

Modification of shellac with polyester resin — I

## Modification with heat convertible polyesters

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*Polyesters based on glycerol and mixtures of phthalic anhydride, and adipic acid or maleic anhydride, are compatible with shellac especially in aqueous ammonical medium. For optimum performance for use in surface coatings, the aliphatic and aromatic polyacids are best used in equimolecular proportions and the varnish blends made containing 75 parts of shellac and 25 parts of the polyester. Improvements in properties are most marked only in baked films, the outstanding improvement being in respect of elasticity.*

MODIFICATION of shellac with its erstwhile rivals viz. synthetic resins, have recently been shown to result in films of improved properties. Typical examples are the modification with urea/formaldehyde resin<sup>1,2</sup> melamine/formaldehyde resin<sup>3,4</sup> and epoxy resin<sup>5-8</sup>, apart from copolymers obtained from acrylamides, etc.<sup>9-16</sup>.

Polyesters are modern synthetic resins, finding increasing use in surface coatings and particularly for solventless coatings, where they are used as a solution in a polymerisable monomer, namely styrene, and cured *in situ* by the presence of initiators, accelerators etc. Wide variations are possible in the properties and performance of polyesters by varying the polyols, saturated and unsaturated polyacids or their mixtures used and their proportions. It was therefore considered that a study of the modification of shellac with such polyesters would be of interest, to see how far such modifications would improve the film properties of either.

Shellac, a natural resin of wide use in surface coatings, has limitations, viz., comparative brittleness, low softening point and poor resistance to water and alkalis. Improvements in the film and moulding properties of shellac by incorporation of polyesters based on glycerol and poly-glycerol, and saturated and unsaturated polyacids have been referred to in literature<sup>17,18</sup>.

Improved film properties have also been claimed by the incorporation, into shellac varnishes, of oxygen convertible polyesters based on hexamethylene glycol and maleic anhydride<sup>19</sup>. These, however, being patents not much information is available about the properties of the various compositions and the optimum conditions under which these are to be prepared, blended and used necessitating a systematic study. The results so far obtained are indicated below.

According to the former patent<sup>17</sup>, suitable polyesters for incorporation into shellac varnishes are produced from glycerol and phthalic anhydride with a proportion of aliphatic acids, saturated or unsaturated, to improve the flexibility of the polyester. Attempts were therefore made, first, to prepare polyesters based on these constituents with a view to correlating the film properties of lac varnishes modified with the different polyesters produced and in different proportions.

## Preparation of the polyesters and shellac/polyester varnish blends

The polyesters described, in the above mentioned patents, were prepared under the simplest of conditions viz. by heating together the various constituents, viz. glycerol as the polyol and phthalic anhydride and the aliphatic acid in an open vessel, in an oil bath. For the sake of uniformity and repro-

ducibility, the size of the batch (and reaction vessel), the temperature and speed of stirring, were kept as uniform as possible. By this, variation of chain length and degree of cross linking were minimised. Adipic acid was used as the aliphatic poly-acid and 10% excess of glycerine over the calculated quantity was used, as usual. The heating (at 180-190°C) was continued till the product lost its stickiness but was still soluble in alcohol and/or acetone and tendency for gelation had not set in (Table I). The resulting clear colourless resins were dissolved in alcohol together with a proportion of acetone or methyl isobutyl ketone to obtain clear solutions of a non-volatile content of 25%. Dewaxed lac varnish, in alcohol of the same concentration was separately prepared and the two mixed in different proportions to yield varnishes (of 25% non-volatiles) containing lac and polyester in different proportions.

It was noticed that the blends were never perfectly clear, irrespective of the amount of ketone incorporated and consequently the films were also not perfectly clear and homogeneous but somewhat translucent.

As the polyesters had substantial residual acidities *vide* column 8 Table I), the possibilities of using them in aqueous (ammonical) solu-

TABLE I  
Preparation of polyesters

SI No	Composition	Composition — Parts equivalent				Time of cooking at 180-190°C. Minutes.	Properties of the polyester produced.	
		Glycerol	Phthalic anhydride	Aliphatic acid used	Equivalent used		A V	solubility
1.	SA	1	0.75	Adipic acid	0.25	165	108	Alcohol + Ketone
2.	SB	1	0.50	"	0.50	150	83.8	" "
3.	SC	1	0.25	"	0.75	130	76	" "
4.	UA	1	0.75	Maleic anhydride	0.25	255	94	" "
5.	UB	1	0.50	"	0.50	240	78	" "
6.	UC	1	0.25	"	0.75	300	63	" "

tion, along with aqueous (ammonical) shellac varnishes was also investigated. There is no reference in literature to these aqueous varnishes. These polyesters could be readily dissolved in ammonical water and, unlike their alcoholic counterparts, the resulting solutions formed clear blends on mixing with aqueous shellac varnishes. Blends of the above varnishes containing different proportions of the polyesters and lac were then prepared. Here again, the concentration was maintained at 25 per cent solids.

