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Shellac modification with urea

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IN small proportions, urea behaves as an efficient accelerator for shellac, about 11 per cent on the weight producing the most rapid curing. With larger proportions, it behaves as a retarder. With 33 per cent and above of urea on the weight of shellac, the two can be heated together for any length of time without gelling. The acid value and water solubles content progressively decrease, and after 20 hours of heating at 165°C, a "permanently" thermoplastic resin of low acid value is obtained which can be further modified, if desired, by cooking with the calculated quantities of fatty acids of drying and non-drying oils. Film properties of none of the products however, show any worth-while improvement over those of the parent shellac, particularly in regard to blush resistance.

THE maximum use of shellac has been in the fields of surface coatings and plastics. But its low softening point and poor water resistance have been serious handicaps for maintaining its position in the face of newer synthetic resins of specialised performance. Several attempts have been made to overcome these limitations by modifying shellac with curing agents or accelerators. Of the several investigated, urea is one of the most efficient and the cheapest.[1]

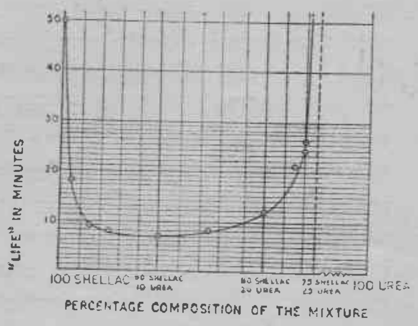

Fig 1

LIFE UNDER HEAT OF SHELLAC MIXED WITH UREA

Presence of as low as 5 per cent of urea brings down the polymerisation (curing time) of shellac from 75 minutes to 8 minutes at 150°C. Addition of urea also increases considerably the viscosity of shellac spirit varnishes. If more than 3 per cent of urea is present, the varnish sets into a gel. Shellac varnishes containing about 3 per cent (on the weight of lac) of urea also produce films of improved heat and blush resistance.[2] Thus, on all accounts, urea behaves as an efficient accelerator or curing agent. It is, therefore, surprising that a patented composition[3] contains 50 to 100 per cent of urea on the weight of lac and the two are fused together at 150°C-165°C for one hour. As smaller proportions would have polymerised the lac much sooner, the presence of large proportions of urea obviously behave differently. It would be very surprising, if such large quantities of urea went into reaction completely with lac during the one-hour treatment, leaving no water soluble matter in the reaction product which would be a source of trouble in any use for which the latter is intended to be put.

As urea is a very attractive modifying agent for shellac in view of its easy availability and cheapness, and as it, apparently, behaves differently in smaller and larger proportions, it was considered desirable to make a systematic study of the modifications of lac with urea especially with larger

TABLE 1

Life under heat (curing time) of shellac at 150°C ± 5°C in presence of urea

Sl. No.	Composition of mixture Shellac g.	Urea g.	Proportion of urea on the weight of the lac — per cent	Life — Minutes
1	10	0.0	0.0	50
2	9.9	0.1	1.01	18
3	9.75	0.25	2.56	9
4	9.5	0.5	5.26	8
5	9.0	1.0	11.1	7
6	8.5	1.5	17.6	8
7	8.0	2.0	25.0	12
8	7.7	2.3	29.8	21
9	7.6	2.4	31.5	22
10	7.57	2.43	32.1	23
11	7.52	2.48	32.9	Does not polymerise
12	7.5	2.5	33.3	—do—
13	7.0	3.0	42.8	—do—
14	6.0	4.0	66.6	—do—
15	5.0	5.0	100.0	—do—

proportions, as smaller proportions have already received considerable attention.

Effect of urea on curing time of shellac

In the first stage, the life under heat of shellac mixed with varying proportions of urea from very small to very large proportions was determined at 150°C±5°C. It was seen (Table 1 & Fig. 1) that there is a very rapid drop in curing time in the initial stages and that with about 10 per cent urea on the weight of the mixture, (or 11.1 per cent on the weight of lac), the curing time is the minimum viz. about 7 or 8 minutes as against 50 minutes in the absence of urea. It was also seen that further increase in the proportion of urea increases the curing time, and it starts behaving as a retarder. It was also seen that with about 24 per cent of urea in the mixture, the curing time is about 23 mins. but that with about 24.8 per cent (i.e. 32.9 per cent on the weight of shellac), the mixture does not polymerise at all. Obviously beyond this proportion, shellac and urea can be heated together for any length of time (for any reaction that may take place between them) without fear of gelling. This proportion works out to 5.5 mols of urea per mol of lac, assuming an average molecular weight of 1,000 for the resin.

