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LAC and cashewnut shell liquid (CNSL) are two bounties of nature indigenous to India; both of them noted for their versatility and multifarious applications. At present, about 140,000 tons of whole cashewnuts are being processed in this country annually, producing about 15,000 tons of CNSL, which is a by-product of the industry. This is exported, mainly to the U.S.A. and Japan, only a small quantity being consumed locally. Internal consumption of lac in the country also presents a similar pattern. Less than ten per cent of our annual production (of about 40,000 tons) is being consumed by the various industries here, the rest going out for export, mainly to the U.S.A., with smaller quantities to the U. K., W. Germany and the U.S.S.R. Both the materials have been the subject of extensive investigations to utilize their unique properties in the fields of surface coatings, plastics, adhesives and cements. Numerous patents and publications suggesting methods for their industrial utilisation bear testimony to their versatility. Both are covered by I.S.I. standards besides international specifications for shellac, for ensuring good and consistent quality to the consumer. Lac is sold in the form of many hand-made and machine made grades, also as dewaxed and decolourised shellacs besides bleached lacs. CNSL is available, both raw as well as 'treated' i.e. after removal of metallic impurities and sulphur compounds.

Shellac, which is one form of refined lac, but a name used synonimously for all forms of refined lac, is a solid solution of inter- and intra-esters of hydroxy carboxylic acids and is thus a very complex material, which perhaps accounts for its versatile nature. An average molecule (molecular weight about 1,000) contains about five free hydroxyls and one carboxyl, which are capable of further reaction with a number of chemicals. Cashewnut shell liquid consists chiefly of (1) cardanol (about 90%), which is formed by the thermal decarboxylation, during the roasting, of anacardic acid originally present in the shell and (ii) cardol (10%.) The former is a mixture of phenolic compounds differing only in the unsaturation of their side chains viz (i) tetrahydro-cardanol (3 pentadecyl phenol) (4%), (ii) 8 mono-olefinic (15%), 8′, 11′ diolefinic (44%) and (iii) 8′, 11′ diolefinic (44%) compound (37%). Cardol, is 5-penta deca -8′, 11′, dienyl-resorcinol.[1]

A number of processes for the conversion of CNSL into solid or semisolid resins suitable for use in the varnish and plastic industries have been worked out and patented in the U.S.A., U.K., Japan and India. The numerous uses are mainly based on the fact that (i) by polymerisation, it can be converted into solid or semisolid synthetic resins and (ii) it forms condensation products with aldehydes and certain other materials, through its phenolic hydroxyl. Both types find use in surface coatings. The processes genearlly employ mineral acids, hydrocarbon sulphates, formaldehyde, hexamine etc. as the reactants or catalysts. Besides, CNSL and its reaction products with the above chemicals also serve as plasticizers helping in copolycondensations with a large number of natural, semisynthetic or synthetic resins.

Shellac-CNSL combinations have been studied by a number of workers with a view to combine the useful features of both shellac and CNSL in surface coatings and plastics industries. These are reviewed below.

SURFACE COATINGS

Excellent water, solvent and weather resistant as well as anticorrosive compositions have been prepared. Most of these do not require elaborate plant for their manufacture, and as colour is not very important in anticorrosive coatings, they should find ready acceptance for their outstanding performance.

(1) WEATHER RESISTANT VARNISH

Varnishes with excellent weathering properties have been described by Ajmani,[2] based on shellac, rosin and CNSL. These have been prepared on the lines of lac-rosin-castor oil varnishes previously described by Bhattacharya,[3], CNSL having been used in place of castor oil to take advantage of the fact that phenolic substances exercise a solubilizing effect on polymerised shellac.

(2) ANTICORROSIVE VARNISH

A satisfactory composition for the protection of metal surfaces from corrosion by sea water has been described by Rajan Pillai and co-workers.[4] The material is prepared by cooking lac and CNSL (previously heated at 120°C for one hour at 120-130°C for 2-3 hours when a solid resinous product is obtained. This can be used as such in the molten condition or as a solution in methylated spirit.

