

## Shellac Graft Copolymers: Part II—Shellac-Ethyl Acrylate-Styrene-Acrylamide Graft Copolymers

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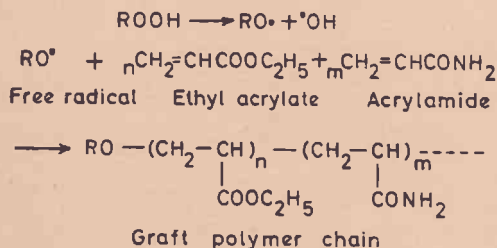
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The possibility of improving the film properties of shellac through its graft copolymerization with different vinyl monomers (acrylates, styrene and acrylamide) and their mixtures has been examined. Of the various monomers and their mixtures tried, best results (in respect of film properties of the resulting copolymer emulsions) have been obtained with ethyl acrylate. However, in the case of films to be baked, a 50:10 per cent mixture of ethyl acrylate and acrylamide (on the weight of shellac) gives the best results.

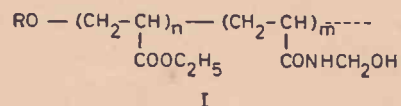
It was reported earlier<sup>1</sup> that shellac can be made to graft copolymerize with ethyl acrylate on treating its hydroperoxide with this monomer in aqueous ammoniacal medium to produce emulsions with improved film properties. The study has now been extended so as to cover other vinyl monomers, namely methyl acrylate, styrene and methyl methacrylate, as well as mixtures of ethyl acrylate and acrylamide, and styrene and acrylamide to examine the possibility of further improving the properties of the films.

In cases where acrylamide was used, hexamethylene tetramine was also later incorporated as a curing agent in the hope that the reaction would proceed as follows: Shellac forms with oxygen the hydroperoxide, which can then graft copolymerize with a mixture of the acrylate and acrylamide according to the following equations:

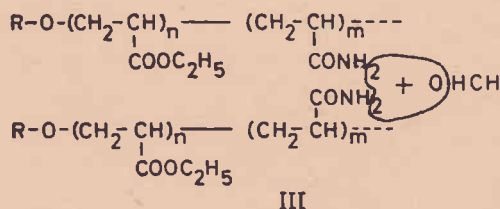
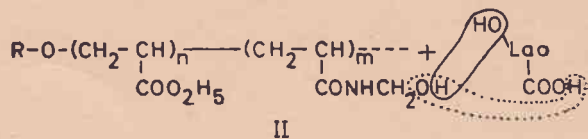


The resulting polymer would further react with the formaldehyde released from hexamethylene

tetramine to form methylol group in the graft copolymer chain (I)



which might lead to the formation of crosslink structures (II) and (III) with the —OH group or —COOH group of the unreacted lac or with another similar graft copolymer chain present in the emulsion product thus



### Experimental Procedure

Shellac was first converted into its hydroperoxide by passing oxygen into its aqueous ammoniacal solution as described earlier<sup>1</sup>. It was then treated

with different monomers, namely ethyl acrylate, methyl acrylate, styrene or methyl methacrylate (60 per cent on the wt of shellac) along with 0.2 g. of sodium sulfoxylate of formaldehyde and the reaction mixture allowed to graft copolymerize at  $40^{\circ} \pm 1^{\circ}\text{C}$ . for 3 hr in a stream of nitrogen. In a similar manner, mixtures of ethyl acrylate and acrylamide, and styrene and acrylamide with different proportions of the monomers, to a total of 60 per cent on the weight of lac were also grafted on to the lac. To the resulting emulsions obtained in the case of mixtures, hexamethylene tetramine was added as curing agent. Films of the emulsions were prepared on glass slides and tin panels by flowing and allowing to drain in an almost vertical position. The films were examined under standard conditions.

### Results and Discussion

The characteristics of the various copolymers are presented in Table 1. For comparison, the characteristics of shellac/ethyl acrylate copolymers are also included.

*Finish* — The films on glass and tin surfaces, both air dried and baked (at  $100^{\circ}\text{C}$ ./1 hr) were smooth and glossy, with no smell of the free monomers. They were also perfectly tack-free.

*Hardness* — Among the copolymers obtained using single monomers, that from ethyl acrylate showed the best performance. Its copolymer with shellac had a scratch hardness of 0.6 kg. against 0.3 for the copolymer from methyl acrylate. The films of the copolymer obtained from styrene and methyl methacrylate exhibited almost zero hardness, the films flaking off from the substrate surface. Air-dried films of the copolymers obtained from mixtures of monomers showed poor performance. However, baked films of these copolymers were superior to the film of copolymer obtained from ethyl acrylate alone. The best copolymer in respect of film hardness was the one obtained from a 40 : 20 per cent mixture (on wt of shellac) of styrene and acrylamide; the scratch hardness of films of this copolymer was above 2.0 kg.

*Flexibility* — In respect of flexibility also, films of the copolymer obtained from ethyl acrylate showed the best performance. The copolymers obtained from methyl acrylate and 50 : 10 per cent mixture of ethyl acrylate and acrylamide also exhibited almost the same film flexibility as the copolymer from ethyl acrylate. The flexibility of films of all other copolymers was low (almost comparable to that of the parent lac).

