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Oil Modified Urethane Coatings from Shellac: Part II—Compositions Based on Shellac Modified by Reaction with Alcoholysis Products of Linseed Oil and Propylene Glycol

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One of the ways of increasing the versatility of shellac in its use in surface coating compositions is through its chemical modification; a variety of modified products are already in commercial use. The present paper reports the results of a study in which shellac has been modified by reacting it with the alcoholysis products of linseed oil and propylene glycol so as to make it suitable as a vehicle for urethane coating systems. Among the various compositions tried, the one containing the various ingredients in the following proportions gave the best performance in respect of hardness, gloss, flexibility of the films obtained as well as their resistance to water, acids, alkalies and organic solvents: Shellac, 50; product of reaction between linseed oil and propylene glycol, 100; white spirit, 100; xylene, 50; toluene diisocyanate, 40; and cobalt naphthenate (6% cobalt), 0·5-1·0 parts.

THE reaction of isocyanates with compounds containing free hydroxyl groups is well known. If a diisocyanate is reacted with a polyhydroxy compound, the resulting product is polyurethane, a high molecular weight material. Polyurethanes afford hard, tough and inert finishes even without stoving.

In recent years there has been considerable interest in curing hydroxyl containing resins with isocyanates for use in surface coatings. Polyesters and polyethers with a wide range of hydroxyl group contents are most commonly used for this purpose. Attempts have also been made to react the free hydroxyl groups present in shellac with organic diisocyanates with a view to improving its surface coating properties[1-3]. The poor solubility of shellac in non-hydroxy solvents as well as its acidic character are drawbacks in formulating a satisfactory urethane coating system from this resin. However, if shellac is suitably modified, satisfactory compositions can be obtained from it by reacting with diisocyanates.

Shellac can be combined with drying or non-drying oils under suitable conditions[4,5]. The resulting products have been reported to be soluble in aromatic solvents, esters, etc. Their acid values are also low.

It was found earlier that by modifying shellac with castor oil, a product soluble in non-hydroxy solvents, such as toluene, butylacetate, methyl isobutyl ketone, etc. can be obtained. The resulting composition when cured with toluene diisocyanate produces films which are extremely hard, glossy and flexible. They also possess excellent resistance to water, chemicals and solvents. However, it suffers from the drawback of having a short pot life (2-3 hr). The suitability of lac/linseed oil/glycerol combinations as vehicles for urethane coating systems has also been investigated[6]. These compositions have also been found to give excellent film performance with relatively better pot life (4-6 hr). The short pot life of these compositions was possibly due to the higher reactivity of the systems. Investigations were, therefore, undertaken to find out if the alcoholysis products from linseed oil and propylene glycol could be used to modify lac to yield products which could subsequently be reacted with isocyanates to give satisfactory products.

Experimental procedure

Alcoholysis of linseed oil with propylene glycol — Linseed oil (alkali refined) was reacted with 10, 15 and 20% of propylene glycol in the presence of 0·5% litharge (on the weight of linseed oil). The reaction was carried out at 220-230°C in a fairly closed system with only a tubular outlet for the escape of fumes. To find out if the alcoholysis is complete, samples were taken out at intervals and diluted with ethanol. The reaction was continued as long as turbidity appeared on dilution of the sample with ethanol. It was found that the reaction was complete in 45-60 min.

Combination of shellac with the alcoholysis products of linseed oil and propylene glycol — The reaction product of linseed oil and propylene glycol was taken in a three-necked flask fitted with a thermometer and a mechanical stirrer and heated to 250°C. After the addition of shellac was complete, cooking was continued and samples were taken out at intervals to determine its solubility in white spirit.

Preparation of coating compositions — Shellac/linseed oil/propylene glycol combination was dissolved in an equal part of white spirit or a mixture of white spirit and xylene and 0·02% cobalt naphthenate was added as drier. Toluene diisocyanate was then added in different proportions and the mixtures were allowed to stand for 30 min at room temperature (25-30°C). Thereafter films were prepared on glass and tin panels and the properties studied.

Results and discussion

It was desirable to find out the minimum quantity of propylene glycol required for the alcoholysis of linseed oil which would make the product compatible with shellac. It was found that a minimum of 15% of propylene glycol (on the weight of linseed oil) should be reacted with linseed oil so as to make it compatible with shellac. The alcoholysis products obtained with 10% of propylene glycol, when cooked with 50% of shellac at 250°C gelled before they could become soluble in white spirit. A maximum of 60% of shellac could be combined with the alcoholysis products obtained from 15 to 20% of propylene glycol. The acid and hydroxyl values of these products were then determined. The results are given in Table 1. The acid and hydroxyl values of the shellac used in these experiments were found to be 70 and 268·5 respectively.

