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Shellac-Dimethylolurea Moulding Composition

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A method for the preparation of a moulding powder composition using shellac and dimethylolurea has been described. The shellac-dimethylolurea moulding composition, whose moulding characteristics are as good as that of lac-urea-formaldehyde powder, is much cheaper to produce because it can be prepared by the dry method which does not require the use of any solvents or machinery other than a pair of hot rollers.

SHELLAC is a thermoplastic resin which, on prolonged heating, slowly polymerizes to an infusible, insoluble product. Based on this property of slow heat polymerization of shellac, various attempts[1-7] have been made to convert it into a thermosetting resin that can cure quickly. So far only partial success has been achieved in this direction. Ranganathan and Aldis[8] observed that many chemicals including urea harden shellac quickly under heat treatment. Ranganathan[6] actually utilized this observation to prepare shellac-urea moulding powders by the wet process, but the compositions were not mouldable by the bakelite technique. Later on, Venugopalan and Sen[7] formulated an improved composition by reacting shellac, first with formaldehyde and then with urea in alcoholic solution. Moulding compositions thus prepared could be moulded hot and ejected hot. Since the process as a whole was rather complicated, time-consuming and costly, attempts were made to evolve an improved process involving the use of the dry[9] instead of the wet method. But attempts to incorporate urea into the reaction product of shellac and formaldehyde (termed 'shellac-formal') by the dry method, i.e. by passing the mix between steam-heated mixing rollers, resulted in premature curing. It was, however, thought that the dry method could be used and the process also improved, if, instead of proceeding separately with formaldehyde and urea, a direct reaction of shellac with dimethylolurea (DU), itself a product of reaction between formaldehyde and urea, were utilized. The present paper reports results of investigations along these lines.

Materials and methods

Shellac — Ordinary shellac having the following properties was used: life (polymerization time) at 150°C., 47 min.; flow, 75 sec.; wax content, 4·20 per cent; and carbonyl value, 17·3.

Dimethylolurea — As commercial DU was not available at the time of starting the investigation it was prepared in the laboratory according to the procedure employed by Einhorn[10,11]. Barium hydroxide (0·4 g.) was dissolved in formaldehyde solution (37·4 per cent; 26·7 g.) to which was added urea (10 g.). The mixture was maintained at 25-30°C. until all the formaldehyde had reacted. On completion of the reaction, carbon dioxide was passed into the solution for 10-15 min. after which the liquid was evaporated to dryness in a desiccator. The dried residue was extracted with warm 80 per cent ethyl alcohol and the solution filtered; on cooling, 10 g. of DU (m.p. 126°C.) crystallized out. DU thus prepared was used in preliminary experiments by the wet process for the determination of the optimum amount of DU necessary for successful moulding compositions, conditions of moulding, etc. Subsequently the commercial product was available which was used in further experiments. It may be noted, however, that both the commercial product and the laboratory-made sample deteriorate slowly on storage during the first six months, and rapidly thereafter, becoming more and more insoluble in alcohol.

Methods of preparation of the moulding powder

Wet process — The wet method of preparing the standard lac-urea-formaldehyde (L-U-F) moulding powder[12] was adopted in the case of shellac-DU compositions (S-DU). Shellac (100 g.) was mixed with varying amounts (0-35 g.) of DU and refluxed with methylated spirit (200 ml.) at 130-40°C. for 3 hr on an oil bath. *Haldu* (*Adina cordifolia*) wood flour (100 g.) and aluminium stearate (2 g.) were then

TABLE 1 — MOULDING TRIALS WITH DIFFERENT PROPORTIONS OF DU (WET METHOD)

