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# Oil modified urethane coating from sehllac

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*Suitability of shellac/linseed oil/glycerol combinations as a vehicle for urethane coating system has been investigated. The alcoholysis products of linseed oil with glycerol (i.e. mono and diglycerides and mixture thereof) have been reacted with 30-60% of shellac (on the wt. of glycerides) and the resulting compositions cured with toluene-di-isocyanate. The surface coating properties of these compositions have been studied. A composition containing 50 parts of shellac and 100 parts of glyceride mixture and cured with 25% of toluene di-isocyanate has been found to give the best properties. Films obtained from this composition were hard, glossy and flexible. They possessed good resistance to 5% sodium hydroxide, 20% sulphuric acid, 95% ethyl alcohol, acetone and toluene.*

SHELLAC, the versatile natural resin, consists of inter — and intra-esters of polyhydroxy carboxylic acids. It has approximately five hydroxyls and one carboxyl groups free in an average molecule. It is a good film forming material, but its utility in the field of surface coatings is limited due to its brittleness and poor resistance to heat, water, solvents and chemicals. Most of these defects could possibly be removed if the shellac molecule could be crosslinked by reaction of several of its functional groups with reactive materials, such as isocyanates.

Isocyanates react readily with compounds containing active hydrogen atoms such as. alcohols, amines, phenols, carboxylic acids etc. If a di-isocyanate is reacted with a polyhydroxy compound, the resulting product is a high molecular weight material, a polyurethane. Polyurethanes afford hard, tough and inert finishes even without stoving.

In recent years there has been considerable interest in the use of isocyanates for curing resins, containing free hydroxyl groups Polyesters and polyethers with a wide range of hydroxyl numbers are most commonly used for such compositions. However, any polymer which contains reactive hydrogen atoms can be crosslinked by a polyisocyanate to form a polyurethane.

## Uses

Use of isocyanates for reaction with shellac appears to be of considerable interest. It has been reported that by reacting shellac with 3.5% toluene di-isocyanate in dry acetone solution, resins with higher softening and melting points are obtained.[1] Films obtained from the alcoholic solutions of these products have been claimed to possess improved hardness and higher resistance but poor elasticity. The quantity of isocyanate used in this investigation was, however, very much less than the stoichiometric requirement (52.7%). A single pack stable composition from shellac and blocked isocyanates has been reported in the patent literature.[2] This composition has been claimed to be suitable for wood but requires heating in an oven at 120°C. In another patent, claims have been made of stable coating compositions based on anhydrous shellac and isocyanates which do not require heat curing.[3]

However, in reacting shellac with isocyanates for coating purposes there are certain practical difficulties. The main disadvantages are: solubility of shellac in common urethane solvents, e.g. esters, ketones and hydrocarbons, is poor (hydroxy solvents cannot be used since they react with isocyanates); and its functionality is relatively high with a reactivity number of about 350 which would require more isocyanate and thus make the composition uneconomical.

In our earlier work[4] we have found that these limitations could be overcome to a considerable extent by modifying shellac with castor oil and then reacting the resulting product with a di-isocyanate. This work has now been extended to shellac linseed oil combinations as vehicles for urethane coatings.

Shellac is not compatible with linseed oil under the usual conditions. However, it combines readily with the alcoholysis products of linseed oil with glycerol (i.e. mono and diglycerides and mixtures thereof). Sankaranarayanan[5] has investigated the suitable conditions for the preparation of a glyceride mixture which would be compatible with lac, using linseed oil and the minimum quantity of glycerol. He has reported that up to about 60 parts of shellac can combine with 100 parts of the above glyceride mixture.

It may be mentioned here that the earliest hydroxylated compounds to be investigated as coreactants with di-isocyanates were the alcoholysis products of drying oils and glycerol. These compositions are commonly known as "urethane oils" or "urethane alkyds". They closely resemble oil modified alkyds in formation and structure. The properties of the cured films of urethane oils are very similar to those associated with alkyd resins except that the former dry much more rapidly.

**Experimental**

**Preparation of mixed glycerides of linseed oil:** The alcoholysis reaction between linseed oil and glycerol was conducted in the manner described by Sankaranarayanan[5]. Suitable reaction conditions are given below.

| | |
|---|---|
| Linseed oil (alkali refined) | 100 parts |
| Glycerol | 20 parts |
| Litharge | 0.5 parts |
| Reaction temp. | 220°C |
| Reaction cycle | 60 mins. |

The reaction was carried out in a closed system with only a long tubular outlet for the escape of fumes. For some experiments, the product of the reaction was washed with boiling water to remove the unreacted glycerol.

**Combination of shellac with reaction product of linseed oil and glycerol:** The reaction products of linseed oil and glycerol were taken in a three-necked flask fitted with a thermometer and a stirring arrangement. It was heated in a heating mantle at 200°C. Powdered shellac was added gradually in small quantities with stirring and the temperature was gradually raised to 250°C. Samples were drawn at intervals to determine the extent of reaction. It was found that if the product gave a clear solution in nine times of its volume of white spirit the combination was almost complete.

Compositions with 30-60 parts of shellac and 100 parts of the glyceride mixture were prepared and their acid and hydroxyl values determined.

**Preparation of coatings:** The products of shellac-glyceride combination were diluted with white spirit and 0-03% cobalt (as cobalt naphthenate) was added.