(3) WATER AND SOLVENT RESISTANT COATINGS

Siddique et al[5] have described a composition, . obtained by interacting shellac and 18-20 per cent of its weight of CNSL, with water in an autoclave for about 1½ hours at 30-40 lbs/sq. inch pressure. The resulting plastic material is insoluble in hydrocarbon solvents and has much better water resistance than shellac. This product may be used in surface coatings as such or in solution in alcohol and the films baked at 110-150°C to obtain alcohol insolubility also.

(4) METAL LACQUERS

Shellac—CNSL varnishes have been used for tinplate lacquering as well as a protective coating on mild steel. While CNSL imparts alkali and sulphur resistance, shellac is noted for acid resistance. When one part each of shellac and ethyl ether of CNSL are heated to 315°C (600°F) and thinned with a solvent such as petroleum spirit, the material obtained is suitable, among others, as an enamels on tin plate, on which it can be baked at about 150 to 200°C (300 to 400°F) for about 30 minutes. Such coatings have good elasticity, toughness and resistance to acids and alkalies.[6]

Oil soluble compositions suitable for can lacquering, have also been prepared from CNSL, shellac, glycerine and formalin.[7]

Varnishes prepared from CNSL and shellac are usually dark; so only black, green and other dark coloured enamels are possible. Paler varnishes may be prepared by using lighter coloured shellacs and cardanol, obtained by vacuum distillation of the raw CNSL at 220-230°C under 15-20 mm. pressure.

(5) HOT-MELT COATINGS

Equally useful combination is the low temperature reaction product[8] of shellac and CNSL, which is suitable for milling on directly to fabric surfaces to produce hard, glossy, flexible and water-resistant coatings. This composition can also be milled into rubbers to enhance resistance of the latter to oils, solvents and chemicals. A recent use for a similar material is as a hot-spread water-proof dressing for hessian.[4] Gunny bags coated with this material are suitable for packing fertilizers, chemicals[9] etc. The same product can also be used for bonding paper and polythene to hessian, and for lamination of fabrics. If hydrolysed lac is used in place of shellac, the compositions[4] become compatible with bitumen.

(6) ELECTRICAL INDUSTRY

(a) *Insulating varnishes*: Shellac is well known for its electrical insulation properties, and especially for its unique non-tracking property. Its usefulness in the electrical industry, is also due to its good adhesion to most materials, as well as its resistance to hydrocarbon oil such as transformer oil. Condensation products of CNSL with aldehydes are stable against moisture, acids and alkalies and, unlike most phenol-aldehyde resins, soften at elevated temperatures even though the products were cured before by baking. Coupled with these properties is the low liberation of volatile products at high temperature. All these have led to the extensive use of CNSL in insulating varish formulations.

Shellac and CNSL further condensed with suitable proportions of formaldehyde and urea in the presence of solvents have been shown[10] to produce varnishes with very good electrical insulation properties, water resistanc, flexibility, adhesion and resistance to weak alkalies. Their poor 'aging' properties could be improved with the incorporation of linseed oil.[11]

Another composition[12] used for insulation in the electrical industry is the reaction product of equal parts of shellac and CNSL at 150°C dissolved in a mixture of butyl alcohol and toluene (1:1). This varnish is applied to bare, enamelled or braided wire by dipping, and dried at 120°C for one minute, after which, the coated wires are wound tightly into coils for transformers etc. Baking such coils at 120°C for 20 hours remelts the insulation coating which then sets into one hard, infusible solid mass.

(b) *Laminated insulators*: The reaction product between shellac and CNSL at 105-160°C described earlier,[8] can also be used as the bond for producing laminated paper tubes of good electrical insulation characteristics and resistance to water, oils and chemicals. They are suitable for use on cores of electrical transformers.

PLASTICS

Shellac and CNSL in combinations with fillers such as wood flour, saw dust, asbestos powder, cotton waste, bagasse, jute waste or the like also form the basis of good plastic moulding powders.[5, 13] The ingredients can be mixed on rolls at a temperature of 110-130°C for about 20 to 30 mins. till a continuous sheet is obtained. The powdered sheet can be com-

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CNSL also improves shellac urea formaldehyde moulding powders.[14] Partially polymerised CNSL (25% on the weight of the lac) produces all round improvement in the moulding properties of the composition, particularly water resistance. The second advantage is that the powder can be made by hot roller-mixing more easily, because the plasticity of the composition allows for a longer time of mixing on the hot rollers, than in the absence of CNSL.

