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Shellac Graft Copolymers: Part I—Shellac-Acrylate Graft Copolymers

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Graft copolymerization of shellac with ethyl acrylate or a mixture of ethyl and methyl methacrylates in aqueous ammoniacal medium yields a product whose films (air-dried and baked) exhibit improved heat, water, impact and chemical resistance as well as adhesion, flexibility and gloss compared to films of shellac. In respect of scratch hardness, however, the graft copolymer films show inferior performance compared to shellac films. In general, graft copolymers prepared using mixtures of ethyl and methyl methacrylates are inferior to those prepared using ethyl acrylate alone.

FOR its outstanding properties, such as gloss, toughness and remarkable adhesion to a variety of surfaces, shellac finds extensive use in surface coatings for protection, decoration and electrical insulation. Several investigators have attempted to overcome its limitations, such as low softening point and poor water resistance. It has been modified with sulphur[1], thiourea[2], urea[2], melamine[3], cashewnut shell liquid[4], urea sulphite[5], etc. The latest trend is to modify it either by admixture with a synthetic polymer[6,7] or to graft copolymerize it with synthetic monomers or their mixtures[8,9]. For example, lac has been modified with spirit-soluble (butylated) melamine[10] and urea formaldehyde resins[11] to produce air-dried and baked films respectively of outstanding water (blush) resistance and improved heat resistance. Lac has also been graft copolymerized with ethyl and methyl acrylates through the intermediate hydroperoxide[8]. It has also been copolymerized with these monomers in the presence of redox catalysts[9]. Outstanding film properties have been claimed for the products.

There are no references in literature to the hydroperoxide of lac, except in one patent[8]. Information available about the optimum conditions for the production of the hydroperoxide is rather meagre. This, being an essential prerequisite for further graft copolymerization, was studied in detail in this laboratory (Sahu, T. & Misra, G. S., unpublished data). The present paper deals with attempts to determine the optimum conditions for the production of graft copolymers with satisfactory performance, through the hydroperoxide. The nature and film properties of the resulting composition have also been studied.

Hydroperoxide of lac was first prepared under the optimum conditions. Methyl methacrylate was then grafted on to the hydroperoxidized lac in the presence of sodium sulphoxylate formaldehyde. The graft copolymer was reclaimed from the resulting emulsion by air drying on a glass plate from which the film could be peeled off easily.

The product was found to contain 18·7 per cent unpolymerized lac (alcohol soluble), 15·4 per cent homopolymer (toluene soluble) and 66·23 per cent of material insoluble in either of the solvents, presumably the graft copolymer. After separating the portions soluble in alcohol and toluene, the remaining insoluble product was analysed and found to have a hydroxyl value of 25·16 and an acid value of 3·39. These values indicate that the lac was in a combined state, or in other words, a graft of the vinyl polymer had formed on a shellac backbone. Further evidence for graft polymerization of the vinyl monomers on lac was obtained as follows. An emulsion polymer of ethyl acrylate only was

TABLE 1 — FILM PROPERTIES OF SHELLAC-ETHYL ACRYLATE POLYMER MIXTURE

[Air-dried films were tested after 7 days' ageing and baked films (at 100°C. for 1 hr) tested after 24 hr of baking]

Ethyl acrylate on wt of shellac %	Scratch hardness (over 1 mm. steel ball) kg.		Flexibility (over 3 mm. mandrel)		Impact resistance		Water resistance (immersion in water at room temp., about 28°C.)					
							Air dried, immersed for			Baked, immersed for		
	Air dried	Baked	Air dried	Baked	Air dried	Baked	24 hr	48 hr	1 week	24 hr	48 hr	1 week
45	0·2	0·5	Cracks	Cracks	Fails	Fails	Blushes	Blushes	Blushes	No blush	No blush	No blush
60	0·1	0·5	do	do	do	do	do	do	Heavy blush	do	do	do
75	0·2	0·3	do	do	do	do	do	do	do	Blushes	Blushes	Heavy blush

prepared by the usual technique and mixed with an ammoniacal solution of lac in the same proportion in which these had been determined for the graft copolymer of the two. The performance of this mixture (Table 1) was quite different from that of the graft copolymer of shellac and ethyl acrylate, indicating that the improvement in the properties of the emulsion is due to the formation of a graft copolymer. Having obtained evidence for graft copolymerization under these conditions, the experiment was repeated with different proportions of ethyl acrylate as well as mixtures of ethyl acrylate and methyl methacrylate in different proportions. The resulting graft polymer films could not be detached from glass plates so readily as the ones where only methyl methacrylate had been used, indicating improved adhesion.

