

Fractionation of Shellac: Part I—Shellac-urea Complexes

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A simple process for the fractionation of shellac by progressive complex formation and precipitation by refluxing a mixture of shellac and urea in acetone is described. Shellac has been fractionated into six fractions by this procedure. Of these, five are solid fractions which are presumably derived from the pure resin portion. The sixth fraction, a honey-like mass, is derived from the soft resin portion. The solid fractions are soluble in alcohol and alkali but insoluble in diethyl ether, and show marked differences in their physical and chemical properties.

A reaction mechanism between urea and shellac is suggested in which urea reacts not only with the free aldehyde group but also with other groups in shellac.

THE chemical constitution of shellac has not yet been fully elucidated. Tschirch and Farner¹, and Farner² were the first to fractionate shellac into two fractions by means of diethyl ether. Harries and Nagel³, employing the same solvent, obtained an insoluble portion, 'pure resin', and a soluble portion, 'soft resin'; the latter had a honey-like consistency. Verman and Bhattacharya⁴ specially recommended the use of toluene and trichlorethylene which were less hazardous than diethyl ether; they called the insoluble portion 'hard resin'. Mild alkalies^{5,6}, salts of weak acids^{7,8} and various other organic solvents^{9,10} have also been recommended for the fractionation of shellac.

Bhattacharya and Heath⁵, from their work on the fractionation of shellac with mild alkalies, concluded that shellac is a mixture of several components with molecular weights varying from 300 to 3000, and that the components, which are more or less similar in chemical nature, are present in the form of an isogel. Their assumption was corroborated by the work of Schaeffer, Weinberger and Gardner⁹ who fractionated shellac by means of different solvents into six fractions having different chemical and physical properties. Two of these were ether-soluble and presumably constituted the soft resin while the rest constituted the pure resin. These results indicate that neither pure resin nor soft resin is a single component but a mixture of several components.

The present work was undertaken with a view to studying the fractionation of shellac in greater detail so that the chemical nature of shellac, in particular,

of the pure resin component on which the excellent qualities of shellac largely depend, may be better understood.

The method employed by Schaeffer *et al.*⁹ for the fractionation of shellac, though preferable to that of Bhattacharya and Heath⁵, is laborious and time-consuming. Also, the final removal of solvents from the individual fractions is not easy and their long contact with the solvents may also lead to some transformation^{3,11-14}. Actually two fractions of pure resin as obtained by Schaeffer *et al.*⁹ were insoluble both in alcohol and alkali, suggesting that some transformation had taken place.

Kamath *et al.*¹⁵ have described a new method of fractionation of shellac in which an ethanol solution of shellac is extracted with butyl alcohol-hexane mixture. They obtained fractions which differed in acidity and fluidity. They claimed their process to be more advantageous than that of Schaeffer⁹. But Kamath's process is apparently not entirely free from objection as it involves the use of a liquid-liquid system for fractionation, which, because of the partition coefficient coming into play, cannot be expected to yield pure individual fractions.

Venugopalan and Sen¹⁶ have observed that the pure resin is rendered insoluble in acetone by treating it with urea. This observation has been made use of in developing a method for the preparation of the pure resin. The method, though simple, requires four days for rendering the pure resin completely insoluble. The present author has observed that by refluxing on a water bath a mixture of any variety of shellac or even seedlac and urea,

the urea complex of pure resin separates completely as a voluminous mass in about 2.5 hr. This finding has been utilized for the fractionation of the pure resin of shellac by progressive precipitation of the urea complex from acetone solution.

However, since urea is known to form complexes with straight-chain hydrocarbons, acids, alcohols and esters, dewaxed decolourized shellac has been used in the present work to guard against the possibility of urea combining with the wax-alcohols and esters of shellac. The optimum quantity of urea to be used in the reaction has been found to be 7-8 per cent on the weight of shellac^{16,17}. In the present study 8 per cent of urea on the weight of shellac has been employed.