#### Film properties

Film properties of all these varnishes were then examined and three sets of films were made, both on glass and on tin panels. One set was allowed to air dry, at room temperature for seven days before the tests. Another set was baked at 100°C for one hour and the third at 150°C for 30 minutes, both these sets being tested 24 hours after the baking.

It was seen (*vide* Tables II and III) that the incorporation of the polyester is definitely advantageous both in spirit and in aqueous varnishes. Although, the spirit varnish blends gave translucent films the films from aqueous varnishes were perfectly clear, glossy and homogeneous. The optimum proportion, in both cases, appeared

to be 75 parts of lac to 25 parts of the polyester. The polyester prepared using 0.5 equivalent of phthalic anhydride and 0.5 equivalent of aliphatic acid produced somewhat superior films than the polyesters in the other proportions.

Modified with such a polyester in the above proportion, films of lac varnishes showed a 50 to 70 per cent improvement in scratch hardness, especially on baking and substantial improvement in elasticity in all films (as can be expected). In regard to water resistance, however, the air dried films were inferior to those of unmodified dewaxed shellac varnish. Improvement in this was obtained only on baking at 100°C in the case of spirit based varnishes, and at 150°C in the case of the water based ones.

#### Polyesters using unsaturated aliphatic acid

The possibility of further improvement by the substitution of unsaturated acid, was next investigated. Polyesters were prepared using maleic anhydride in place of adipic acid described above (UA, UB and UC of Table I). The resulting products were then blended, as before, with lac varnishes, both in alcohol and in aqueous ammonia. It was found that the blends in organic solvents and the films

produced from these, were cloudy and translucent whereas in aqueous ammonical medium, homogeneous and clear blends were obtained which also gave clear and transparent films.

The film properties were next studied. It was seen (*vide* Table III) that, in these cases also, the optimum proportion was 75 parts of the polyester. There did not appear to be much difference in the performance of the polyesters produced using different proportions of the aliphatic and aromatic polyacids. Although for use in aqueous media, the proportion of 25 equivalents of the former to 75 of the latter appeared to be somewhat superior. The improvement in respect of hardness was of the same order as with the saturated acid polyesters, as far as spirit based varnishes were concerned, although in the case of the aqueous varnishes, the improvement was somewhat less, the improvement in respect of elasticity was equal in both cases. In regard to water resistance, the air dried films were again inferior to those of unmodified lac, and similar to the films of the saturated acid polyester blends. In respect of the baked films, the improvement was somewhat superior as even films baked at 100°C (for 1 hour) were perfectly bluish resistant on 24 hours continued immersion.