Experimental Procedure

Hydroperoxidation — A solution of dewaxed decolourized shellac (20 g.) was prepared in a mixture of water (80 ml.) and aqueous ammonia of density 0·91 (3 ml.) by warming on a water bath to 60°C. for 50 min. The solution (50 ml.) was then taken in a three-necked flask fitted with a water condenser, a mercury seal stirrer and an inlet tube for passing oxygen. The flask was immersed in a thermostatic bath maintained at 50° ± 1°C. Oxygen gas was passed into the solution for 3 hr with constant stirring. After this period, the excess oxygen was displaced by passing nitrogen for 30 min.

Grafting of the monomers — The monomer (ethyl acrylate) or mixture of ethyl acrylate and methyl methacrylate (6 g.) was then added dropwise into the flask, the contents of which were kept stirred and nitrogen gas passed for another 30 min. Sodium sulphoxylate of formaldehyde (0·2 g.) was then added and the contents of the flask were allowed to graft copolymerize, by stirring in a stream of nitrogen gas for 3 hr. The resulting graft polymer emulsion was a thin translucent liquid possessing a faint odour of the monomer. It had a viscosity of about 0·5 poise at 20°C.

Films of the emulsion were prepared on glass and tin panels by flowing and allowing to drain in an almost vertical position. Films on wooden panels were made by the French polishing technique. These films were examined under standard conditions.

Results and Discussion

The possible mechanism of grafting is as follows. When oxygen is passed into a shellac solution under appropriate conditions, it gets hydroperoxidized:

$$\underset{\text{Shellac}}{RH} + O_2 \rightarrow \underset{\text{Shellac hydroperoxide}}{ROOH}$$

This shellac hydroperoxide then breaks up into two free radicals, either one of which can initiate the polymerization of vinyl monomers. Shellac grafts result as follows:

$$ROOH \rightarrow RO^* + {}^*OH$$

$$\underset{\text{Free radical}}{RO^*} + \underset{\text{Monomer}}{nCH_2 = CHX} \rightarrow \underset{\text{Graft polymer chain}}{RO(CH_2-CHX)_n-}$$

The chain then gets stabilized by one of the several possible cessation mechanisms.

Finish — The films on glass and tin, both air dried and baked (100°C./ hr), and the French polished surfaces on wood were smooth and glossy with no smell of the free monomers. They were also perfectly tack-free.

Hardness — Scratch hardness of the films (on tin panels) was determined by a Sheen automatic scratch hardness tester. The scratch hardness of the air dried films of the graft copolymers with ethyl acrylate increased gradually with increasing proportion of the monomer (Tables 2 and 3). Surprisingly enough, there was hardly any improvement in the case of baked films. In the case of graft copolymers with the mixture of ethyl acrylate and methyl methacrylate, there is actually a drop in the value of scratch hardness, except when ethyl acrylate and methyl methacrylate are present in the proportion 50 : 10.

Flexibility — Flexibility, on the other hand, definitely improves in both air dried and baked films (Tables 2 and 3), although here also the performance of the graft copolymers with mixtures of methyl methacrylate and ethyl acrylate is poor.

Impact resistance — Impact resistance was found to be of the same order as flexibility in both the cases.

Water resistance — The water resistance of the films was determined by applying them on glass slides and immersing in water at laboratory temperature (about 28°C.) for one week. The air dried as well as baked films could resist water action for one

TABLE 2 — FILM PROPERTIES OF SHELLAC-ETHYL ACRYLATE GRAFT COPOLYMER

[Air-dried films were tested after 7 days' ageing and baked films (at 100°C. for 1 hr) tested after 24 hr of baking]