The required amount of toluene di-isocyanate (Suprasec C), calculated on the basis of the total reactivity (acid and hydroxyl values) of the products, was added, and the mixture allowed to stand for 10 minutes. Thereafter films were prepared on glass and tin plates and properties studied.

**Results and discussion**

During the alcoholysis of linseed oil a certain amount of glycerol remained unreacted. It was found that only about 60% of the total glycerol was utilised in the reaction and the remaining 40% could be recovered by washing with boiling water. To find out if the presence of unreacted glycerol had any undesirable effect on the surface coating properties, different compositions with washed and unwashed glycerides were prepared and their properties compared.

The acid and hydroxyl values of the various compositions are shown in Table I. It will be seen that the acid values of the combinations are quite low indicating the esterification of free carboxylic groups of shellac. There is also considerable decrease in the hydroxyl content of the products (apart from the hydroxyls utilised for esterification). This is possibly due to the formation of ether linkages. The hydroxyl values of the compositions prepared from unwashed glycerides are higher by 60-70 units presumably due to the presence of unreacted glycerol.

In our experiments, toluene di-isocyanate was used for curing the coating compositions. The isocyanate requirement was calculated on the basis of the total reactivity of the composition i.e. the sum of the hydroxyl and the acid values. However the use of a slightly less than the stoichiometric requirement was preferred to ensure that no unreacted isocynate was retained in the coating.

It was observed that after the addition of di-isocyanate the viscosity of the coating compositions increased gradually and finally gelation occurred. The pot life decreased with increasing proportions of shellac. Compositions prepared from washed glycerides were found to have relatively better pot life.

**Film properties**

Films prepared from these com-

TABLE I
THE ACID AND HYDROXYL VALUES OF SHELLAC-LINSEED OIL GLYCEROL COMPOSITIONS

| Parts of shellac combined with 100 parts of linseed oil-glycerol combination | Compositions with unwashed glycerides | | Compositions with washed glycerides | |
|---|---|---|---|---|
| | A.V. | OH value | A.V. | OH value |
| nil | 2.10 | 268.60 | 2.96 | 191.00 |
| 30 | 3.50 | 136.50 | 3.80 | 78.50 |
| 40 | 3.70 | 149.00 | 4.10 | 89.50 |
| 50 | 5.50 | 168.20 | 6.70 | 99.60 |
| 60 | 6.40 | 169.60 | 6.90 | 102.20 |

positions were air dried in 3-4 hours. The properties were tested after one week of conditioning. Resistance to solvents was tested by applying 50 hard rubs with a cotton pad soaked in 95% ethyl alcohol, acetone & toluene. The results are summarised in Table II. Films obtained from compositions from 40-60 parts of shellac and 100 parts of unwashed glycerides were hard, glossy and flexible. The scratch hardness and resistance to water, alkali, acid and solvents increased as the proportion of shellac was increased. With lower percentage of shellac the films were soft and showed poor resistance to water and chemicals. Films obtained from a composition containing 60 parts of shellac were quite hard (scratch hardness, 2 kg) and possessed good resistance to water, 5% NaOH, 20% sulphuric acid and solvents. However, the pot life was poor. Unsuccessful attempts were also made to react more than 60% of shellac with the glyceride mixture as the product gelled during cooking of the material.

With washed glycerides, the results were not so promising. Films were glossy and flexible but were not so hard. Resistance to chemicals and solvents was also relatively poorer.

The best results were obtained with 50 parts of shellac and 100 parts of unwashed glyceride mixture cured with 25% of toluene di-isocyanate. Films obtained from this composition were hard (scratch hardness 1800-2000), glossy, flexible and resistant to water, 5% NaOH, 20% sulphuric acid, 95% ethyl alcohol, acetone and toluene.

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3 Skeist I., Martel, Rock F., & Kuebler R., U.S. Pat. Chem. Abstr., 64 (1966) 8499.

4. Mani Tripathi, S. K., Misra G. S., under publication.

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**TABLE II**

Film properties of the compositions from unwashed and washed glyceride mixtures

| Parts of shellac reacted with 100 parts of glyceride | TDI* added per 100 gm. of product | Pot life | Scratch hardness | Elasticity (condition of the film on bending double) | Water resistance (condition of the film after 7 days immersion | Resistance to 5% sodium hydroxide | Resistance to 20% sulphuric acid |
|---|---|---|---|---|---|---|---|
| | | With unwashed glycerides | | | | | |
| 30 | 20 | > 8 hours | 400-500 | good | blushes | dissolves in 3-4 hrs. | blushes in 3-4 hrs. |
| 40 | 22 | 6-7 ,, | 1300-1400 | good | good | slight blushing after 24 hrs. | good |
| 50 | 25 | 5-6 ,, | 1800-2000 | good | good | film neither blushes nor dissolves even after 10 days. | |
| 60 | 25 | 3-4 ,, | > 2000 | good | good | —do— | good |
| | | With washed glycerides | | | | | |
| 30 | 12 | > 16 ,, | 200-300 | good | blushes | dissolves within 1 hr. | blushes |
| 40 | 14 | 10-12 ,, | 400-500 | good | blushes | —do— | —do— |
| 50 | 16 | 8-10 ,, | 800-900 | good | good | dissolves in 3-4 hrs. | good |
| 60 | 16 | 4-6 ,, | 1100-1200 | good | good | —do— | good |

* TDI = Toluene di-isocyanate