Experimental procedure

Dewaxed and decolourized shellac (200 g.) was dissolved in acetone (1 litre) (A.R., B.D.H.; moisture content, 1 per cent) by warming. A solution of urea (16 g.) (B.D.H.) in acetone (500 ml.) containing a few drops of water was prepared by warming the mixture. These two solutions were mixed together and refluxed on the water bath. After about 15 min. a solid separated (first fraction) which was immediately filtered off through cotton wool. The filtrate gave a second solid product (second fraction) on slight cooling and a third product (third fraction) on cooling to room temperature. The mother liquor was again refluxed for a further period of 2 hr and on cooling overnight, it gave a solid fraction (fourth fraction). These solid fractions were finely powdered, placed inside separate packets and extracted together with acetone to remove the adhering soluble resin; on cooling the extract to room temperature a precipitate separated (fifth fraction). The acetone solutions (the one left after separation of the fourth fraction, and the other left after separation of the fifth fraction) were mixed and, on removal of acetone, yielded a honey-like thick syrup (sixth fraction). To remove the combined urea, the first and the second fractions were heated with boiling water under pressure, while the

remaining fractions were repeatedly washed with boiling water.

Results

The percentage yield, and the physical and chemical properties of the urea-free fractions are given in Table 1. Nitrogen was absent in all the fractions.

Discussion

Fractions I-V (Table 1) are pale coloured brittle products which could be powdered easily and are completely soluble in alcohol and alkali but insoluble in diethyl ether. Obviously, these fractions constitute the pure resin portion of shellac. The softening points of the fractions lie between 91° and 97°C. and the melting points between 96° and 111°C., which are much higher than those of the original shellac. The acid values of the fractions gradually decrease from 74.8 for original shellac to 60.9 in the case of fraction III, to rise again to 82.2 in the case of fraction V. The saponification values of these fractions did not vary much except in the case of fraction II. The hydroxyl values, in the fractions, however, show considerable variation. The observation that the solid complexes, from which fractions I and II were obtained, did not sufficiently soften in boiling water during removal of urea while the others did, suggests that urea forms insoluble complexes much more easily with fractions I and II, which have high molecular weights than with other fractions. Thus the properties of the individual fractions suggest that these are all different components of the pure resin.

Fraction VI was a soft, honey-like, pale yellow mass soluble in alcohol, alkali and diethyl ether. Presumably, this is the soft resin portion of shellac mentioned earlier. The properties of this fraction were also found to be almost identical with those recorded for soft resin.

This method of fractionation of shellac, through the formation of urea complexes, is quicker than the method of Venugopalan and Sen¹⁶, and may be used for obtaining pure and soft resins of shellac in their

TABLE 1 — PROPERTIES OF INDIVIDUAL FRACTIONS OF SHELLAC

FRACTION	YIELD %	SOFTENING POINT °C.	M.P. °C.	ACID VAL.	SAP. VAL.	ESTER VAL.	HYDROXYL VAL.
Original shellac	—	78-80	85-6	74.8	220.4	145.6	243.4
I	11.0	93.4	105.6	74.0	232.6	158.6	236.4
II	17.0	95.6	110.1	70.2	252.5	182.3	238.5
III	22.4	96.7	103.4	60.9	224.2	163.3	266.3
IV	5.9	91.2	96.7	64.4	224.5	160.1	270.4
V	17.8	95.6	106.7	82.2	223.6	141.4	184.5
VI	24.4	—	—	100.8	187.3	86.5	104.7

purest forms, since the pure resin is rendered completely insoluble in acetone by means of urea. Besides acetone, methyl ethyl ketone, mixture of butyl acetate (85 per cent) and butyl alcohol, and mixture of ethyl acetate and ethyl alcohol could be used for effecting fractionation.

