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Modified Shellac-based Polyurethane Coatings

K NARASINHA RAO* & B B KHANNA
Indian Lac Research Institute, Namkum, Ranchi 834010

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Shellac-based polyurethane coatings with good flexibility and resistance to chemicals and solvents have been developed. Shellac-based polyesters were prepared by chain extension by reacting shellac with ethylene glycol or diethylene glycol and dicarboxylic acids, such as adipic, terephthalic and phthalic or maleic anhydride. These polyesters were subsequently reacted with 2,4-tolylene diisocyanate to yield modified shellac-derived polyurethane coatings. The properties of the shellac-based polyesters, such as the acid and hydroxyl numbers and of the modified shellac-derived polyurethanes, such as solubility, gelation time, flexibility, and resistance to water, hydrochloric acid and sodium hydroxide have been studied.

Shellac is considered to be a mixture of polyesters made up of various hydroxy aliphatic and sesquiterpenic acids[1]. The structure for pure lac resin has been recently proposed by Sukh Dev[2]. Shellac is prized due to its outstanding properties, such as high dielectric strength, low thermal conductivity, good adhesion on a variety of surfaces, resistance to many organic solvents, gloss, dimensional stability, easy fusibility on heating and non-toxic nature. It is used in the form of varnishes, polishes, finishes, lacquers, primers and paints. However, inspite of its having many desirable properties, shellac suffers from some inherent drawbacks, such as brittleness, low softening point, poor resistance to many solvents and chemicals and insolubility in common non-hydroxy solvents[3-5]. To overcome these drawbacks, attempts have been made to modify shellac in several ways, viz. with chemicals, synthetic resins, monomers and drying oils[6].

Urethanes are the reaction products of isocyanates with materials possessing hydroxyl groups[7,8]. The reaction is capable of being adapted to the production of polymeric compounds from which coatings, fibres, foams, elastomers and adhesives can be developed. Coatings based on polyurethanes have excellent adhesion, good flexibility, weatherability and resistance to impact, abrasion and solvent attack. Polyester-derived urethane coatings are generally superior in regard to tear strength and resistance to ageing. They can be cured at lower temperatures than those necessary for alkyds and have high gas permeability. Due to their excellent dielectric properties, these resins are suitable for use in making wire coatings and insulating materials[9].

Shellac possesses hydroxyl groups and as such can react with tolylene diisocyanate[10]. Stable coating compositions have been prepared from shellac and blocked diisocyanates[11-14]. Shellac modified with drying or non-drying oils[15-17] and shellac esters[18] have also been reacted with diisocyanates.

Shellac has also been used for preparing rigid polyurethane foams[19], textile coatings and electrical insulating varnishes[20,21].

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*Present address: Indian Agricultural Research Institute, New Delhi.

The paper describes results of a study aimed at improving the coating properties of shellac by first reacting it for chain extension with ethylene glycol or diethylene glycol and dicarboxylic acids, such as adipic, terephthalic and phthalic or maleic anhydride to yield polyesters and subsequently with 2,4-tolylene diisocyanate to prepare polyurethanes and studying their film properties.

Materials and methods

Shellac used was D.O. (dewaxed orange) obtained from Angelo Bros., Calcutta; 2,4-tolylene diisocyanate (TDI) (synthesis grade 97%) was obtained from E. Merck, Germany. Other reagents used were of L.R. grade.

Shellac-based polyesters were prepared by two methods. In the first method (one-step process), shellac, glycol and dicarboxylic acid were reacted at the same time, while in the second method (two-step process), ethylene glycol ester of shellac was prepared first and subsequently reacted with a dicarboxylic acid.

The methods of analysis adopted are available in literature[22].

Preparation of polyesters—The reaction was conducted in a three-necked flask equipped with a reflux condenser, electrical stirrer and a thermometer.

Shellac (powdered – 40 mesh), glycol and the dicarboxylic acid were heated to 120°C with constant stirring until all the shellac had dissolved. The temperature was thereafter lowered to 80°C and *p*-toluene sulphonic acid was added, after which the temperature was

Table 1—Preparation of Shellac-Based Polyesters and Their Properties

[Catalyst, 0.5 g, *p*-toluene sulphonic acid; heating period, 6-8 hr; temp., 175 ± 5°C]

Composition No.	Shellac g	Ethylene glycol ml	Diethylene glycol g	Adipic acid (one-step process) g	Adipic acid (two-step process) g	Terephthalic acid (one-step process) g	Phthalic acid (one-step process) g	Maleic anhydride (one-step process) g	Acid value	Hydroxyl value
1	100	38	—	—	—	—	—	—	32.41	208.63
2	do	do	—	—	10	—	—	—	34.01	180.22
3	do	do	—	—	15	—	—	—	42.61	—
4	do	do	—	—	25	—	—	—	57.82	—
5	do	do	—	10	—	—	—	—	19.45	170.10
6	do	do	—	15	—	—	—	—	20.18	—
7	do	do	—	20	—	—	—	—	32.68	145.50
8	do	do	—	—	—	10	—	—	27.98	—
9	do	do	—	—	—	20	—	—	41.48	—
10	do	do	—	—	—	—	10	—	43.04	185.30
11	do	do	—	—	—	—	20	—	56.63	—
12	do	do	—	—	—	—	—	10	48.14	189.34
13	do	—	54	10	—	—	—	—	28.35	—
14	do	—	do	10	—	—	—	—	28.05	—
15	do	—	do	20	—	—	—	—	47.68	—
16	do	—	do	—	—	10	—	—	30.16	—
	(Shellac D.O.)	—	—	—	—	—	—	—	72.20	264.40

gradually raised. The mixture was heated at 175 ± 5°C. Samples were withdrawn at regular intervals for the determination of the acid value. The heating was continued till the acid value was constant.

