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Modification of Lac with Epoxy Resins

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The modification of lac with epoxy resins for improving its properties, particularly surface coating properties has been investigated. The product obtained by fusing together a 70 : 30 mixture of lac and epoxy resins for 15-20 min. at 150°C. has been found to have the best surface coating properties. It is soluble in a 45 : 55 mixture of alcohol and toluene ; baked films from it are superior to those of lac alone or a physical mixture of lac and epoxy resins. The chemical constants and infrared spectra of the fusion product indicate that the epoxy group of the resin reacts with the carboxyl group of lac, and on further curing of the product cross-linking takes place.

IN recent years, lac has been losing its commercial importance due to increasing competition from synthetics. Despite some excellent properties and versatility, the utility of lac has been limited in many fields due to its brittleness, low softening point and poor resistance to water, alkalies, etc. Several attempts have been made to modify lac to overcome these limitations. The latest technique adopted involves copolymerization with monomers or admixture with polymers, both of which have shown promise.

Epoxy resins are among the most versatile of all modern synthetics. The main commercial application of epoxy resins is in surface coatings which they owe to their outstanding chemical resistance, adhesion and toughness. For most surface coating formulations, epoxy resins are esterified with organic acids. Shellac is also acidic, containing about one free carboxyl group for every average molecule (mol. wt 1000) apart from about five hydroxyls, both of which can react with epoxies.

Some work on lac-epoxy combinations has already been reported in literature. Such products have been found useful for electrical insulation[1], and possess high resistance to alkalies and other chemicals[2]. A detailed study was, therefore, taken up to determine the optimum conditions for the modification of lac through epoxidation.

Experimental Procedure

During preliminary experiments shellac (platina) of varnishes were prepared in dioxane containing different proportions of commercial epoxy resins of different (average) molecular weights, viz. 450, 1000, 1400 and 3000, by either mixing their solutions in appropriate proportions or mixing lac and epoxy resin solids and dissolving the mixtures in the solvent, both in the cold. Films of the varnishes were prepared on glass and tin panels and their properties studied.

Effect of conventional curing agents — Small quantities of some conventional curing agents, viz. *p*-toluenesulphonic acid, phosphoric acid, benzoic acid, *m*-phenylenediamine, *n*-butylamine and tetraethylene pentamine, were added to the shellac-epoxy varnishes containing 50-90 parts of shellac and 10-50 parts of epoxy resins and the film properties of the products studied.

Effect of heat treatment — Mixtures of shellac and epoxy resins containing 50-90 parts of shellac and

10-50 parts of epoxy resins were dissolved in dioxane and boiled under reflux for different periods (1-6 hr) and their film properties studied. The non-volatiles of the varnishes refluxed for 6 hr were isolated by evaporating off the solvent and the products analysed for acid values and epoxide contents[3].

Dry fusion of lac-epoxy mixtures — The convenient range of temperature for fusion of lac is 150-70°C. At lower temperatures, the process of polymerization is very slow, whereas at higher temperatures the life of shellac is inconveniently short. Hence, as a first step, the gelation period for mixtures of shellac and epoxy resins in various proportions were determined at 150° and 170°C. The effect of partial combination was next examined. Mixtures with 50-90 parts of shellac and 10-50 parts of epoxy resins of different (average) molecular weights were fused at 150°C. for 10, 15 and 20 min. The fused products were taken out and powdered and their solubility in different solvents studied. Varnishes were prepared from the completely soluble products and their film properties studied. The physical and chemical constants of these products were also determined.

Results and Discussion

Study of the film properties of lac-epoxy varnishes led to the following conclusions: (1) As far as air-dried films are concerned, addition of epoxy resins does not produce much improvement in the properties of the films. (2) In the case of baked films, considerable improvement in respect of hardness, flexibility and resistance to alkalies, as compared to shellac, is obtained. (3) Addition of curing agents does not effect any improvement in the properties of air-dried films. During baking, however, amine accelerators reduce the curing time but the resulting films are brittle. (4) There is no appreciable difference in the film properties of the varnishes prepared by refluxing for different periods. (5) Varnishes containing 70 parts of shellac and 30 parts of epoxy resin (av. mol. wt 1000) show best performance.

