THE HEAT CURING OF SHELLAC

PART II.

"DEPOLYMERISATION"

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In the first part of this paper (6) it was indicated that the process of heat 'curing' of shellac was considerably retarded by pressure. In view of the significance of this with respect to the practical utility of shellac it was considered desirable to investigate the phenomenon further.

Preliminary experiments were conducted on the effect of heating shellac in an autoclave under varying conditions of pressure and temperature. The interesting observation was recorded that heat 'cured' shellac and old infusible shellac could be reconditioned and rendered soluble in alcohol if heated under suitable conditions. Some of the possibilities which are opened up by such a process have been examined in this paper.

Experimental.

Depolymerisation of 'Cured' Shellac.—When shellac is heat 'cured' up to the stage when it is 'rubbery' while hot, it is never completely insoluble in alcohol. The amount of insolubles may vary over a wide range depending on the conditions of heating. Rapid heating without stirring may give a 'cured' shellac with an insoluble content as low as 30%. Complete insolubility is, of course, never obtained owing to the presence of the ether-soluble resin which is non-heat-convertible. To obtain a sample of 'cured' shellac with a reasonably high 'insolubles', it was found convenient to heat small batches of 40—50 gms. with stirring until 'cured', finally powdering and mixing.

High insolubles can be readily obtained by baking 'cured' shellac but this introduces complications which will be discussed later.

The sample of 'cured' shellac prepared as described above was analysed for 'alcohol insolubles' by the usual method (A. S. T. M.) and heated in an autoclave under varying conditions of temperature and pressure. In a few trial experiments it was indicated that certain precautions were necessary, *e.g.* (*a*) the sample should not be heated in a narrow tube which did not encourage condensation of, and give free access to, moisture, (*b*) the steam pressure should not be too rapidly released since this results in the autoclave cooling more rapidly than the sample, leaving it at an elevated temperature under atmospheric pressure which, of course, results in the shellac again polymerising, (*c*) the air should be expelled from the autoclave by allowing steam to escape for a short period before closing. In all subsequent experiments these precautions were taken. To ensure sufficient moisture being present, the samples were immersed in water.

After treatment in the autoclave the samples were dried in a desiccator for 48 hrs. and the alcohol insolubles determined. The results obtained are indicated in Table I.

TABLE I.

Steam pressure in Kilos/Sq.cm.	Steam temperature in °C.	Time of heating in minutes.	Alcohol insolubles %.
1. Control	—	—	60·6
2. 5	148	10	25·6
3. ,,	,,	20	13·5
4. ,,	,,	30	9·3
5. ,,	,,	40	6·5
6. ,,	,,	50	3·8
7. ,,	,,	75	1·3
8. ,,	,,	120	2·2
9. 10	174	10	6·2
10. ,,	,,	20	3·6
11. ,,	,,	30	2·5
12. ,,	,,	40	2·0
13. ,,	,,	60	2·9
14. ,,	,,	90	0·45
15. 15	193	10	2·8
16. ,,	,,	20	1·9
17. ,,	,,	30	1·5
18. ,,	,,	45	1·5
19. 20	208	10	1·8
20. ,,	,,	15	1·1
21. ,,	,,	20	0·56

It will be seen from the table that it is possible to obtain a 'depolymerised' lac with an insoluble content of only 0·5% by choosing suitable conditions. It is also interesting that, although not complete, there is considerable depolymerisation at low pressures such as 5—10 atmospheres.

Depolymerisation of 'Baked' shellac.—The above experiments refer only to shellac which has been heated up to the 'cured' stage *i.e.* the stage at which it is 'rubbery' while hot. If heated for longer periods the shellac slowly loses this 'rubbery' texture and changes to a material which is hard and crisp while hot. This change from rubbery while hot to hard while hot is a slow one and is accompanied by a small continual loss in weight. This small loss in weight may continue for a long time *e.g.* 3 gms. of shellac heated at 180°C had not come to constant weight after 800 hrs.

The possibility of depolymerising shellac which had been heated past the 'cured' stage, *i.e.* 'Baked' shellac, was accordingly examined.

Samples of shellac were baked at different temperatures. At intervals, a small sample was removed from the oven and autoclaved for 20 minutes at 20 atmospheres. After a certain time, depending on the temperature of baking, it was found that this amount of autoclaving was insufficient to depolymerise the shellac to a fusible resin. The results are indicated in Table II.

TABLE II.

Temp. of baking.	100°C	130°C	180°C	210°C
Hours of baking to resist autoclaving at 20 atm. for 20 mins.	170 hrs.	31 hrs.	$\frac{3}{4}$ hr.	$\frac{1}{4}$ hr.

If the samples were baked for longer intervals than those indicated in the table, the time of autoclaving had to be increased to effect depolymerisation. A few results are indicated in Table III.

TABLE III.