It is seen from Table 1 that the acid and hydroxyl values drop considerably during the combination of shellac with the alcoholysis products obtained from linseed oil and propylene glycol. Obviously, the reaction occurs through both carboxyl as well as the hydroxyl groups of shellac. Since the total carboxyl groups consumed during the combination is much less than the hydroxyl groups, it appears that some ether is also being formed along with the esters.

Isocyanate requirement — The theoretical requirement of isocyanate was calculated on the basis of acid and hydroxyl values

Table 1 — Acid and hydroxyl values of lac/linseed oil/propylene glycol compositions

Propylene glycol used during alcoholysis %	Shellac used parts/100 parts linseed oil/propylene glycol combination	Acid value	Hydroxy value
10	nil	7·2	123·8
15	nil	7·7	209·5
20	nil	8·4	239·3
15	50	5·4	152·6
15	60	6·8	159·4
20	50	6·2	153·5
20	60	7·6	165·3

of the shellac/linseed oil/propylene glycol compositions. The optimum requirement was also determined by adding different proportions of toluene diisocyanate to the coating compositions and testing the properties of the resulting films. It was found that the amount of isocyanate required for a satisfactory performance was a little higher than the calculated amount. Best results were obtained with —OH/—NCO ratio of 1:1·2. There could be two possible reasons for this: (1) When the coating is exposed to the atmosphere in thin films it picks up moisture very readily and consumes some isocyanate. The reactivity of an isocyanate group is approximately the same as its reactivity towards a secondary hydroxyl group; and (ii) The urethane link formed by the reaction of hydroxyl and isocyanate groups might react with another isocyanate group to form an allophanate, thereby consuming more isocyanate without further participation of hydroxyl groups. The reaction could be explained as follows:

$$R{-}NHCOOR' + R{-}NCO \rightarrow R{-}N(CONHR)COOR'$$

$$+R{-}NCO \rightarrow R{-}N(CONR(CONHR))COOR'$$

After the addition of isocyanate, the viscosity of the composition increased gradually and finally it gelled after 12-16 hr. The change in the viscosity of the composition, which was found to give the best results, has been shown in Fig. 1.

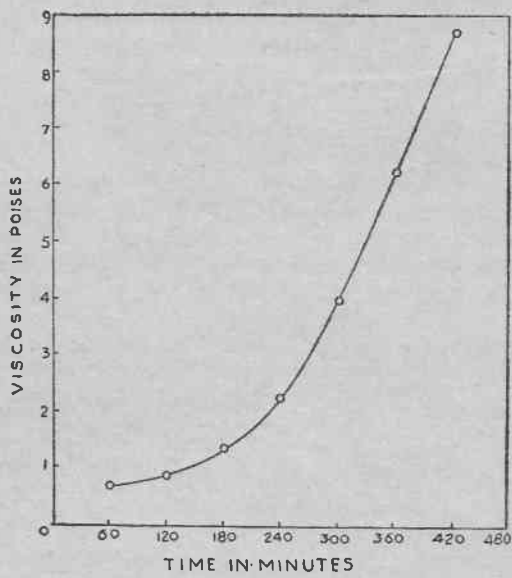

Fig. 1 — Viscosity versus time

Surface coating properties —From a comparative study of the film properties of the various compositions, the following composition was found to give the best performance:

Alcoholysis products of linseed oil with 15% propyleneglycol	100	Cooked at 250°C for 45 min
Shellac	50	
White spirit	100	
Xylene	50	
Toluene diisocyanate	40	
Cobalt naphthanate (6% cobalt)	0·5-1·00	

The above composition had a pot life of 10-12 hr. Films obtained from the composition dried in air in 2-3 hr. After one week of usual conditioning, the films were found to be highly glossy and smooth. The scratch hardness was 1800 g and there were no cracks when films were bent double. They also possessed excellent resistance to water, 5% sodium hydroxide, 20% sulphuric acid and solvents such as denatured spirit, toluene, acetone, etc.

When no isocyanate was added the films remained soft even after one week.

References

1. Rao, V. S. & Sankaranarayanan, Y., *Res. & Ind., New Delhi*, **10** (1964), 299.
2. Skeist, I., Martel, Rock, F. & Kuebler, R., *U.S. Pat.* 3,215,551, 2 Nov. 1965; *Chem. Abstr.*, **64** (1966), 3044.
3. Skeist, I., Martel, Rock, F. & Kuebler, R., *U.S. Pat.* 3,228,782; *Chem. Abstr.*, **64** (1966), 8489.
4. Aldis, R. W., *Indian Lac Research Institute, Research Note No.* 5, 1933.
5. Sankaranarayanan, Y., *Paintindia*, **2**(1) (1952), 81.
6. Mani Tripathi, S. K. & Misra, G. S., *Paintindia*, **17**(10) (1968), 7.