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Shellac allyl ether/ester

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ABSTRACT

WHEN shellac is treated with allyl alcohol in the presence of concentrated sulphuric acid, the alcohol reacts with the carbonyl, carboxyl and hydroxyls of lac. The resulting ether/ester, in alcohol or toluene solution, with 0.2 per cent cobalt, dries in the air or on baking yielding hard, glossy and elastic films, but only the baked films are water and solvent resistant. The ether/ester, in toluene solution, also cold cures in the presence of tolylene diisocyanate to yield films of improved properties.

THE discovery of Nicholas and Yanovsky¹ in 1944 that allyl ethers of carbohydrates on exposure to air form insoluble and infusible resins, gave the first industrial encouragement for using the material in coatings, adhesives and plastics and a substantial research effort has since followed in regard to the preparation and polymerisation of allyl ethers.

Shellac is a natural resin which finds considerable use in surface coatings. It possesses outstanding protective, decorative and electrical insulating properties. However, its comparative brittleness, low softening temperature and poor water resistance limit its utilisation in certain industries. Modifications of the resin of improved properties have been produced by the use of chemicals, admixture or chemical combination with other film forming materials² and graft/copolymerisation with synthetic monomers.³ Shellac is a polyfunctional material having, in an average molecule (molecular weight 1,000), about five hydroxyl groups, a little more than one carboxyl and about one third carbonyl group free. The carboxyl has been esterified with mono and polyfunctional alcohols and the hydroxyls esterified with acids and etherified by alcohol to modify its properties. Both the esters and ethers produced are sticky balsam like materials, which do not exhibit much drying properties; in fact the esters do not dry at all, whereas the ethers dry only when baked at high temperatures for long periods. It was hoped that the use of unsaturated alcohols, such as allyl-alcohol would result in more satisfactory drying and better film properties.

The desirability of introducing unsaturation into shellac molecule to facilitate its further modification into improved products had long been recognised. Venugopalan⁴ reacted lac with allyl alcohol in the presence of hydrochloric acid to produce a soft resinous ester. He also obtained a hard brittle resin by

carrying out the reaction in presence of *p*-toluene sulphonic acid as the catalyst and using a Stark and Dean separator. Both the products had identical acid values and iodine numbers, and formed films from alcoholic solution which air dried in the presence of a small quantity of benzoyl peroxide but became hard and water resistant only on baking at 70°C. Puntambekar and Venkatachalam⁵ repeated this study in the presence of hydrochloric acid. But the sticky material they obtained did not dry in the air but dried only on baking.

Despite the presence of unsaturation thus introduced in the molecule, neither of these workers used any conventional drier like cobalt to enhance the air drying nor attempted any further modification of the products with polymerisable monomers or other reactants to further improve the performance of the material. Systematic investigation was therefore taken up to study the reaction product of shellac with allyl alcohol under various conditions of treatment. Because of non-volatility and ease of handling, sulphuric acid was preferred as the catalyst for the treatment.

Experimental

Dewaxed decolourised shellac (10 g.) was dissolved in anhydrous allyl alcohol (25 ml) and varying amounts of the catalyst (1, 2, 3, 4 & 5% on the weight of shellac) were added and the product boiled under reflux for about 12 hours. The resulting solution was poured into water and unreacted allyl alcohol and catalyst washed out. The resulting resinous material was dried by heating in an open dish to 120°C or under vacuum. The dried product was soluble in the usual shellac solvents as well as in ether, aromatic hydrocarbons, ketones, esters etc. It was insoluble in aliphatic hydrocarbons.

The acid and hydroxyl values of the product were 17.7 and 136.6 respectively and the iodine values 80.6. It had no carbonyl value. The drops in acid and hydroxyl values and carbonyl number indicate the formation of ester, ether and acetal groups simultaneously. This would also account for the change in solubility characteristics.

Based on the above data, it has been calculated that 3.03 mols. of allyl alcohol have reacted with each mol. of shellac (assuming a molecular weight of 1,000 for the resin), to form the ether/ester of which 0.8932 mol. has reacted to form the ester,

0.4464 mol. the acetal, and the remaining (by calculation) 1.6904 mols. presumably the ether. Calculated indirectly, on the basis of a drop in hydroxyl value, this works out to 1.661 mols. a good agreement considering the nature of the products.