As urea is a very water sensitive material and somewhat hygroscopic, the effect of the associated moisture, if any, on the curing time was next investigated. Lac and dry urea in various proportions were taken and various amounts of water added to the mixture, and the life under heat then determined. It was found that the change in the curing time due to the water added was only of the order of 2 to 3 minutes. The effect of moisture obviously is insignificant.

Shellac-urea combinations

The nature of the reaction products obtained by heating together shellac and 33 per cent of its weight of urea, as well as double and treble this proportion at different temperatures for different periods, was next examined. For the sake of convenience, three parts of shellac and one, two and three parts of urea were used. Urea was taken in a glass or stainless steel beaker kept in an oil bath at 150°C±5°C. and allowed to meet completely. Then shellac in powder form was gradually added in small lots keeping the melt mechanically stirred. Immediately after addition of each lot, the lac appeared to polymerise but later gradually went into solution. It was also found that fully polymerised lac dissolved readily in molten urea and behaved in a similar way. After addition of all the lac, samples were removed at known intervals and the acid value and water solubles determined in each. It was seen that both these progressively decreased with increase in time of heating.

The experiments were repeated at 165°C and 180°C. At 150°C, reaction was comparatively slow and the product appeared greasy The products obtained at 180°C were partly insoluble in spirit or other organic solvents or their mixtures. At 165°C, the reaction was smooth and the product completely soluble in spirit. The products obtained using 50 and 100 per cent urea on the weight of lac were also softer than with 33.3 per cent (and consequently less suitable for possible use in surface coatings), the softness increasing with increasing proportions of urea. Therefore, further studies were restricted to the reaction temperature of 165°C and to the proportion of three parts of shellac to one of urea, which is the smallest quantity of the latter which can be treated with shellac at high temperatures for long periods without any risk of gelling.

The chemical constants of the products obtained were then determined. As water solubles in the products would be undesirable for most uses, they were also removed by washing the products with water, and the constants of the residue also determined. It was seen (Table 2) that the acid value and

TABLE 2.

Properties of the reaction products of shellac heated with a third of its weight of urea for different periods at 165°C±5°C.

Sl. No.	Duration of of heating hours	Properties of the product		Properties of the product after washing free from water solubles		
		A.V.	Water solubles per cent	A.V.	Melting point °C.	Nitrogen content, percent
1	1	26.87	23.16	35.95	122-125	—
2	3	21.95	11.08	33.68	105	—
3	4.5	20.43	8.08	28.76	100	—
4	10	11.35	6.08	18.16	—	—
5	20	7.81	5.80	12.54	98	8.5

water solubles contents of the product steadily decreased with progressive heating and that they reached very low figures (7.81 and 5.80 per cent respectively) after 20 hours of heating. It was also found that the drop in the values was not appreciable after 10 hours of heating, being of the order of only 3.54 and 0.28 per cent respectively during the subsequent 10 hours. It was thus clear that further heating would not be of any practical utility.

Acceleration of reaction

As 20 hours is a long reaction period for practical purposes, the possibility of accelerating it was investigated. As it has been seen that high temperature was not satisfactory, catalysts were tried. Both acidic and basic catalysts were used viz. p-toluene sulphonic acid and α-naphthylamine, but neither of these produced any noticeable acceleration.

Properties

The product obtained after 20 hours of heating was a hard brittle mass with a melting point of 78°C. After removing the water solubles (5.8 per cent), the melting point increased to 98°C. It was completely soluble in alcohols but only partially in aromatic hydrocarbons, esters, ketones etc. and was thus similar to the parent shellac in solubility characteristics in organic solvents. It was however, almost insoluble in aqueous ammonia and other mild alkalies, quite understandably, because of its low acid value. Boiling with strong caustic alkali, however, readily released ammonia. In the case of the material freed from water solubles, this amounted to the equivalent of 8.5 per cent of nitrogen, that is 18.24 per cent of combined urea. The product showed considerable tendency to soften in contact with water.