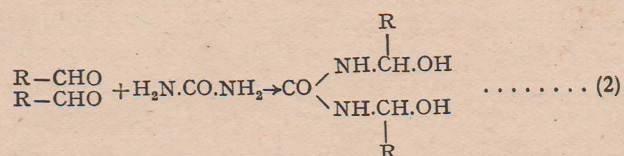
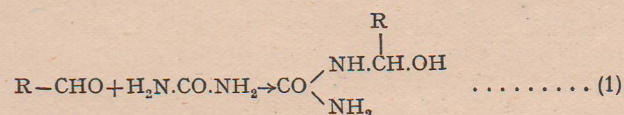
Boiling with water under high pressure or mere washing with boiling water releases urea from the complex. This shows that urea is rather loosely bound to the shellac fractions. Complex formation between urea and shellac takes place because shellac contains carboxyl, hydroxyl, ester and aldehyde groups as well as a straight chain of at least 7 carbon atoms. Bhattacharya¹⁷ has found that the amount of urea (7.3 per cent) in the complex is in close agreement with the calculated value (7.5 per cent) necessary for salt formation with the free acid groups of shellac (acid val., 70). He, therefore, favoured salt formation with the carboxyl group as the main reaction. Sankaranarayanan and Sen¹⁸, from their study of the action of melamine on shellac, concluded that a loose salt formation occurs as in the case of urea. Bhattacharya¹⁹ also came to the conclusion that the reaction is due to addition of urea to the carboxyl group with the formation of a shellac salt. Sreenivasaya and Sarma²⁰ studied the reaction of bleached lac with urea in butyl alcohol and found that the complex, which was soluble in the solvent, contained about 2.8 per cent urea. This amount is much lower than what (7.3 per cent) had been found by previous workers; they attributed this difference to a difference in the combining capacity of the bleached lac employed. On the basis of this finding, Gidvani²¹ suggested that 2 molecules of lac combine with 1 of urea to form an additive salt (theoretical, 2.91 per cent of urea if the molecular weight of lac is 1000). According to him, the lac-urea salt on boiling with water is decomposed into urea and lac which is soluble in alcohol.

The idea of salt formation involving the combination of urea with the free carboxyl groups of shellac appears to be untenable for a number of reasons. Sreenivasaya and Sarma²⁰ obtained acid values of 57.94 and 63.81 respectively for the complex and the original bleached lac, which shows that a few, if at all, of the carboxyl groups participate in the reaction. The present author also finds that the acid values of the original shellac and the complex differ very little, and further that dimethylolurea behaves in a similar manner to urea in complex formation. These findings suggest a type of reaction which is altogether different from salt formation. The combination of urea with the hydroxyl and the ester groups of shellac also seems to be improbable since the resulting compounds would then be stable and, more-

over, a higher temperature would be necessary for these types of combination.

There is, however, another possibility, namely that of urea combining with straight-chain fatty acids, having at least 7 carbon atoms in the chain, to produce a distinct type of complex. Shellac contains butolic acid, which has a straight chain of 9 carbon atoms, and hence might form such complexes. But actually such complex formation does not appear to have taken place, since the urea complex from shellac, unlike urea complexes with other straight-chain fatty acids, does not decompose in the presence of water at room temperature.

Another possibility in the formation of urea complex is one which involves the aldehyde group in shellac. The presence of one aldehyde group per molecule of shellac (average molecular weight, 1000), partly in the free state and partly in the combined state, has been established by Kamath and Mainkar²² (the carbonyl value of shellac was 29.33 which increased to 52 during alkaline hydrolysis). It is well known that urea easily reacts with aldehydes. Further, dimethylolurea, the product of combination between urea and formaldehyde, is easily decomposed by boiling water²³. This, coupled with the facts that the carbonyl value of shellac-urea complexes has been found to be nil, and that the complexes could be decomposed by boiling water, suggests that urea reacts with the aldehyde group of shellac or its fractions to form compounds of the following types of complexes:



where R-CHO = an average molecule of shellac or a component of shellac.

On the basis that the average molecular weight of shellac is 1000 and that nearly half of an aldehyde group in it is free, the amount of urea necessary for reactions (1) and (2) will be of the order of 3.0 and 1.5 per cent respectively. This amount will be doubled if during reaction the combined aldehyde group, after liberation, also reacts with urea. Since it has been found that the carbonyl values of the original and the regenerated shellac are practically the same, it may be concluded that the combined aldehyde group does not take part in the reaction.

Though the theoretical amount of urea necessary for the first reaction agrees with Sreenivasaya's finding²⁰, the amounts are very much smaller than those actually found by other investigators^{16,17}. Hence to account for the higher percentage of urea found in the complex, urea may be assumed to react with other groups in addition to the free aldehyde group of shellac. Further work is in progress on these aspects, the results of which will be reported elsewhere.

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