It will be noted that the previous workers did not look for the ether and acetal formations. The acid and hydroxyl values of the present product are also lower than these recorded by Puntambekar and co-worker and iodine value higher, indicating that the reaction of the lac with allyl alcohol had proceeded to a greater extent than in the present case.

As the product had residual hydroxyls which could still be etherified with allyl alcohol to introduce more unsaturation, alternate methods of treatment were tried.

First, the conditions⁶ recommended for the preparation of α -allyl glucoside by modified Fischer method were tried. Dry hydrogen chloride gas (3 g.) was dissolved in dry allyl alcohol (100 g.) and product treated with dry dewaxed decolourised shellac (50 g.) on a water bath under reflux for 8 hours. The product was then neutralised with ammonia and most of the allyl alcohol distilled off. The remaining allyl alcohol and volatile products were removed by steam distillation and, finally, the whole mass was dissolved in ether, washed with water and dried over anhydrous sodium sulphate. The residue obtained after evaporating off the ether was a sticky balsam like mass with the chemical constants A.V. 21.22, H.V. 153.5, I.V. 70-74. Obviously, this was no improvement upon the earlier product.

This product was then taken for further treatment in order to obtain complete etherification. It was dissolved in toluene and treated with the equivalent quantity plus a slight excess of metallic sodium and refluxed for five hours at 125°C. Allyl bromide, equivalent to the sodium used, was then added dropwise after which the refluxing was continued at 80°C for a further four hours. Thereafter, the toluene, excess allyl bromide etc. were removed by steam distillation and the residue dissolved in ether, the ether solution washed with water and dried and the ether distilled off. A sticky residue was obtained which had A.V. 13, H.V. 110 and I.V. 83-84. The slight improvement is, obviously, hardly worth the while.

The ether/ester obtained in the first instance using sulphuric acid as catalyst was therefore used for all further studies.

Oxygen convertibility

One of the objectives aimed at by introduction of unsaturation in the shellac modification was oxygen convertibility of the product. The ether/ester was therefore examined for this property.

The material was taken in an Ostwald viscometer

(No. G. T. 3) immersed in a thermostatically controlled glycerine bath, maintained at $100 \pm 2^\circ\text{C}$ and its viscosity determined at the end of 1, 2,..... 6 hours, bubbling a steady stream of nitrogen (freed from the last traces of oxygen by passing through alkaline pyrogallol), all the time (except during the actual viscosity determined). This was to serve as control. The experiment was repeated with another lot of the same sample bubbling oxygen in place of nitrogen at as nearly the same rate as possible. Both the experiments were repeated with fresh lots into which 0.2 per cent of cobalt (as naphthenate) had been incorporated. The data obtained are indicated graphically in Fig. 1.

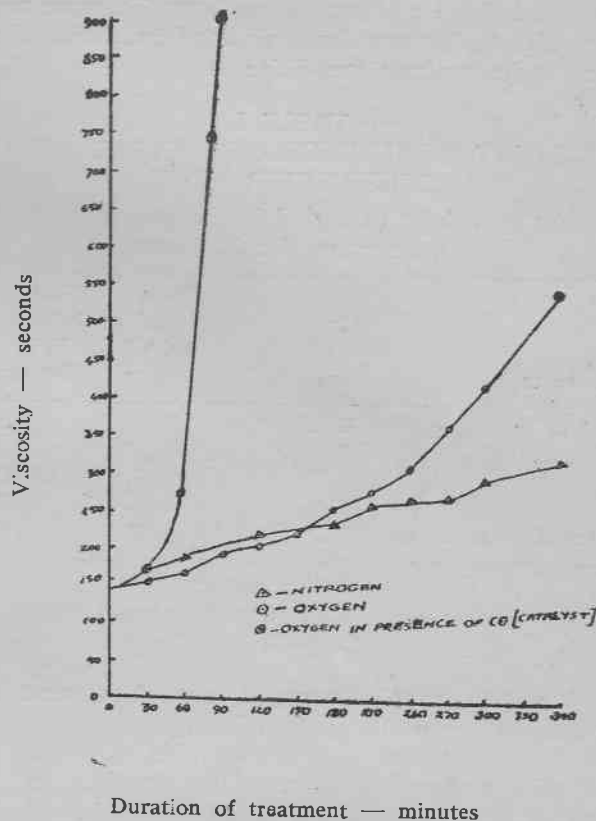


FIG. 1

It will be seen that while there is hardly any increase in viscosity (thickening) with nitrogen (there was no difference even with the presence of cobalt) there is a rapid increase when oxygen is bubbled through which is further accelerated greatly in the presence of cobalt indicating rapid oxygen conversion. In fact, the product with cobalt gelled within 75 minutes.