DU used *g./100 g. shellac*	Moulding quality	Hot alcohol-insolubles of the moulded product %	Cold alcohol-insolubles of the moulded product %	Impact strength *cm. kg./sq. cm.*	Remarks
5	Bad	—	—	—	Too soft; blisters found on moulded articles even after prolonged baking at 90-95°C. for 6 hr
10	do	42·60	73·15	3·07	Soft during ejection
15	Good	53·17	76·80	4·17	Satisfactory moulding at 140°C., 1 ton/sq. in. pressure and 3 min. moulding time
20	do	59·58	81·42	4·19	Satisfactory moulding at 140°C., 1·5 tons/sq. in. pressure and 3 min. moulding time
30	do	70·30	84·10	4·19	do
35	do	71·86	85·40	4·38	Satisfactory moulding at 140°C., 2 tons/sq. in. pressure and 3 min. moulding time

added. The resulting composition, after drying at room temperature, was powdered to 80 mesh and baked at 90-95°C. for 2 hr before putting it into moulds. The results of moulding trials are given in Table 1.

It will be seen from the results presented in Table 1 that as the amount of DU per 100 g. of shellac is increased beyond 15 g., the moulding pressure goes on increasing without, however, any improvement in the impact strength. The optimum amount of DU per 100 g. of shellac may, therefore, be taken as 15 g. It is to be noted that compositions obtained with this proportion of DU could be satisfactorily moulded even without the help of any modifier. A large sample containing this proportion of DU was prepared to study the optimum time, temperature and pressure necessary for satisfactory moulding. In determining these conditions, it should be remembered that from the production point of view the time required for moulding should be as short as possible. Further, the better the moulding powder, the less soluble should it be in alcohol after moulding, as a result of chemical transformation in course of curing. In Table 2 are given the solubility of the original powder and the moulded product in hot and cold alcohol under varying conditions of moulding.

It will be observed from the results given in Table 2 that while other conditions were varied the curing time was kept at 3 min., since this was found to be optimum in this as well as in the case of the standard L-U-F powders. Similarly the optimum pressure and temperature of moulding were respectively 1·5 tons/sq. in. and 140-50°C. The hot alcohol-insolubles content in the moulded product (composition 30-35 g. of DU per 100 g. of shellac) was higher, but the slight increase is more than counter-balanced by the increased cost of DU. Hence for all practical purposes the use of 15 parts of DU per 100 parts of shellac has been considered to be the optimum. This agrees closely with the previous findings in the case of L-U-F moulding compositions (unpublished data), namely that, although 15 per cent urea and 50 per cent formalin on the weight of lac gave the best moulding compositions, the optimum amounts of urea and formalin required for satisfactory moulding were 9 and 25 per cent respectively.

TABLE 2 — HOT AND COLD ALCOHOL-INSOLUBLES IN MOULDED COMPOSITIONS

Moulding conditions			Hot alcohol-insolubles %	Cold alcohol-insolubles %
Pressure *ton/sq. in.*	Curing time *min.*	Temp. *°C.*		
Original powder (without treatment)			42·41	75·47
1·0	1	140	43·12	74·35
1·0	2	140	44·36	75·46
1·0	3	140	53·17	76·80
1·5	3	140	53·87	81·19
1·5	3	150	57·21	81·59
2·0	3	140	57·99	81·50
2·0	3	150	57·61	80·50

Dry process — Having established the optimum conditions for the wet process, the optimum conditions for the dry process were determined. For this, all the ingredients used in the wet process, with the exception of methylated spirit, were intimately mixed between hot rollers (90-95°C.) for 10 min. The hot-rolled mass was taken out in sheet form, powdered