CHEMICAL REACTIONS INVOLVED

Not much attention has been paid to the investigation of the chemical reactions involved during the combination of shellac with CNSL, although some study has been made of the effect of heat and chemicals on both shellac and CNSL individually.

As is well known, on heating alone at 160-300°C, with or without catalysts, CNSL changes into a resinous mass. This is accompanied by reduction in unsaturation indicating that selective polymerisation takes place presumably of the more highly unsaturated components. When condensed with formaldehyde, CNSL behaves like a typical phenol, anacardanol (cardanol) being very similar to *m*-cresol with the only difference that there is an unsaturated chain of 15 carbon atoms in the former in place of the methyl group in the latter. Incidentally, the presence of this side chain influences the properties of the reaction products imparting hydrocarbon solubility, greater elasticity etc.

In the case of shellac, thermal polymerisation has been shown to be accompanied by the elimination of water resulting in inter-esterification at a rapid rate and interetherification comparatively slower. According to Gidvani,[15] the following reactions probably occur. (i) Two carboxyl groups reacting with each other forming anhydrides (ii) A carboxyl of one molecule reacting with a hydroxyl of another forming esters or lactides (iii) Two hydroxyls reacting with each other to form ethers and (iv) a hydrogen and a hydroxyl of two adjacent carbon atoms reacting to produce an unsaturated linkage thus giving rise to some active centres of polymerisation. The part played by the carbonyl group, the presence of which has been confirmed only recently, is yet to be determined.

The rate of thermal polymerisation of shellac can be accelerated or retarded by means of various chemicals. When shellac is subjected to heat in the presence of solvents, its thermal polymerisation is considerably retarded. If sufficient solvent is present, the thermal polymerisation into the familiar rubbery product is prevented altogether, shellac in the meanwhile undergoing some (as yet undetermined) chemical change[16] which makes the product oil soluble. When shellac is heated with CNSL, the lac first goes into solution, the CNSL behaving as a solvent like any other phenol. Thereafter, perhaps, reaction sets in between the hydroxyl of the CNSL and carboxyl (and carbonyl) of shellac. In any case, when heated sufficiently long at adequate temperature (say 30 minutes at 280-300°C) the product becomes oil soluble and does not pass into the rubbery infusible stage. The influence of the side chain of the CNSL in rendering the product lipophillic cannot also be overlooked. Further studies would therefore be of considerable interest to elucidate the reactions involved in the above observations.

The chief shortcoming of CNSL resins are their dark colour and comparatively slow drying rate, probably due to the phenolic nature of the constituents. Colour cannot be improved much, but the drying properties can be enhanced by the judicious use of other resins. Shellac is one of those resins which can perform this function well.

REFERENCES

1. Paul V. J. & Yeddanapalli, L. M., *Nature*, 1954, 174, 604.
2. Ajmani G. M., *J. Sci. Ind. Res.*, 1945, 3, No. 8, 354.
3. Bhattacharya R., *Oil & Col. Trades J.*, 1939, 96, 1447.
4. Rajan Pillai & Indrajit Daw, *Paintindia*, Shellac Suppl., 1962, 12, No. 1, 24-25.
5. Siddique, Saran & Varma, Indian Pat. 41, 338/1951.
6. The Harvel Corpn., U.S. Pat. 2,264,373.
7. Kulkarni R. K., Chowdhary K. K. & Asthana S. K., *Paintindia* 1964, 14, No. 1, 108-119.
8. The Harvel Corporation, U.S. Pat. 2,269,347.
9. Bhattacharya R., Technical notes on new uses of shellac, Shellac Export Promotion Council, Calcutta-8.
10. Venugopalan M. and Sen H K., Practical Applications of Recent Lac Research, Orient Longmans, 1948, 71.
11. Indian Lac Research Institute, Annual Report, 1948-49, 15.
12. The Harvel Corpn., U.S. Patent 2,225,034.
13. Siddique, Saran & Varma, Indian Pat. 41,339/1951.
14. Indian Lac Research Institute. Annual Report, 1944-45, 4.
15. Gidwani, B. S., London Shellac Res. Bureau, Tech. Paper No. 17 (1939).
16. Aldis, R. W., Indian Lac Res. Inst., Bull. No. 12, (1933).