The details of the preparation of polyesters and their properties are given in Table 1.

The solubility of the polyesters prepared was determined in different solvents and mixtures of solvents with a view to finding a suitable solvent medium for treating these polyesters with diisocyanate. All the polyesters prepared with ethylene glycol were found to dissolve freely in cold methyl ethyl ketone and methyl isobutyl ketone, but none of the non-hydroxy solvents or mixture of solvents was found to completely dissolve shellac-based diethylene glycol polyesters.

Preparation of polyurethane films—For the preparation of polyurethanes, shellac-based polyesters as prepared above were dissolved in pure dry methyl ethyl ketone to make a 25% solution and reacted with 2,4-tolylene diisocyanate at room temperature. After thorough mixing and allowing to stand for 15 min, films were prepared on clean and dry glass slides and tin panels. The films thus obtained were highly glossy, hard and smooth. The gelation period was noted in each case. After allowing to stand at room temperature for one week, the films were tested for flexibility, resistance to water, 1% HCl and 1% NaOH at room temperature. A set of films on glass slides and tin panels was also baked in an oven at 150°C for 30 min and tested.

The properties of the modified shellac-derived polyurethanes are given in Table 2.

To determine the most favourable reaction conditions, polyaddition reaction of the enumerated esters with 2,4-tolylene diisocyanate was conducted with different percentages of the isocyanate.

Table 2—Properties of Modified Shellac-Based Polyurethanes

Toluene diisocyanate used on the wt of the polyester, %		COMPOSITION NO.*																							
		1		2		3		4		5		6		7		8		9		10		11		12	
		A.D. hr min	B. hr min	A.D. hr min	B. hr min	A.D. hr min	B. hr min	A.D. hr min	B. hr min	A.D. hr min	B. hr min	A.D. hr min	B. hr min	A.D. hr min	B. hr min	A.D. hr min	B. hr min	A.D. hr min	B. hr min	A.D. hr min	B. hr min	A.D. hr min	B. hr min	A.D. hr min	B. hr min
Gelation period	20	2-20	—	1-50	—	2-05	—	2-20	—	0-25	—	0-50	—	1-0	—	0-35	—	1-10	—	1-30	—	2-0	—	1-50	—
	30	1-30	—	1-20	—	1-30	—	1-40	—	0-15	—	0-30	—	0-35	—	0-20	—	0-40	—	1-0	—	1-20	—	1-20	—
Period for blush in water	20	0-20	15 (days)	24-0	NB	6-0	NB	4-0	NB	0-40	NB	0-35	NB	0-30	NB	1-40	NB	1-15	NB	0-20	NB	0-15	NB	0-35	NB
	30	0-30	20 (days)	30-0	do	7-0	do	5-0	do	0-50	do	0-45	do	0-40	do	2-0	do	1-30	do	0-30	do	0-20	do	0-50	do
Period for blush in 1% HCl	20	0-15	12 (days)	1-40	NB	1-10	NB	0-50	NB	0-30	NB	0-30	NB	0-25	NB	1-0	NB	1-10	NB	0-15	NB	0-10	NB	0-20	NB
	30	0-20	15 (days)	2-0	do	1-20	do	1-0	do	0-40	do	0-40	do	0-35	do	1-10	do	1-20	do	0-25	do	0-15	do	0-30	do
Period for blush in 1% NaOH	20	0-10	1-40	0-30	2-0	0-25	0-50	0-20	0-45	0-20	0-55	0-10	0-20	0-15	1-10	0-20	1-50	0-30	—	0-15	1-50	0-10	2-0	0-30	2-30
	30	0-15	2-0	0-40	2-10	0-35	1-0	0-30	1-0	0-25	1-10	0-20	0-30	0-25	1-20	0-25	2-10	0-40	2-0	0-20	2-20	0-15	2-30	0-40	2-50

A.D.: Air-dried; B.: Baked; NB: No blush after 1 month.

*Composition numbers correspond to those in Table 1.

Results and discussion

Compared to plain shellac, a good deal of improvement in film properties was noticed for the resultant polyurethane films. Whereas films obtained from plain shellac were brittle and blushed in water in 30 min and in acid or alkali within 5 min, polyurethane films were superior in these respects.

During the preparation of shellac-based polyesters, it was found that the use of high proportions of dicarboxylic acid, e.g. more than 25% on the weight of shellac, leads to gelation. As the amount of dicarboxylic acid was increased, the acid values of the resultant polyesters also increased. However, the one-step process gave polyesters with comparatively low acid values. Lowest acid values were obtained using adipic acid, and the highest with maleic anhydride. No noticeable improvement in the film properties of the resultant polyurethanes was observed on using more than 10% of the dicarboxylic acid. The performance of adipic acid-modified composition was the best. The optimum proportion of diisocyanate for obtaining polyurethanes, taking into consideration the pot life, is 30% on the weight of the polyester. Polyurethane films prepared from polyesters from adipic acid by the two-step process had better resistance to water and hydrochloric acid as compared to those obtained by the one-step process.

All the modified shellac-based polyurethane coatings were found to show good flexibility. No cracks were observed in the films when they were subjected to double bend test on the conical mandrel (3 mm). They were also unaffected by normal organic solvents. A marked improvement in the properties of the films was noticed after baking.

The polyurethanes obtained from shellac are much superior to plain shellac as regards film properties and are likely to become products of interest, opening new channels for shellac in the surface coating industry.

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