TABLE 1.—FILM PROPERTIES OF GRAFT COPOLYMERS OBTAINED FROM SHELLAC AND DIFFERENT VINYL MONOMERS USED SINGLY OR AS MIXTURES

[Air-dried films were tested after 7 days' air ageing and baked films (at  $100^{\circ}\text{C}$ . for 1 hr) 24 hr after baking]

Monomer used	Qty of monomer % (on wt of shellac)	Scratch hardness (over 1 mm. steel ball), kg.		Flexibility (over 3 mm. mandrel)		Impact resistance*		Water resistance†					
		Air dried	Baked	Air dried	Baked	Air dried	Baked	Air dried			Baked		
								24 hr	48 hr	1 week	24 hr	48 hr	1 week
SINGLE MONOMERS													
Nil	—	0.3	0.6	C	C	F	F	NB	B	HB	NB	NB	NB
Ethyl acrylate	60	0.6	0.7	P	P	P	P	NB	NB	NB	NB	SB	SB
Methyl acrylate	60	0.3	0.4	P	P	P	P	B	B	B	NB	SB	B
Methyl methacrylate	60	0	0.2	C	C	F	F	PO	PO	PO	NB	SB	B
Styrene	60	0	0.3	C	C	F	F	PO	PO	PO	NB	SB	B
MIXTURES OF MONOMERS													
Ethyl acrylate + Acrylamide	40 } 20 }	0.3	1.2	F	P	F	F	B & PO	B & PO	B & PO	PO	PO	PO
Ethyl acrylate + Acrylamide	50 } 10 }			0.3	0.9	JF	P	F	JF	SB	B	B	NB
Ethyl acrylate + Acrylamide	30 } 30 }	0.2	0.7			F	P	F	F	SB	B	B	NB
Styrene + Acrylamide	40 } 20 }			0	>2.0	F	F	F	JF	PO	PO	PO	NB
Styrene + Acrylamide	50 } 10 }	0	1.0			F	F	F	JF	PO	PO	PO	NB
Styrene + Acrylamide	30 } 30 }			0	0.9	F	F	F	F	PO	PO	PO	NB

C, cracks; P, passes; F, fails; JF, just fails; B, blushes; NB, no blush; HB, heavy blush; SB, slight blush; PO, peels off.

\*Determined by the falling block method.

†Determined after immersion in water at room temperature ( $28^{\circ}\text{C}$ .) for the specified time interval.

TABLE 2 — FILM PROPERTIES OF GRAFT COPOLYMERS OBTAINED IN THE PRESENCE AND ABSENCE OF THE CURING AGENT

(Curing agent used, hexamethylene tetramine; only properties of baked films are given; films baked at 100°C. for 1 hr and tested 24 hr after baking; abbreviations used have the same significance as in Table 1)

Monomer used	Qty of monomer % (on wt of shellac)	Scratch hardness (over 1 mm. steel ball), kg.		Flexibility (over 3 mm. mandrel)		Impact resistance		Water resistance					
		With curing agent	Without curing agent	With curing agent	Without curing agent	With curing agent	Without curing agent	With curing agent			Without curing agent		
								24 hr	48 hr	1 week	24 hr	48 hr	1 week
Ethyl acrylate + Acrylamide	30	0.7	0.6	P	F	F	F	NB	PO	PO	PO	PO	PO
Ethyl acrylate + Acrylamide	40	1.2	0.9	P	P	F	F	PO	PO	PO	PO	PO	PO
Ethyl acrylate + Acrylamide	50	0.9	0.8	P	P	JF	F	NB	NB	NB	NB	SB	SB
	10												

*Water resistance* — In respect of water resistance also, the films of the copolymer obtained from ethyl acrylate showed the best performance among the copolymers prepared using single monomers. However, baked films of copolymers obtained from 50 : 10 per cent mixture of ethyl acrylate and acrylamide (on the wt of shellac) and mixtures of styrene and acrylamide in all proportions showed somewhat superior performance; these films were almost completely bluish resistant.

*Resistance to other solvents* — Films of the same copolymers which showed high water resistance showed high resistance to the dissolving action of spirit, benzene, toluene, acetone and methyl ethyl ketone for more than 24 hr, but the films peeled off in dilute alkali and dilute soap solutions within a few minutes.

*Action of the curing agent* — To determine the role of the curing agent and to examine whether the crosslink between the graft copolymer and shellac was really taking place, the film properties of the copolymers were studied in the presence and absence of hexamethylene tetramine. The results presented in Table 2 show that the baked (cured)

films of copolymers obtained in the presence of hexamethylene tetramine were definitely superior to those obtained in its absence, though the improvement is not substantial. Increase or decrease in the proportion of hexamethylene tetramine beyond that actually used (1 mole of HCHO/mole of acrylamide) did not result in any marked variation in the film properties.

The results of the present study indicate that for graft copolymerization of shellac aimed at improving its film properties, ethyl acrylate gives the best results among the various monomers tried. Even mixtures of monomers do not fare better. However, for obtaining films which are to be baked, a 50 : 10 per cent mixture of ethyl acrylate and acrylamide (on the wt of shellac) is to be preferred.

#### Acknowledgement

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#### References

1. SAHU, T. & MISRA, G. S., *Indian J. Technol.*, **4** (1966), 370.