**TABLE II**  
 Film properties of dewaxed lac — saturated polyester combinations in  
 spirit and aqueous varnishes

Polyester used	Composition of blend		Scratch hardness, in kg.			Flexibility			Water Resistance						
	Shellac	Polyester	Air dried	Baked at		Air dried	Baked at		Time for initial blush in hours			Recovery time, in hours, after 24 hours immersion.			
				100°C	150°C		100°C	150°C	Air dried	Baked at		100°C	150°C	Baked at	
										100°C	150°C			100°C	150°C
<b>Spirit varnishes</b>															
S A	100	0	0.6	0.6	0.7	CP	CP	CP	4.5	6.0	6.0	0.58	0.50	0.50	
	75	25	0.7	0.9	0.8	P	P	P	0.25	NB	NB	0.17	—	—	
	50	50	0.7	0.9	1.0	TP	TP	P	0.25	0.50	NB	0.17	0.17	—	
	25	75	0.6	0.8	0.8	TP	TP	P	0.25	0.75	1.0	0.17	0.17	0.25	
	0	100	0.6	0.6	0.6	TP	TP	TP	0.25	0.50	0.50	0.17	0.17	1.0	
S B	75	25	1.0	0.9	1.2	P	P	P	0.25	NB	NB	0.25	—	—	
	50	50	0.8	0.9	0.8	P	P	P	0.25	0.33	NB	0.17	0.41	—	
	25	75	1.0	0.8	0.9	P	P	P	0.25	0.50	NB	0.25	0.75	—	
	0	100	0.9	0.7	0.9	TP	TP	TP	0.25	0.75	NB	0.25	0.50	—	
	75	25	0.9	1.0	1.0	CP	P	P	0.50	1.0	NB	No	2	—	
S C	50	50	1.0	1.1	1.0	P	P	P	0.25	0.50	0.50	Recovery	24	0.92	
	25	75	0.9	1.0	0.9	P	P	P	0.25	0.50	0.50	„	24	24	
	0	100	0.6	0.7	1.5	TP	TP	P	0.08	0.08	NB	0.50	0.75	—	
<b>Aqueous varnishes</b>															
S A	100	0	0.6	0.6	0.6	CP	CP	CP	3.5	4	4	0.66	0.50	0.50	
	75	25	0.8	0.8	1.0	P	P	P	0.50	1	NB	0.25	0.25	—	
	50	50	0.7	0.9	0.9	TP	TP	P	0.25	0.50	NB	0.50	0.50	—	
	25	75	0.7	0.6	0.7	TP	TP	P	0.25	0.50	NB	0.50	0.50	—	
	0	100	0.8	0.7	0.8	TP	TP	TP	0.25	0.50	1.5	0.50	0.50	0.50	
S B	75	25	0.8	1.0	1.2	P	P	P	0.25	0.50	NB	0.33	0.25	—	
	50	50	0.8	0.7	1.1	TP	P	P	0.25	1.0	NB	0.75	0.50	—	
	25	75	0.7	0.7	0.8	TP	P	P	0.25	1	NB	0.75	0.66	—	
	0	100	0.8	0.7	0.9	TP	TP	P	0.25	0.50	NB	0.83	0.25	—	
	75	25	0.5	0.5	0.7	CP	P	P	0.08	1.33	NB	0.33	1.0	—	
S C	50	50	Separation of resin in colloidal form												
	25	75	Precipitation of resin takes place.												
	0	100	0.5	0.5	0.9	TP	TP	P	0.08	0.08	0.17	0.50	0.75	0.75	

**Effect of drier and catalyst**

The effect of the addition of cobalt as drier and benzoyl peroxide as catalyst to these unsaturated acid polyester/dewaxed lac varnish blends was investigated. As 75 parts of lac blended with 25 parts of polyester, gave the best overall performance, this study was confined to varnishes of this composition and to spirit based varnishes only as cobalt got precipitated in aqueous alkaline medium. It was found (*vide* Table IV) that addition of cobalt improved the hardness of the air dried films (as can be expected), 0.1 per cent on the weight of the polyester content being the

optimum. The maximum improvement was observed in the blend containing the polyester based on phthalic and maleic anhydrides in equal proportions. Cobalt did not have any influence in the case of the baked films. Elasticity and water resistance were also practically unaffected.

Addition of benzoyl peroxide did not improve the film properties of these blends in any way.

**Solvent resistance**

Resistance to solvents other than water of the films of dewaxed lac polyester blends containing 75 parts of the former, to 25 parts of the later, both in spirit and in aqueous

media, which had proved the best of the lot, was then investigated.

It was found that the air dried films were again poor, but the baked films (baked at 150°C) were definitely superior. They were comparable to those of the parent unmodified lac in respect of their resistance to benzene, toluene, white spirit and dilute (5 per cent) hydrochloric and sulphuric acids, but superior in their resistance to acetone and alcohol. They also resisted dilute (2 per cent) sodium carbonate solution for 24 hours, but not caustic soda of the same concentration.