It was found that there was hardly any change in epoxide contents and acid values of the varnishes obtained by refluxing for 6 hr as compared to the parent mixtures, showing thereby that there has been no appreciable reaction on refluxing. However, the improvement in the properties of the baked films of lac-epoxy mixtures indicates the possibility of modification at higher temperature.

Dry fusion of shellac-epoxy resin mixtures indicated that the gelation time of shellac first decreases with increasing proportion of epoxy resin and again goes up (Fig. 1). Minimum gelation time (25 min. at 150°C. and 14 min. at 170°C.) was recorded with a mixture containing 20 parts of epoxy resin and 80 parts of lac. There was, however, very little change in gelation time of mixtures containing up to 30 parts of epoxy resin and 70 parts of shellac. Gelation time of original shellac was found to be 35 min. at 150°C. and 23 min. at 170°C., whereas the epoxy resin alone does not gel even after 8 hr at these temperatures.

The products of fusion for 10 and 15 min. were completely soluble in dioxane, methyl ethyl ketone, alcohol-benzene (32: 68) mixture and alcohol-toluene (45: 55) mixture, whereas the product of 20 min. fusion was only partly soluble in these solvents.

From the study of the film properties of the completely soluble products it was observed that baking of the films was necessary to bring about the improvement. Optimum baking schedule was found to be 170°C. for 15 min. or 190°C. for 10 min. It was also confirmed that the epoxy resin of mol. wt 1000 is most suitable and the optimum proportion for modification is 30 parts of epoxy resin to 70 parts of lac.

Baked films (baked at 170°C. for 15 min.) of the product obtained by fusion for 15 min. were found superior to those from shellac alone or a physical mixture of shellac and epoxy in respect of gloss, scratch hardness and resistance to the action of alkalies. Scratch hardness of the films (1500-1600) was found to be much improved as compared to the parent shellac (800-900) or the physical mixture (1100-1200). The resistance of the films to the action of alkalies was also remarkably good. Films (baked) of the fused product were found unaffected even after 10 days of immersion in 20 per cent sodium carbonate solution whereas the film of pure shellac failed within 6 hr. They were also found resistant to 4 per cent sodium hydroxide solution for more than 10 hr, whereas the films obtained from the physical mixture failed within 4 hr and those of pure shellac in less than 1 hr.

It is thus clear that for bringing about maximum improvement in the film properties of shellac modified with epoxy resin, it is necessary to fuse them together at 150°C. for about 15 min.

Possible reactions involved — The physical and chemical constants of the fused products are given in Table 1.

The data presented in Table 1 show that there is a gradual fall in acid values and epoxide contents during fusion. After 10 and 15 min. of fusion the acid value of the mixture came down by 9·2 and 12·77 units respectively. Decrease in epoxide

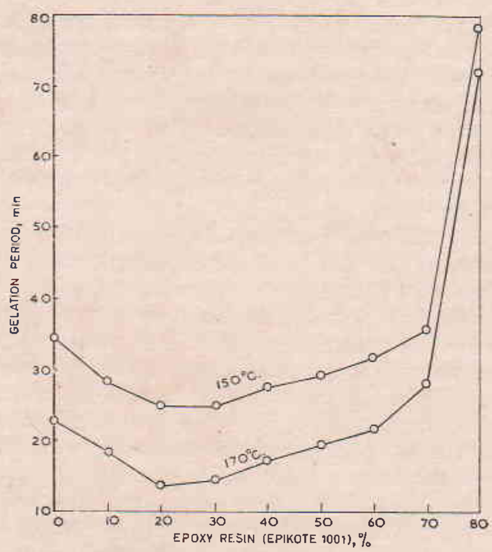


Fig. 1 — Variation in gelation time with epoxy content

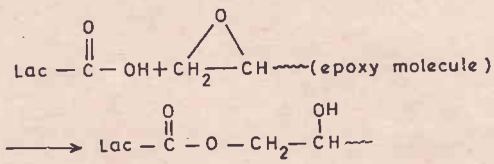
TABLE 1 — PHYSICAL AND CHEMICAL PROPERTIES OF FUSION PRODUCT OF SHELLAC AND EPOXY RESIN (EPIKOTE 1001)

(Fusion temp., 150°C.)