Film properties

As mentioned above, this ether/ester is soluble in all types of solvents except aliphatic hydrocarbons. Film properties of the material, however, were studied

only from its solutions in alcohol and toluene for obvious reasons. The films from either solvent did not air dry even after several days exposure. They did not also dry on baking under the usual schedules of 100°C for one hour or of 150°C for 30 minutes. Incorporation of cobalt, however, made the difference. With 0.2% of the metal (as naphthenate), incorporated in toluene solution, the film dried in the air overnight or when baked at the above mentioned schedules. Both the air dried and baked films were glossy, hard and elastic. However, only the baked films were water resistant. The air dried films blushed under water within 15 minutes although, even after 24 hours immersion, the films recovered completely on air drying for about half an hour. To some organic solvents, however, both air dried and baked films were quite resistant (see Table I).

TABLE I
SOLVENT RESISTANCE OF SHELLAC ALLYL
ETHER/ESTER FILMS

Films were kept immersed in the solvent at room temperature for 24 hours

Solvents	Air dried films	Films	Films
		baked at 100°C/ 1 hour	baked at 150°C/ 30 mins.
White spirit	U.A.	U.A.	U.A.
Toluene	U.A.	U.A.	U.A.
Alcohol	D.O.	S	U.A.
Ethyl acetate	U.A.	U.A.	U.A.
Methyl ethyl ketone	D.O.	S	U.A.

U.A.=Unaffected
D.O.=Dissolved out.
S=Softened

Urea⁷, as is well known, is one of the most efficient accelerators for shellac. Incorporation of as low as 3 per cent into shellac varnishes eliminates the blushing tendency completely. The possibility of urea behaving in a similar way in spirit varnishes of shellac allyl ether/ester was therefore investigated but without success. The possibility of using the ether/ester as an oxygen convertible plasticiser for shellac/urea films was also investigated but with no better results.

Pigmentation

Incorporation of pigments to a pigment volume concentration of 15 to 35 per cent into both spirit and toluene solutions of the ether/ester resulted in films of poor gloss and flexibility, whether baked or air dried.

Treatment with polyisocyanate

As mentioned already, the ether/ester has a substantial amount of residual hydroxyl groups. It was therefore considered possible that treatment with hydroxyl reactive compounds like polyisocyanates might result in improved products. Preliminary experiments have, in fact, shown that treatment with the equivalent amount of tolylene diisocyanate yields cold curing films of outstanding elasticity and resistant to heat, water, solvents and even to dilute (5 per cent) caustic alkali. If the isocyanate is added after the varnish (in toluene) is pigmented, the paints produced have all the above properties in addition to exceptional levelling and gloss. As similar performance was, however, also noticed with other alkyl esters of shellac, the matter is being studied in detail and will form the subject of a later communication.

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REFERENCES

- 1 N'chols, P.L., Jr & Yanovsky, E., *J. Am. Chem. Soc.*, **67**, (1945), 46.
- 2 Shrahan Kumar & Sankaranarayanan, Y., *Paint India*, **15**, (1965), 123.
- 3 Schmalz, M. & E. M. Hoffman. *Ger. Pat.* 1,151,381 (to Resart Gesellschaft, Kalkhof to Rose), July 11, 1963; *Chem. Abstr.*, **59** (1963), 103, 446.
- 4 Venugopalan, M., *Indian Lac Res. Inst.*, A. R. 1949-50, 17.
- 5 Puntambekar, S. V. & Venkatachalam, T. K., *Indian J. Technol.*, **6** (1963), 231-233.
- 6 Talley, E. A., Vale M. D. & Yanovsky E., *J. Am. Chem. Soc.*, **67**, (1945), 2037.
- 7 Venugopalan, M., Ranganathan, S., Aldis R. W., *Indian Lac Res. Inst.*, Research Note No. 14, 1934.