TABLE 3 — MOULDING TRIALS WITH SHELLAC-DU (AGED) MOULDING COMPOSITION WITH DIFFERENT MODIFIERS

Modifier *g./100 g. shellac*	Duration of hot rolling at 90-95°C. before addition of modifier *min.*	Duration of hot rolling after addition of modifier *min.*	Duration of baking at 90-95°C. for blister-free moulding *hr*	Moulding characteristics of composition moulded at 145°C., 1·5 tons/sq. in. pressure for 3 min.
Control	20	—	9	Soft composition with blisters; sticks to mould and unsuitable for hot moulding
Oxalic acid, 3·0	5	5	3	Blister-free moulding; very dull in appearance
Cinnamic acid, 3·0	10	2	3½	do
Phthalic anhydride, 3·0	10	16	4	do
Maleic anhydride, 3·0	10	13	3	Does not fuse properly; sticks to mould
Maleic acid, 0·5	10	20	7½	Composition rather soft for hot moulding
Maleic acid, 1·5	10	12	3	Hard composition; blister-free moulding; dull in appearance
Maleic acid, 3·0	10	6	1½	do
Lime, 1·0	10	2	6½	Very good gloss and flow, but had blisters which could not be cured by longer baking
Maleic acid, 1·0 + lime, 1·0	10	10	2	Good gloss and flow; slightly soft composition
Maleic acid, 2·0 + lime, 1·0	10	8	1½	Good gloss and flow; composition suitable for hot moulding
Maleic acid, 3·0 + lime, 1·0	10	8	1½	Good gloss and flow; composition suitable for hot moulding; gloss slightly inferior to preceding composition 11; suitable for hot moulding

TABLE 4 — MOULDING CHARACTERISTICS OF COMPOSITIONS WITH DU AGED FOR DIFFERENT PERIODS

Sl No.	Duration for which DU was aged	Modifier (on the wt of shellac)	Duration of hot rolling *min.*	Duration of pre-heating at 90-95°C. for blister-free moulding *min.*	Impact strength *cm. kg./sq. cm.**	Moulding characteristics of compositions moulded at 145°C. at 1·5 tons/sq. in. pressure for 3 min.
1	Freshly prepared (alcohol-soluble)	nil	5	120	4·30	Satisfactory moulding
2	do	Maleic acid, 2%; CaO, 1%	10	45	4·33	Satisfactory moulding; slightly better gloss and flow than No. 1
3	One year (partially alcohol-soluble)	nil	12	120	—	Could not be properly moulded; soft composition
4	do	Same as in No. 2	15	60	4·33	Satisfactory moulding
5	Two years old (alcohol-insoluble)	nil	20	120	—	Could not be properly moulded; soft composition which sticks to mould
6	do	Same as in No. 2	18	90	4·33	Satisfactory moulding
7	Above three years (alcohol-insoluble)	nil	15	300	—	Very soft composition which sticks to mould; unsuitable for moulding
8	do	Same as in No. 2	47	180	4·20	Soft and sticky composition; moulding unsatisfactory

*Impact strengths for compositions which could not be properly moulded were not determined.

and pre-heated before moulding. The compositions thus obtained did not differ materially either in respect of moulding characteristics or properties of moulded products from those prepared by the wet process.

To explore the commercial possibilities of this process, moulding compositions were prepared employing the commercial grades of DU (15 parts per 100 parts of shellac) which was almost insoluble in alcohol. These compositions were found to be rather soft and hence unsuitable for moulding by the bakelite technique. Known methods of hardening, e.g. longer heat treatment during mixing between hot rollers, pre-heating before putting in moulds, or reaction with higher amounts of DU (30 parts), did not improve their moulding characteristics. On the other hand, identical compositions made with freshly prepared DU (alcohol-soluble) were quite satisfactory in all respects. In practice, however, the moulding compositions prepared should be based on the use of commercial or aged DU. To achieve this, various modifiers were tried, taking the following composition as the basis: shellac (100 parts), *Haldu* saw dust (100 parts), DU (stored for one year and alcohol-insoluble) (15 parts), aluminium stearate (3 parts), and pigment (4 parts). The ingredients were mixed between hot rollers at 90-95°C. and various modifiers added. Hot rolling was continued till the compositions left the rollers and came out in a sheet form. Of the various modifiers tried, the results obtained with the promising ones are given in Table 3.

It will be seen from the results of moulding trials given in Table 3 that with a single modifier, the moulded product was either dull in appearance or soft with blisters. Thus maleic acid, though promising, gave dull products; similarly lime imparted gloss but blisters appeared which could not be eliminated even by longer pre-heating. However, by incorporating a mixture of maleic acid and lime in the respective proportions of 2 parts and 1 part per 100 parts of shellac, satisfactory products could be obtained; the baking period for obtaining blister-free mouldings of such a modified composition was also found to be much shorter (1·5 hr). It may be mentioned that during hot rolling no smell of formaldehyde was noticed.