Film properties

Films were prepared from alcoholic solutions by flowing on tin panels and glass slides and allowing to stand in an almost vertical position. Air dried films were moderately hard and glossy but blushed very badly and almost instantly on immersion in water. On baking at 100°C, there was no worth-while improvement. On baking at 150°C, film continuity was lost and a number of pin holes developed, although the blushing tendency under water was eliminated. Use of solvent mixtures in place of alcohol alone as well as with incorporation of plasticisers did not improve the varnish in any way.

Modification of varnish

The varnish (in alcoholic solution) was therefore further modified by boiling under reflux with paraformaldehyde to the equivalent of 1 and 2 molecules of formalin per mol of combined urea. The resulting varnishes produced clean homogeneous films which remained as such on baking and were also hard, flexible and water resistant and almost similar to those of shellac varnish modified by the addition of spirit soluble urea/formaldehyde resin.[4] [5]

Modification of resin

It will be seen that unlike the parent lac, lac modified by heating with a third of its weight of urea at 165°C for 20 hours, can be further heated for any length of time without fear of gelling. This material had still free hydroxyls to the extent of 4.97 per cent (hydroxyl value being 163.9). The possibility of modifying these by esterification with the calculated quantities of fatty acids of drying and non-drying oils was therefore investigated in order to improve the drying and flexibility of the resulting films.

It was found that when the material was heated together with the fatty acid under mechanical stirring at 180°C, esterification proceeded smoothly, rapidly at first and more slowly later, to produce esters of low acid values. The esterification was considerably accelerated by catalysing with 0.5 per cent p-toluene sulphonic acid. All the esters were found to be tough elastic masses soluble in alcohol but not in aliphatic or aromatic hydrocarbons. Alcoholic varnishes produced clear homogeneous films which retained their appearance, flexibility and gloss on baking but their water resistance was still not satisfactory. Incorporation of cobalt drier into the drying oil fatty acid modified material made some difference.

Heating of shellac with excess of urea for short duration

It will be seen that despite its low acid value and water solubles content, the material obtained by heating shellac with a third of its weight of urea at 165°C for 20 hours, freed or not from water solubles content, has not shown much promise as a surface coating material.

It may have other possible uses particularly because of its permanent thermo-plasticity. The possibility of improving the prospects of the material in surface coatings was next investigated by limiting the duration of heating to the minimum to obtain complete (alcohol) solubility. It was found that if the heating was continued only for about two hours, the modified product became completely soluble in alcohol and, unlike the earlier product, in aqueous ammonia also, although the water solubles content was necessarily excessive (about 15-20 per cent). This material had an acid value of 23.8 and melting point of 80 to 85°C and after freeing from water solubles, they were 30.95 and 92 to 105°C respectively. Both spirit and aqueous varnishes could be made of both the materials. Study of the film properties of the spirit varnishes, with and freed from water solubles, revealed that the air dried films were distinctly inferior to those of the parent lac in regard to adhesion, scratch hardness and blush resistance. Baked films of both, however, were more or less like those of the parent lac.

In regard to aqueous varnishes, the viscosity of a 25 per cent solution of the materials was so high that the varnishes set to a gel on cooling to room temperature. Clear homogeneous solutions were obtained at lower concentrations but the films obtained were necessarily thin. Water thinnable varnishes of workable viscosity producing good films were obtained by replacing part of the water with ethyl alcohol. A typical varnish was produced by dissolving 10 parts of resin in 10 parts of spirit and diluting the varnish with stirring with a solution of 1 part of ammonia (d 0.88) in 19 parts of water. Varnishes of the parent lac similarly made flaked off completely from glass and tin panels whereas those of the modified resin showed better adhesion although elasticity was still far from satisfactory.

Apparently, modification of lac with large proportions of urea under the above conditions does not produce any worth-while improvement for use in surface coatings. The only result is the formation of a "permanently" thermoplastic resin which should be capable of further modification without fear of gelling.

References

1 Ranganathan S & Aldis R.W., Indian Lac Res. Inst., (1936), Bull No. 14.

2 Venugopalan M., Ranganathan S. & Aldis R. W., Indian Lac Res. Inst., **Res. Note**. No. 14 (1934).

3 Bassford H. H. (Jr.), **U.S. Pat.** 2,387,048/1945 (to U.S. Shellac Importers' Assoc.).

4 Legrand B., **French Pat. 861,185**, 3 Feb., 1941.

5 Shravan Kumar & Sankaranarayanan Y., **Paintindia, 15, (1966)**, No. 1, 123.