**TABLE III**  
 Film properties of dewaxed lac — unsaturated polyester combinations  
 in spirit and aqueous varnishes

Polyester used	Composition		Scatch hardness, in kg. of films			Flexibility			Water Resistance					
	Polyester	Shellac	Baked at			Baked at			Time for initial blush in hours			Recovery after 24 immersion in hours		
			Air dried	Baked at		Air dried	Baked at		Air dried	Baked at		Air dried	Baked at	
				100°C	150°C		100°C	150°C		100°C	150°C		100°C	150°C
<b>Spirit varnishes</b>														
U A	100	0	0.6	0.6	0.7	CP	CP	CP	4.5	6	6	0.58	0.50	0.50
	75	25	0.9	1	1.2	P	P	P	0.25	NB	NB	0.50	—	—
	50	50	0.9	0.8	1	P	P	P	0.25	NB	NB	0.50	—	—
	25	75	0.9	1	1.2	P	P	P	0.25	1	1.5	0.50	0.33	0.41
	0	100	1.0	1.2	1.1	P	P	P	0.25	1	1.25	0.75	0.50	0.50
U B	75	25	0.9	1	1.1	P	P	P	0.25	NB	NB	0.50	—	—
	50	50	0.7	0.7	0.7	P	P	P	0.25	NB	NB	0.25	—	—
	25	75	0.9	0.8	0.9	P	P	P	0.25	NB	NB	0.33	—	—
	0	100	1.0	1.2	1.2	P	P	P	0.25	NB	NB	0.41	—	—
U C	75	25	0.9	1	1.2	P	P	P	0.25	NB	NB	0.25	—	—
	50	50	0.7	0.7	0.8	P	P	P	0.25	NB	NB	0.50	—	—
	25	75	0.8	0.9	1	P	P	P	0.25	NB	NB	0.58	—	—
	0	100	0.8	1	1.2	P	P	P	0.25	NB	NB	0.33	—	—
<b>Aqueous varnishes</b>														
U A	100	0	0.6	0.6	0.6	CP	CP	CP	3.5	4	4	0.66	0.50	0.50
	75	25	0.7	0.8	1	P	P	P	0.25	NB	NB	0.50	—	—
	50	50	0.5	0.6	0.6	C	C	P	0.25	0.50	NB	0.50	0.50	—
	25	75	0.6	0.8	0.7	C	C	P	0.25	2.50	24	0.50	0.66	0.08
	0	100	0.6	0.7	0.6	TP	P	P	0.25	0.50	1	0.75	0.50	0.50
U B	75	25	0.7	0.8	0.8	P	P	P	0.25	NB	NB	0.50	—	—
	50	50	0.6	0.6	0.5	P	P	P	0.25	NB	NB	0.50	—	—
	25	75	0.7	0.8	0.9	TP	TP	P	0.25	24	NB	0.50	0.08	—
	0	100	0.8	0.7	0.9	TP	TP	P	0.25	NB	NB	0.50	—	—
U C	75	25	0.6	0.8	0.9	P	P	P	1	NB	NB	0.50	—	—
	50	50	0.7	0.8	0.7	P	P	P	0.25	1	NB	0.50	0.17	—
	25	75	0.6	0.6	0.5	TP	P	P	0.25	1	NB	0.50	0.17	—
	0	100	0.8	0.8	0.9	P	P	P	4	NB	NB	1	—	—

**TABLE IV**  
 Film properties of dewaxed lac and unsaturated polyester combination  
 in spirit medium with cobalt as drier

Polyester used	% of cobalt as dried, Sample No.	Scatch hardness in kg.			Flexibility			Water Residence					
		Baked at			Baked at			Time for initial blush in hours			Recovery after 24 hours immersion, in hours.		
		A.D.	Baked at		A.D.	Baked at		A.D.	Baked at		A.D.	Baked at	
			100°C	150°C		100°C	150°C		100°C	150°C		100°C	150°C
U A	0.05	0.7	0.8	0.7	P	P	P	0.41	1	24	2.5	0.50	0.17
	0.10	0.8	1.2	1.1	P	P	P	0.41	1	NB	2.5	0.41	—
	0.25	0.8	0.8	0.8	P	P	P	0.41	1	4	2.5	0.50	0.33
	0.50	1.3	1.2	1.9	P	P	P	0.33	0.41	4	2.5	—	—
U B	0.05	1.2	1	0.7	P	P	P	0.41	NB	NB	0.50	—	—
	0.10	1.3	1	0.9	P	P	P	0.41	NB	NB	0.50	—	—
	0.25	1.3	1	0.8	P	P	P	0.41	NB	NB	0.50	—	—
	0.50	1.3	1	0.7	P	P	P	0.41	4	24	0.50	—	—
U C	0.05	1.2	0.9	0.7	P	P	P	0.41	NB	NB	0.50	1.5	1
	0.10	1	0.9	0.7	P	P	P	0.41	NB	NB	0.50	0.33	0.17
	0.25	1	0.7	0.7	P	P	P	0.41	2	NB	0.50	0.17	—
	0.50	0.8	0.9	0.7	P	P	P	0.41	24	NB	0.50	0.17	—

### Improved film properties

From the above it will be clear that incorporation of these heat convertible polyesters into shellac varnishes, definitely results in improved film properties. For spirit varnishes, a certain proportion of ketone is also necessary. Still, the varnish blends are not clear and homogeneous but only translucent. Aqueous ammoniacal blends, on the other hand, are perfectly clear and produce films which are smooth, homogeneous and glossy. For the polyester, the optimum proportions of the aliphatic and aromatic polyacids are about 50:50 mols. In the former, there is hardly anything to choose between the saturated and unsaturated. The optimum proportion of shellac to polyester in the blend is 75:25 and the improvement in properties are most perceptible only in baked films. While there is a 50-70 per cent increase in respect of hardness and some improvement in solvent resistance, the most outstanding improvement is in respect of elasticity. The use of these blends is, therefore, particularly indicated as water thinned finishes of the baking type requiring good adhesion and elasticity.

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