Since the transformation of DU on storage from alcohol-soluble to alcohol-insoluble form progresses with time, several types of DU, aged for different periods, were used. The results of moulding trials with these compositions, with or without modifiers, are given in Table 4.

The results given in Table 4 show that DU stored for two years may conveniently be used in combination with a modifier. Further, the use of modifiers along with freshly prepared (alcohol-soluble) DU, which by itself ensures satisfactory moulding, results in slightly improved compositions requiring much less baking time. The properties of such compositions (Table 5) are also comparable with those of standard L-U-F compositions prepared by the wet method using methylated spirit as solvent.

TABLE 5 — PROPERTIES OF MOULDING COMPOSITIONS

PROPERTY	STANDARD L-U-F COMPOSITION	S-DU COMPOSITION	S-DU COMPOSITION WITH MODIFIER
Sp. vol. of moulding composition (25 g.), ml.	47	48	48
Impact strength of moulded articles, cm. kg./sq. cm.	4·8	4·3	4·7
Water absorption of moulded articles (24 hr), %	0·97	1·20	0·98
Heat resistance of moulded articles (Marten's oven), °C.	82	82	82
Dielectric strength of $\frac{1}{8}$ in. thick specimen, V./mil	450	—	428
Surface resistivity at 3% humidity, ohm/cm.	$3{\cdot}2\times10^{15}$	—	$3{\cdot}0\times10^{15}$

Discussion

The efficiency of urea in reducing the polymerization time of shellac is well known. In the absence of any solvent, the rate of polymerization of shellac with urea is rapid and during hot rolling (90-95°C.), even if shellac had been pre-treated with formalin, the rate of polymerization becomes uncontrollable, and infusible products are obtained. On the other hand, DU has been found to have a milder reaction and the polymerization of shellac proceeds at a reasonably slow rate so that shellac-DU moulding compositions, almost as good as the standard L-U-F compositions, can be prepared by the dry method (Table 5).

One apparent disadvantage of DU is its tendency to undergo a sort of progressive change on storage under tropical conditions, as is evident from its gradual transformation from alcohol-soluble to alcohol-insoluble condition. This means that the use of commercial-grade DU, stored for varying periods, might give bad or non-uniform compositions. However, the use of modifiers (2 per cent maleic acid and 1 per cent lime on the weight of shellac used) practically eliminates this difficulty and gives successful moulding compositions, provided the age of stored DU does not exceed two years (Table 4). It is

interesting to note that shellac-DU moulding compositions have much better keeping properties than DU itself; a moulding composition made with freshly prepared DU and stored for more than three years showed uniform moulding characteristics during the whole period of storage. In view of the satisfactory keeping quality of shellac-DU moulding powders, it would be worthwhile to utilize fresh DU in the manufacture of shellac-DU moulding powders, and at the same time incorporate modifiers so that the powders would have uniform moulding properties for durations as long as three years or more. The preparation of DU for this purpose should not prove difficult, since as stated earlier, the method is simple and needs no elaborate equipment or costly machinery. A further point of interest is that, as subsequent investigations have shown, the process of making DU need not be continued till the crystals of DU are obtained, but that the solution obtained by adding urea in a solution of formalin and barium hydroxide may be straightway used in place of DU. This greatly simplifies the manufacturing process.

In conclusion it may be stated that, with respect to the quality of the powder, or the performance of the moulded product, there is little to choose between S-DU composition prepared by the dry method or L-U-F moulding composition prepared by the wet method. Since solvents and machinery such as kneading and mixing machine, solvent recovery plant, etc., are not required for the preparation of S-DU — the only machine to be used is a pair of hot rollers—it can be prepared quickly, thereby lowering the overall cost of its preparation. The S-DU composition should, therefore, be preferred to the standard L-U-F powder on grounds of economy.

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