Temp. of baking.	Time. of baking.	Time of autoclaving at 20 atmos.
210°C	½ hr.	¾ hr.
	1 ,,	1 ,,
	1½ ,,	1½ ,,
	2 ,,	2 ,,
	3 ,,	2½ ,,
	4 ,,	3 ,,
	5 ,,	3½ ,,
245°C	½	2
	1	2½
	1½	3½

It will be seen that over the small range of baking conditions examined the shellac can always be depolymerised if autoclaved for sufficient time.

It must be pointed out, however, that shellac baked for 300 hrs. at 210°C cannot be considered completely hardened. It will be realised, therefore, that this table is very incomplete and gives scope for considerable further investigation.

Effect of accelerators.—In the first part of this paper (6) it was indicated that a number of chemicals were capable of accelerating the heat 'curing' of shellac. A number of samples were prepared by heating shellac up to the 'cured' stage in the presence of accelerators. All these samples were readily depolymerised by autoclaving at 20 atmospheres for 20 minutes. No accelerator has yet been found which can prevent this depolymerising effect.

"Porous" Moulds.—This phenomenon of depolymerisation offers a ready explanation for the big retarding effect of pressure on the heat hardening of shellac. Presumably the water given off in the early stage of the 'curing' of shellac is sufficient to produce autoclave conditions in the mould and tends to depolymerise the shellac. Equilibrium is set up and the sample can be heated for many hours with no apparent effect.

The effect of removing this water during the heat treatment of shellac in the mould has been examined. A mould was prepared with a porous base of "Plaster of Paris". Moulding powders containing shellac and accelerators such as urea and rosolic acid were heated for a few minutes at 170°C and 1 ton./sq. in. pressure. On opening the mould the samples were found to have hardened and could be ejected while still hot. The samples were not sufficiently hard, however, to prevent deformation if ejected when too hot. Prolonged heating in the mould could not overcome this difficulty.

Effect of dry pressure.—The need for free access to water during heating in the autoclave has already been mentioned. To demonstrate this further, a sample of 'cured' shellac was dried and heated in a closed mould under pressure. Many hours of such heat treatment produced no sign of depolymerisation. A sample of 'cured' shellac was moistened with water and heated in a closed mould. This shellac showed signs of softening but was not completely depolymerised. Apparently quite an appreciable amount of water is required for complete depolymerisation. This is understandable since as much as 5% of the weight of shellac may be lost during the 'curing' process, and this presumably has to be replaced. Evidence for this view was obtained by weighing a sample of shellac before 'curing' and again after depolymerising and drying by desiccation. No appreciable change in weight was observed.

Properties of Depolymerised Shellac.—The quality of the shellac obtained by depolymerisation was next investigated. A fresh sample of good quality shellac was 'cured' as described above and then 'depolymerised' by autoclaving at 20 atmospheres for 20 minutes. The sample was dried by desiccating for 48 hrs. and then subjected to the usual shellac analysis. The results are indicated in Table IV.

TABLE IV.

	Control.	Depolymerised.
Alcohol insolubles % (A. S. T. M).	0·68	1·24
Wax % (McIlhiney)	2·82	2·67
Iodine value (Wijs)	14·11	19·85
Acid value	64·96	80·90
Fluidity in secs. (Vickers)	106	183
Life under heat at 180°C (6)	38	18
Colour index	8·6	15·6
Bleaching test (c.c. bleach required)	100	162

It will be seen from the table that the shellac has been modified to a certain extent by depolymerisation. There is an appreciable increase in iodine and acid values. The colour is considerably darker as indicated by the colour index and more reagent is required to bleach it. There is also an appreciable shortening of 'life under heat'. This indicates that the 'ageing' property of the shellac might have been modified. The rate of change of fluidity with storage was accordingly examined.

Two samples were chosen, one depolymerised at medium pressure *i.e.* 10 atmospheres for 1½ hours and one at high pressure *i.e.* 20 atmospheres for 20 minutes. Two methods of drying were examined (*a*) drying in a desiccator (*b*) fusing and stirring at 120°C until a drop of the lac gave a hard bead when dropped on a glass plate. The fluidity of these samples w~~ere~~as examined periodically. The results are indicated in Table V.

TABLE V.

Time of storage.	Method of drying.	Fluidity (Metropolitan Vickers Method.)	
		Depolymerised at 10 atmos. for 1½ hrs	Depolymerised at 20 atmos. for 20 mins.
8 days	Fusion	375 secs.	232
28 ,,	,,	462	263
46 ,,	,,	514	272
100 ,,	,,	584	386
4 ,,	Desiccation	427	236
100 ,,	,,	700	286

The alcohol insolubles were determined before and after 100 days' storage and in each case showed a small increase. Results are shown in Table VI.

TABLE VI.

