consists chiefly of the xanthoresinotannol ester of paracoumaric acid. Free paracoumaric and cinnamic acids are present also.⁴

Apart from the difference in colour the presence of cinnamic acid distinguishes the yellow resin from the red.

Both resins are examined for percentage soluble in alcohol. It is very difficult to cleanse the solutions of extraneous matter, and the only really satisfactory way is to remove the large insoluble matter by rough straining and to pass the remainder through a centrifuge. This will not remove the very fine dirt, but the condition of the solution may be such as to permit its use for certain purposes. If more bit-free solutions are desired it is best to allow the solutions to stand and settle. The clear supernatant liquor is then removed. Attempts to filter press these solutions often result in rapid clogging of the papers.

Yellow accroides has a melting-point of 97° C. compared with 110° C. for the red resin.

The resins are soluble in alcohol, but insoluble in aliphatic and aromatic hydrocarbons. The resins are only partly soluble both in chloroform and ether. Like shellac the resins are soluble in alkali. They are not very resistant to water and darken on stoving. They have poor durability.

Accroides resins are used in yellow and red spirit stains, in which the natural colours of the resins are exploited. The red resin especially may form the basis of cheap black air-drying lacquers involving the use of black pigment or dye. Their insolubility in hydrocarbons suggests their incorporation in petrol-resisting lacquers. They may be used instead of rosin for sizing paper and for sealing wax. They are sometimes used in cheap metal lacquers.

BENZOIN

Benzoin, which has been described as a resin, gum or balsam, is not of very great importance to the spirit varnish manufacturer. Several different types of benzoin are available. Siam benzoin obtained from styrax benzoin of Siam is generally regarded as the best type. Other



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types are Palembang, Padang, Sumatra, and Penang benzoin. Sumatra benzoin, like Siam benzoin is obtained from styrax benzoin in Sumatra. Penang benzoin is believed to be obtained from styrax subdenticulata of Farther India. The origins of Palembang benzoin and Padang benzoin are uncertain.

Palembang benzoin is the next grade to Siam, with Sumatra as the inferior of these two. The constituents of benzoin have been given by Lüdy.⁵ Benzoin is an exudation obtained on incision. It is a soft resin, melting below 100° C. Siam benzoin may be obtained in the form of very pale tears or as a mixture of white and yellow resinous matter. Sumatra benzoin is a darker mixture consisting of pale and reddish-grey matter.

Benzoin resins are soluble in alcohol, but only partly soluble in hydrocarbons. They have a distinct "vanilla" smell.

Benzoin resins normally contain substantial amounts of dirt and the precise amount present should be determined in each consignment before use.

Benzoin is used in spirit varnishes to give the resulting films a pleasant aroma and it also acts as a glossy softening agent.

ELEMI

Elemi is obtained from *Icica Icicariba*, *Amyris Plumieri* and *Canarium commune*. The resin is collected in the Philippines (Manila), West and East Indies, South America, Central America and Africa. The elemi from the Philippines is known as Manila elemi; from America as Rio, Mexican, Vera Cruz or Brazilian Almessega elemi; from the East Indies as East Indian elemi, and from Africa as Luban Matti elemi.

Elemi resins may be subdivided further into two grades, soft and hard. Bulungu resin from the Belgian Congo is stated by Stock to be similar to elemi. Because of the fact that it chars on heating and by reason of its insolubility in linseed oil it is not a satisfactory varnish resin.⁶

According to Dieterich, fresh elemi is a solution of resins in an ethereal oil. Part of the resins may be in crystalline form. The crystalline deposition explains the turbidity of the resin. Phellandrene and dipentene are obtained by distilling elemi.⁷

Lieb and Mladenovic have examined the constitution of Manila elemi.⁸

The colour of elemi varies, depending on its source, from white, through golden-yellow to greyish-black. The white grades are Manila and Yucatan elemi.

The smell of elemi is characteristic and is said by some to be of a terpenic nature. Others have stated that it is reminiscent of lemons.

Its acidity varies from 1.2 to 39.4, depending upon the source of the resin.

Elemi is soluble in alcohols, ether, benzol, acetone, turpentine,



petroleum hydrocarbons, chloroform and carbon disulphide. Solubility in petroleum hydrocarbons is apt to be variable.

Elemi deteriorates on exposure.

Its most important uses are as a plasticiser for spirit varnishes and as a plasticising resin for nitrocellulose lacquers or enamels, particularly of the brushing type.

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GUM THUS

Gum thus is the oleoresin which exudes from the rosin-producing trees and which adheres to the tree and hardens. Gum thus is sometimes known as "scrape" and it contains less volatile matter (turpentine) than the original oleoresin.

Gum thus is not used to any appreciable extent in the manufacture of modern varnishes. Its chief use is in spirit varnishes where it performs the function of a plasticiser.

VENICE TURPENTINE

Source.—Venice turpentine is an exudation of the larch tree (*Pinus larix*, *Larix decidua*). The sources of Venice turpentine are the Tyrol and Piedmont although larch forests occur also in Poland.

Production.—The oleoresin is not obtained by incision but by drilling into the heart wood. It is a clear pale greenish-yellow viscous liquid.

Composition.—According to Morrell it consists of resin acids (60–64 per cent), essential oils (20–22 per cent), resenes (14–15 per cent) and other constituents (2–4 per cent).¹ Dieterich gives the constituents as caffeic acid, ferulaic acid?, abietic acid, formic acid, vanillin, ethereal oil, bitter principle and water.² Schmied gives the composition as larinolic and larinolic acids and laricoresene.³

Properties

The acid value of Venice turpentine varies from 65 to 100. Schmied gives 70 as an average figure. It is soluble in petroleum and aromatic hydrocarbons, alcohols, ether, acetone, chloroform and turpentine. By steam distillation a turpentine can be obtained from Venice turpentine which resinifies on exposure to air.

Artificial Venice turpentines have been made and consist chiefly of mixtures of rosin, rosin oil and turpentine.⁴



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Uses

The chief function of Venice turpentine is as a plasticiser in spirit and other varnishes. Venice turpentine is also used in the manufacture of sizes for fabrics, in sealing wax, in cements, and in artists' colours.

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