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Oil Modified Urethane Coatings from Shellac—Modification with Castor Oil

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The suitability of shellac-castor oil combinations as vehicles for urethane coating systems has been investigated. A composition containing shellac and castor oil in the ratio 55 : 45 and cured with 30 per cent tolylene diisocyanate has been found to give the best results. The films obtained were hard, glossy and flexible and possessed good resistance to water, 1·25*N* sodium hydroxide, 6*N* sulphuric acid, 95 per cent ethyl alcohol, toluene and acetone.

THE common constituents of the two-component systems of urethane coatings are a hydroxy bearing polymer and a polyisocyanate. A typical coating composition of this type is obtained by mixing the solution of an alkyd resin with the solution of a diisocyanate at the time of use. However, any polymer which contains reactive hydrogen atoms can be crosslinked by a polyisocyanate to form a polyurethane. The physical properties of the polyurethane and its suitability for a particular application depend on the chemical structures of both the components.

Shellac whose behaviour is akin to that of a polyester consists of inter- and intra-esters of polyhydroxy carboxylic acids with about five hydroxyl groups and one carboxyl group free in an average molecule. Thus it should be possible to react shellac with polyisocyanates to form a polyurethane.

Shellac reacted with 3-5 per cent tolylene diisocyanate (suprasec C) in dry acetone solution is reported to give resins with high softening and melting points[1]. Films obtained from the alcoholic solutions of these resins are claimed to possess improved hardness and blush resistance, but poor elasticity. Since the quantity of isocyanate used in this case was very much less than the theoretical requirement (52·7 per cent), it could not produce the desired effect. Another one-pack stable composition from shellac and blocked isocyanates has been reported in patent literature[2]. This composition requires oven heating at 120°C., and surprisingly it has been claimed to be suitable for use with wood.

A two-pack urethane coating composition based on shellac does not seem to have been tried so far. From practical point of view, shellac as such can hardly make a good vehicle for such a coating system because of the following drawbacks: (i) Its solubility in the common urethane solvents such as ketones, esters and hydrocarbons is poor (hydroxy solvents cannot be used since they react with isocyanates); and (ii) its reactivity number is considerably high requiring more isocyanate for complete cure, and thereby increasing the cost. Moreover, the resulting products are likely to have a high degree of crosslinking and to be obviously more brittle. Thus for using shellac as a vehicle for urethane coatings, it has to be so modified that the above drawbacks are eliminated.

Castor oil is widely used in the preparation of urethane polymers. Its incorporation in urethane coatings improves their water resistance and elasticity. Incidentally castor oil is a good plasticizer for shellac. Castor oil can be incorporated in shellac at about 250°C. using certain metallic oxides as incorporating agents. Since castor oil molecule contains on the average about 2·7 hydroxyl groups, its incorporation can be expected to lower the reactivity of shellac to the desired extent. Shellac-castor oil combinations are also likely to have high solubility in nonhydroxy solvents. The object of the present study was to examine the suitability of shellac-castor oil combinations as vehicles for the urethane coating system.

The conditions for combining shellac with oils have been investigated by different workers[3-6]. It has been reported that for combining shellac with oil it is necessary to employ certain incorporating agents. Lime and/or litharge have been reported to give satisfactory results[4]. It has also been suggested that no major change takes place in the overall structure of shellac during its incorporation in oils[5]. The authors have also observed that very little castor oil combines with shellac even when the two are heated together to 250°C. or above. Moreover, with prolonged heating, shellac gets polymerized and becomes insoluble and infusible. However, if castor oil is first heated with 4-5 per cent calcium hydroxide or sodium hydroxide at 250°C., it combines with shellac in any ratio. Therefore studies were conducted to determine the optimum ratio of shellac to castor oil so as to get a product with the desired solubility and the requisite number of reactive groups.

Experimental procedure

Castor oil was heated to 250°C. in a stainless steel beaker fitted with a mechanical stirrer and calcium hydroxide (4-5 per cent on the weight of shellac) was added to it. As soon as lime dissolved completely, shellac (dewaxed) was added by parts with speedy stirring so as to avoid overflow of the material due to frothing. The temperature was maintained at 250 ± 5°C. till a clear melt was obtained. Combinations with different shellac-castor oil ratios were made and their solubilities in ketones, hydrocarbons and esters were determined. The acid and hydroxyl values of the products were also determined.

Preparation of coating compositions — Solutions of shellac-castor oil combinations were prepared in dry methyl isobutyl ketone, butyl acetate or toluene. A solution of tolylene diisocyanate in methyl isobutyl ketone was prepared separately. Requisite amounts of tolylene diisocyanate solution, calculated on the basis of total reactivity, were added to the solutions of shellac-castor combinations and mixed thoroughly. The mixed solutions were allowed to stand at <30°C. for 10 min. Thereafter films were prepared on glass and tin panels. The films were allowed to dry in air for at least 48 hr and then subjected to the common mechanical and chemical tests.