Sample.	Insolubles.	
	Before	After.
Depolymerised at 10 atmos. and fused	1·22	1·34
Depolymerised at 10 atmos. and desiccated	1·23	1·36
Depolymerised at 20 atmos. and fused	1·29	1·60
Depolymerised at 20 atmos. and desiccated	1·42	1·64

The results indicate that a certain amount of 'ageing' takes place *i.e.*, the shellacs are slowly re-polymerising. This 'ageing' is somewhat rapid in the case of shellac treated at the lower pressure but is not so serious in the case of the high pressure samples.

Another polymerised sample was treated at 20 atmospheres for 30 mins. and dried by fusing at 120°C. This had a high initial fluidity which decreased somewhat rapidly to a steady figure of about 200 secs. The progressive 'ageing' is indicated in table VII.

TABLE VII.

Time of storage in days ...	nil.	26	49	83	100	130
Fluidity (Metropolitan Vickers in secs.)	60	90	117	210	200	226

Undoubtedly this 'ageing' is somewhat more rapid than a normal shellac sample, but it is too early to estimate the full magnitude of the effect.

The varnishing qualities of depolymerised lacs were next examined. 4 lb. cut. varnishes were prepared from the samples and films made on glass slides by the spinning method, the conditions being adjusted to give approximately the same film thickness in each case. Results are indicated in Table VIII.

TABLE VIII.

	Control.	Depolymerised at 20 atmos.
1. Appearance of film	Light colour	Somewhat darker, better gloss.
2. Adhesion on glass	Good	Good.
3. Effect of water immersion	Milkiness after about 4 hrs.; adhesion fairly good.	Same as control.
4. Water absorption as % of wt. of dry film after 48 hrs.	11·8	9·8
5. Sward Rocker Hardness %.	56	56
6. Scratch Hardness after 4 days' drying.	1100 gms, clean scratch.	900 gms, slightly jagged scratch.
7. Abrasion factor after 4 days' drying.	267	296
8. Bending test.	Fairly long straight cracks; adhesion good.	Same as control.

It will be seen from the table that the change in varnishing properties due to depolymerisation is small.

Discussion.

The possibility of reconditioning polymerised shellac to a fusible and soluble resin has been demonstrated. Shellac therefore, apparently falls into the class of organic gels which include rubber, metastyrene, heat-converted alkyd resins, and heat converted drying oils which are capable of depolymerisation when heated under pressure (5).

A notable feature of the process in the case of shellac, however, is the part played by water. The usual explanation of the depolymerisation of these other gels is the production of high boiling decomposition products which solvate and eventually liquify the gel. In the case of shellac the reaction approximates more nearly to a reversible one :

$$\text{shellac} \rightleftharpoons \text{'cured' shellac} + \text{water.}$$

The possibility of some decomposition occurring and influencing the process under autoclaving conditions must not be overlooked. It is known that prolonged heating in air at 180°C or over decomposes shellac slowly and at least one constituent, *viz.*, shellolic acid, is known to decompose fairly readily at 202—203°C (4).

That this effect must be very small, however, is indicated by the negligible change in weight when shellac is 'cured' and then depolymerised.

The similarity in properties of depolymerised and ordinary shellac indicates how nearly this reaction may be considered reversible. The essential difference is the small increase in iodine and acid values. It is difficult to decide if these changes are produced during the curing process or during depolymerisation.

A small rise in iodine value by moderate heat treatment has been recorded (1) ; it is possible that this may amount to several units during the last stage of 'curing'. This unfortunately cannot be proved experimentally since the 'cured' shellac is insoluble in the reagents used. It is possible, therefore, that the increase in iodine value is due to a non-reversible unsaturation produced during the 'curing' process and is not an effect of depolymerisation.

A possible explanation of the increase in acid value is that the breakdown of the lactide and anhydride linkages during depolymerisation into carboxyl and hydroxyl groups is carried to a stage somewhat further than that of ordinary shellac and hence depolymerised lac may show greater free acidity.

The process of reconditioning shellac by autoclaving may possibly be of commercial importance. It appears to be superior to the other methods which have been recommended by this Institute (2) (3) in that all types of shellac, even 'baked' shellac, can be treated.

Used in conjunction with the solvent extraction process depolymerisation may have valuable use. An 'over-cooked' shellac may possibly be converted into a useful substance. Yield of shellac on solvent extraction may be increased by preliminary autoclaving.

It is reported that large stocks of Burma stick lac exist which have been stored so long that they are practically infusible and useless to the country shellac manufacture. The depolymerisation process suggests a means of dealing with this material.

In the phonograph industry old record stock may possibly be rendered more fluid and fusible by autoclaving.

Finally, it may be mentioned that in this paper conditions have been described which make the reaction of 'curing' and depolymerising as nearly reversible as possible. The effect of more drastic heat treatment and prolonged autoclaving has not been described. Interesting modifications of shellac may well result from such variations in the process.

Summary.

Shellac which has become infusible and insoluble by heating, age or chemical treatment can be converted into a material very similar to ordinary shellac by autoclaving under suitable conditions.

References.

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