Ethyl acrylate (on wt of shellac) %	Scratch hardness (over 1 mm. steel ball), kg.		Flexibility (over $\frac{1}{8}$ in. mandrel)		Impact resistance		Water resistance (immersion in water at room temp., 28°C.)						Heat resistance*	Gloss on wooden panel %
							Air dried, immersed for			Baked, immersed for				
	Air dried	Baked	Air dried	Baked	Air dried	Baked	24 hr	48 hr	1 week	24 hr	48 hr	1 week		
0	0·3	0·6	Cracks	Cracks	Fails	Fails	No blush	Blush	Heavy blush	No blush	No blush	No blush	Sticks badly with circular mark	36·5
28	0·4	0·8	do	do	do	Slight cracks	do	No blush	Slight blush	do	do	do	Slight sticking, marks	42
45	0·4	0·9	do	Passes	do	do	do	do	do	do	do	do	No sticking, no mark	51·5
60	0·6	0·7	Passes	do	Passes	Passes	do	do	No blush	do	Slight blush	Slight blush	do	58
75	0·7	0·7	do	do	do	do	do	do	Slight blush	do	do	do	do	52
100	1·1	1·0	do	do	do	do	Slight blush	Blush	Heavy blush	Slight blush	Blush	Blush	do	57

*Determined by placing a boiling water breaker on air-dried polished wooden panel for 2 min.

TABLE 3 — FILM PROPERTIES OF SHELLAC-ETHYL ACRYLATE AND METHYL METHACRYLATE GRAFT COPOLYMER

[Air-dried films were tested after 7 days' air ageing and baked films (at 100°C. for 1 hr) tested after 24 hr of baking]

Acrylate added (on wt of shellac)		Scratch hardness (over 1 mm. steel ball), kg		Flexibility (over $\frac{1}{8}$ in. mandrel)		Impact resistance		Water resistance (immersion in water at room temp., 28°C.)						Heat resistance*	Gloss on wooden panel (air dried) %
								Air dried, immersed for			Baked, immersed for				
Ethyl acrylate %	Methyl meth-acrylate %	Air dried	Baked	Air dried	Baked	Air dried	Baked	24 hr	48 hr	1 week	24 hr	48 hr	1 week		
—	—	0·3	0·6	Cracks	Cracks	Fails	Fails	No blush	Blush	Heavy blush	No blush	No blush	No blush	Sticks badly with circular mark	36·5
30	30	0·2	0·5	do	do	do	do	Peels off	Peels off	Peels off	do	do	do	Sticks slightly with a little mark	48
20	40	0·1	0·5	do	do	do	do	do	do	do	do	do	do	No sticking, no mark	65
10	50	0·0	0·3	do	do	do	do	do	do	do	do	do	do	do	41
50	10	0·4	0·4	Fine cracks	Passes	do	Passes	No blush	No blush	No blush	do	do	do	Sticks slighly with a little mark	50

*Determined by placing a boiling water beaker on air-dried polished wooden panel for 2 min.

week, when 45-60 per cent of ethyl acrylate on the weight of lac was grafted; further increase in the proportion of ethyl acrylate during graft copolymerization decreased the water resistance, whereas in the case of a mixture of ethyl acrylate and methyl methacrylate the air dried films of only one particular composition, ethyl acrylate: methyl methacrylate :: 50: 10 were found to be water resistant. Baking improved the films of other compositions.

Heat resistance — Heat resistance was determined by placing a beaker containing water, kept boiling by an immersion heater, over the French polished surface on wood. The extent of sticking and disfiguring of the surface, when the beaker was removed after 2 min. was noted. The data presented in Tables 2 and 3 show that there is a substantial improvement in this respect in the films of the graft copolymers as compared to those of the parent lac.

Gloss — The gloss of the air dried films on French polished wooden panels was measured by Lange's glossmeter. The gloss of the films of the graft copolymers was superior to that of films of the parent shellac in all cases.

Chemical and solvent resistance — In addition to water resistance, baked films of the emulsions were found to resist the action of spirit, benzene, toluene, acetone, methyl ethyl ketone, etc., for more than 24 hr, but the films peeled off in dil. alkali and dil. soap solutions. The air dried films, however, did not have any resistance against the above chemicals and solvents.

The above results indicate that the graft copolymer emulsion of shellac with ethyl acrylate is a substantial improvement over the parent lac in all respects, particularly when it is used as a French polish for wood. The performance of the baked films is rather disappointing in respect of scratch hardness. With the possible exception of the proportion of 50 parts of ethyl to 10 parts of methyl methacrylate, mixtures of ethyl acrylate and methyl methacrylate are inferior to ethyl acrylate as far as graft polymerization with lac is concerned.

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