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Lac-melamine & Lac-melamine-formaldehyde Resins

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LAC-MELAMINE & LAC-MELAMINE-FORMALDEHYDE RESINS

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The main use of shellac is in the production of gramophone records — a process of hot and cold moulding. With the coming of bakelite into the field of plastic moulding and the consequent rapid development in the moulding of thermosetting resins, attempts were made to use lac for similar purposes. The main difficulty was obviously the comparatively slow curing of lac (about 30-60 minutes at 150°C). Several investigations [1-5] have been undertaken to accelerate this "curing" of lac, and a fairly long list of the so-called accelerators including urea, dicyandiamide, various metallic oxides, etc., is available today. Of these, urea is far and away the most effective, the "curing" time with this chemical being as low as 3 minutes at 150°C, and a workable moulding powder using urea as the accelerator has already been developed at the laboratories of the Indian Lac Research Institute [6,7] and is available now in commercial quantities in this country. The rapid development of melamine-formaldehyde resins, and their close analogy with and enhanced properties over urea-formaldehyde resins naturally suggested the investigation of melamine as an accelerator for lac.

The life under heat of lac with varying proportions of melamine was determined and it was found that the "life" decreases with increasing amounts of melamine as shown in Table I.

TABLE I

% Melamine on lac	Life	% Melamine on lac	Life
0 ..	37 minutes	6 ..	21 minutes
1 ..	34 ,,	7 ..	20 ,,
2 ..	32 ,,	8 ..	18 ,,
3 ..	29 ,,	9 ..	17 ,,
4 ..	26 ,,	10 ..	16 ,,
5 ..	22 ,,		

Melamine is therefore an accelerator for lac, though in this respect *apparently* it is far inferior to urea, the miscibility of melamine in molten shellac being extremely small.

The action of melamine on alcoholic solutions of lac was then investigated. Melamine is practically insoluble in alcohol and so suspending it in the cold in alcoholic solutions of lac has no effect. When, however, the solution is boiled under reflux, the melamine goes into solution and on cooling a thick viscous solution is obtained depending upon the amount of melamine used. If the amount of melamine used exceeds 3½ to 4%, the viscosity of a 25% solution of lac in alcohol goes on increasing till after a few days (depending upon the atmospheric temperature) the solution sets into a gel. If about 6% melamine is used, the solution gels within a few hours, which is then not soluble in alcohol and can be dissolved with dilute hydrochloric acid only with difficulty (cf. urea-shellac gel [8]).

Films obtained from melamine-treated lac varnishes show improved heat- and water-resistance over the ordinary lac films. Table II indicates the comparative heat- and water-resistance. The varnish was applied to clean polished wooden panels by brushing and to glass panels by flowing in an almost vertical position.

TABLE II

Test	Melamine-treated lac film		Urea-treated lac film		Control : ordinary dewaxed lac film	
	Unbaked	Baked at 90°-95°C for 1 hour	Unbaked	Baked	Unbaked	Baked
Boiled water in a beaker and placed the hot beaker with water on the wooden panels after the film has aged for 48 hours.	Two very faint marks.	No marks or sticking.	Two bold marks:	No marks or sticking:	Thick ring of blistered film formed, the resin coming off in shreads.	Practically same as unbaked.
Films on glass slides, after ageing for 72 hours, were kept immersed in cold distilled water.	No blushing for 24 hours or even longer.	Same as unbaked.	No blushing for 24 hours. Begins to blush slightly after a week.	The film peels off from the plate in about ½ hour after dipping (poor adhesion)	Blushes in 3 to 4 hours.	Blushes in 3 to 4 hours.
After ageing for 72 hours, the glass slides were dipped in boiling distilled water.	Blushes in 3 to 4 minutes followed by pitting and coalescing of the resin.	Blushes in 3 to 4 minutes and thereafter remains otherwise unaffected for 10 minutes.	Blushes in a few seconds and the film melts and coalesces.	Blushes in a few seconds and the film melts and is pitted badly.	Blushes and the film melts.	Same as unbaked
Water was boiled in a 400 cc. beaker and then placed on the film surface (only the films on glass slides were baked) and the water was kept boiling by means of an immersion heater.	Two faint marks, slight sticking of the beaker; otherwise, the film was unaffected.	Same as unbaked	A circular blistered patch where the bottom of the beaker touched the panel, The beaker was forcibly detached with difficulty.	Unaffected and no sticking.	The film melts and when the beaker is removed the resin comes off in shreads.	Same as unbaked.
Scratch hardness (films aged 1 week). Load on 1 mm. steel ball.	3500-3600 gms.		1700-1800 gms.		700-800 gms.	

From this table it is clear that melamine-treated lac films are definitely superior to plain lac films as also to unbaked urea-treated lac films. There appears to be practically no difference between baked and unbaked melamine-lac films. Baked urea-lac films, however, showed greater *dry* heat-resistance though poorer adhesion.