Isocyanate requirement — The quantity of tolylene diisocyanate required for curing the coating compositions was calculated on the

Table 1 — Some chemical constants of the shellac-castor oil combinations

Composition (%)		Acid value		Hydroxyl value		Reactivity No.
Shellac	Castor oil	Calc.	Obs. (A)	Calc.	Obs. (B)	(A+B)
60	40	40·8	37·6	219·0	187·6	225·2
55	45	37·4	35·8	213·3	182·5	218·3
50	50	34·0	32·5	207·5	167·8	200·3
40	60	27·2	27·1	196·2	156·1	183·2
30	70	20·4	19·6	184·5	143·8	163·4
20	80	13·6	13·4	173·0	135·0	148·4

basis of the total reactivity of the compositions. The optimum requirement was also determined using different proportions of the isocyanate. It was found that on increasing the proportion of isocyanate, the pot life of the composition as also the gloss and elasticity of the resulting films were adversely affected. On the other hand, on lowering the quantity of isocyanate to an appreciable extent than the calculated requirement, there was some improvement in the pot life, but the hardness and the chemical resistance were poor. It was, however, considered safe to use slightly lesser quantities in order to prevent any unreacted isocyanate remaining in the coating.

Results and discussion

The solubility of the combinations in ketones, hydrocarbons and esters decreased with increase in the proportion of shellac. However, the products with shellac-castor oil ratio of up to 55 : 45 dissolved freely in methyl isobutyl ketone, toluene and butyl acetate. The observed acid and hydroxyl values of the combinations are given in Table 1. Whereas there is a close agreement between the observed and the calculated values (presuming no reaction of the carboxyl groups), there is a drop of 30-40 units in the hydroxyl values during the incorporation of shellac with castor oil. Sankaranarayanan reported a similar drop in hydroxyl values of shellac-drying oil combinations[5]. Incidentally, the lowering of the hydroxyl values is advantageous since it helps in reducing the reactivity of shellac to the desired level.

Films of compositions with shellac-castor oil ratio less than 40 : 60 remained soft even when allowed to dry in the air for 7 days. The hardness of the films increased with increase in the proportion of shellac. With shellac-castor oil ratio 60 : 40, the scratch hardness of the films was quite good (>2000 g.), but the films were very brittle. The best results were obtained when 55 parts of shellac (dewaxed) were blended with 45 parts of castor oil and the resulting composition was cured with 30 parts of tolylene diisocyanate. The films obtained from this composition were hard (scratch hardness, 1600-1700), glossy and flexible. There was no damage to the films when the

Table 2 — Surface coating properties of shellac-castor oil urethanes

Composition (%) Shellac	Composition (%) Castor oil	Calc. requirement of TDI* per 100 g. resin (shellac + castor oil) g.	TDI* added per 100 g. resin	Pot life *min.*	Scratch hardness *g.*	Elasticity (condition of the film on bending double)	Water resistance (condition of the film after 7 days' immersion)	Resistance to 5% caustic soda soln	Resistance to $6N$ sulphuric acid
40	60	28·4	28·0	180-200	800-900	Good	No blush	Failed within 2 hr	No blush
50	50	31·05	30·0	120-150	1500-1600	do	do	Film did not dissolve even after 7 days	do
55	45	33·80	33·0	60-80	1800-1900	Fine cracks	do	do	do
55	45	33·80	30·0	80-90	1600-1700	Good	do	do	do
60	40	34·90	33·0	40-50	>2000	Cracks and peeling off	do	do	do
60	40	34·90	30·0	50-60	1900-2000	Cracks	do	do	do

*TDI stands for tolylene diisocyanate.

surfaces were rubbed hard more than 50 times with cotton pads soaked in 95 per cent ethyl alcohol, acetone or toluene. The films also possessed good resistance to water, 5 per cent sodium hydroxide solution, and 6N sulphuric acid. The only drawback with this composition was a relatively poor pot life. The surface coating properties of the compositions with different shellac-castor oil ratios using the optimum quantities of tolylene diisocyanate for curing are given in Table 2.

References

1. RAO, V. S. & SANKARANARAYANAN, Y., *Res. & Ind.*, **10** (1964), 299.
2. SKEIST, I., MARTEL, R. F. & KUEBLER, W. R., *US Pat.* 3,215,551 (to Gillespie-Rogers-Pyatt Co., Inc.), 2 Nov. 1965; *Chem. Abstr.*, **64** (1966), 3844.
3. ALDIS, R. W., *Paint Mf.*, **3** (1933), 105.
4. ALDIS, R. W., *Indian Lac Research Institute Res. Note*, No. 5, 1933.
5. SANKARANARAYANAN, Y., *J. scient. ind. Res.*, **7B** (1948), 87.
6. SANKARANARAYANAN, Y., *Paintindia*, Annual Number (1952), 81.