	Shellac	Epoxy resin	Physical mixture	Mixture fused for		
				10 min.	15 min.	20 min.
Softening point, °C.	68-70	64-65	—	74-76	85-87	96-98
Acid val.	74·5	nil	51·05	41·85	38·28	—
Epoxide equiv./100 g.	nil	0·179	0·053	0·043	0·039	—
Conversion, %*	nil	nil	nil	18·87	26·40	—
Mol. wt (Rast method)	960	1040	—	1200-1300	1400-1500	2000-2200

*Calculated on the basis of epoxide consumption.

content of these products is almost equivalent to the drop in acid values. This indicates that the reaction is between the epoxy group of the epoxy resin and the carboxyl group of lac. The reaction may be represented as

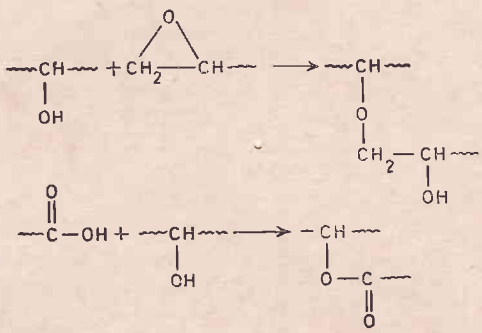


Based on epoxide consumption, it is found that of the total carboxyl present, about 26 per cent has reacted with epoxy group during the 15 min. fusion at 150°C.

The above findings were further confirmed by infrared spectra of the products. The infrared spectrum of a 70: 30 physical mixture of shellac and epoxy resin shows characteristic bands of both the resins. Prominent absorption bands for shellac are in evidence at 3500 $cm.^{-1}$ due to —OH group and at 1715-1760 $cm.^{-1}$ due to carbonyl groups[4].

Absorption bands characteristic of epoxy resin (epikote 1001) are seen at 3030, 1344, 1250, 1105, 916, 862 and 834 $cm.^{-1}$. The bands at 1250, 915 and 862 $cm.^{-1}$ have been attributed to epoxy group and the band at 3030 $cm.^{-1}$ to the methylene group[5,6].

Absorption spectrum of the product obtained by 15 min. fusion at 150°C. shows marked change in absorption at 1250, 915 and 862 $cm.^{-1}$, indicating a decrease in epoxide content, whereas the bands at 3500 and 1730 $cm.^{-1}$ show increased absorption. The increase in the 3500 $cm.^{-1}$ region indicates creation of more hydroxyl groups as expected by the reaction mentioned above. This is also supported by increase in intensity in the region 1730 $cm.^{-1}$ which indicates formation of ester groups. In the case of the product obtained by carrying out the fusion for 30 min., the intensity of most of the absorption bands is reduced to a marked extent and many of them disappear. This is possibly due to crosslinking of the molecules which incidentally makes the product insoluble. During the later stages of curing, —OH groups of shellac or nascent hydroxyls produced by the above-mentioned reaction are probably reacting with epoxy and/or with the carboxyl, thus forming a three-dimensional network as indicated below:



It is thus clear that during the fusion of lac-epoxy resin (70: 30) mixture at 150°C., the foremost reaction is between the epoxide group of the epoxy resin and the carboxyl group of lac. When fusion (or baking) is continued, crosslinking takes place resulting in insoluble and infusible products, presumably due to the reaction between the hydroxyl and carboxyl groups or between the hydroxyl and epoxy groups, or both.

References

1. FLOWERS, R. G. & HOLMBERG, G. D., *US Pat.* 2,769,739, 6 Nov. 1956; *Chem. Abstr.*, **51** (1957), 3187.
2. SRINIVASAN, S. R. & KAPUR, S. L., *Indian J. Technol.*, **2** (1964), 71.
3. BURGE (JR), R. E. & GEYER, B. P., *Analytical chemistry of polymers: High polymer series*, Vol. XII, Part I, edited by G. M. Kline (Interscience Publishers Inc., New York), 1959, 123.
4. STAIR, R. & COBLENTZ, W. W., *J. Res. nat. Bur. Stand.*, **15** (1935), 295.
5. LEE, H. & NEVILLE, K., *Epoxy resins* (McGraw-Hill Book Co. Inc., New York), 1957, 22.
6. NAKANISHI, K., *Infrared absorption spectroscopy* (Holden-Day Inc., San Francisco & Nankodo Co. Ltd, Tokyo), 1962, 155.