Regarding gloss, however, the order seems to be plain lac, urea-treated lac and melamine-treated lac, the plain lac varnishes yielding the glossiest films among the three.

Regarding flexibility, after about a week's ageing all the three films are brittle. Urea- and melamine-treated lacs tolerate a good deal more plasticiser without excessive softening, but the flexibility of the films is not much improved.

The melamine-treated shellac resin may be precipitated from its alcoholic solutions by pouring into excess of slightly acidulated water, filtering and washing the resin free from acid. On drying in the air, a fine powder is obtained. The powder when fresh is quite soluble in alcohol and the usual lac solvents. Its softening point, however, is considerably raised and depends upon the percentage of melamine used (softening point determined by the mercury surface method).

Per cent melamine	Softening point
1	120-130°C
2	150-160°C
3	180-190°C
4	Does not soften.

Thus it will be seen that with more than 3% melamine, there is practically no tendency to soften or fuse at the ordinary pressure. The resin may, however, be fused under high pressure at temperatures above 100-120°C. A very brittle, fairly transparent resin is obtained.

Lac-formaldehyde-melamine

The reaction of melamine with lac in presence of formaldehyde or directly with lac-formal appears to proceed in an entirely different way. Whereas melamine reacts with lac at the carboxyl group (cf. urea)[8], melamine reacts with the formal grouping in the lac-formal and results quite analogous to the lac-formaldehyde-urea resins are obtained. The resin obtained (after drying in the vacuum oven) may be moulded at 140-150°C at 1½ tons per square inch. The colour is the characteristic golden yellow colour of lac if dewaxed lac is used. The articles are quite transparent but very brittle and it is very often impossible to remove them from the moulds where they crack. Several plasticisers like santicisers, camphor, castor oil, tricresyl phosphate, etc., have been used, but so far without success [9].

The alcoholic solution obtained by reacting shellac-formal with melamine may, however, be mixed with fibrous fillers like wood flour, and/or mineral fillers and dried, after which the powder works exactly like shellac-urea-formaldehyde powder. Several proportions have been tried, but the best composition was found to be :

Shellac	100 gms.
Formalin	20 cc.
Melamine	5 gms.
Wood flour	100 ,,
Calcium stearate or stearic acid	3 ,,
Pigment	3 ,,

The shellac is first dissolved in spirit and formalin added. After one hour's boiling under reflux, in a Baker-Perkins mixer, the melamine is added. After further 1 to $1\frac{1}{2}$ hours' refluxing, the rest of the components are added and thoroughly kneaded, recovering at the same time as much of the alcohol as possible by reduced pressure distillation. The residue is then taken out of the mixer and after air-drying is finally dried in a vacuum oven at about 85°C for 1 to $1\frac{1}{2}$ hours. The powder may be moulded practically under the same conditions as lac-formaldehyde-urea (viz. 140-145°C at 1 to $1\frac{1}{2}$ tons per square inch). The articles are quite strong and sufficiently glossy.

Test pieces 9 gave the following figures :

Impact strength	6·5 to 7 kg. cm./sq. cm.
Heat-resistance (Martens) ..	72-74°C.
Water absorption	0·8-1% (Discs immersed in distilled water for 24 hours.)

The powder has been used in regular commercial presses at Bombay and Calcutta and pronounced as satisfactory.

Conclusion

The action of melamine on lac appears to be quite similar to the action of urea, viz. a loose salt formation. Ordinary lac as well as its acetyl or methoxy derivatives reacts with melamine, whereas when melamine is refluxed with any shellac ester, the whole of the melamine is recovered unchanged showing that the reaction is at the carboxyl group. Melamine has considerably more power of 'gelling' lac solutions than urea, the gels forming even in fairly dilute alcohol.

A lac-melamine solution containing 6% of melamine on the weight of lac dissolved in spirit to effect a 20-25% solution, gels within a few hours, whereas a similar solution with urea may be preserved practically indefinitely without gelling. Again, a lac-urea gel (in acetone) reverts to a solution in a few minutes if a drop or two of dilute HCl is added, while in the case of the lac-melamine gel the reversion is exceedingly slow. From these observations it may be concluded that, weight for weight, melamine is a better accelerator for lac than urea, and the only eplanation why urea gives a much shorter life under heat is the fact that at the conditions of the determination (150°C) urea melts and forms an intimate mixture, if not a solution, with the fused lac while melamine does not melt at this temperature nor does it go into solution in the molten lac.

The reaction of melamine with shellac in the presence of formaldehyde or with the shellac-formal itself, appears to proceed differently as has been pointed out earlier, the melamine reacting at the formal grouping and not at the carboxyl.

This conclusion is supported by the fact that whereas melamine does not combine with the esters of lac (where the carboxyl is "protected" by ester formation), the lac esters do combine with melamine in the presence of formaldehyde giving rise to soft sticky resins which, however, become tack-free on prolonged baking. The tack-free films are, however, brittle.

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