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STUDIES ON THE CONSTITUTION
OF THE
SHELLAC COMPLEX

PART II
UNSATURATION IN SHELLAC

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PART II

Unsaturation in Shellac

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While studying the action of halogens in general on shellac it was found that direct chlorination of shellac in more common solvents gave a product having a chlorine content of 11.2%. Calculated in terms of iodine on shellac, this would correspond to 45%. Wijs' method of determining unsaturation in fats, oils and resins is generally considered to be standard, and the unsaturation in shellac came to be examined by this process as a means of detecting its adulteration with rosin, as the latter has a very high iodine value compared with that of shellac. Iodine values of normal (*i. e.*, unpigmented and unrosinated) shellac are generally found to lie between 14-18 by this process. If an average value of 16 by Wijs' process be considered as due to unsaturation in normal shellac, the difference between 45 and 16 may be considered as due to substitution in the shellac complex. On prolonged contacts with the prescribed volume of reagent, and 0.2 gram of shellac, however, higher iodine absorption values were obtained, as high as 58 to 60 after 7 to 9 days' contact, but on isolating the halogenated lac no more than 8-9% total halogen calculated on shellac as iodine could be found. But as there was no equivalence between the iodine and the chlorine contents in the shellac after contact with Wijs' reagent, doubt arose as to whether the total halogen content in the isolated shellac really represented the additive portion of the reaction. This is in view of the general acceptance that in Wijs' reaction the addition of I Cl on the double bond takes place (*Vide* Table I).

TABLE I.

WIJS' IODINE VALUES AND HALOGEN CONTENTS.

Sample taken 0.2 gram, 20 c.c. acetic acid (m.p. 14.8°C.), 10 c.c. chloroform and 20 c.c. Wijs' solution at 22°C.

(1) Sample—Kusum Shellac.

Time of contact	Iodine value.	Percentage of Iodine in		Iodine equivalent of chlorine in percent on		Total percentage of halogens as Iodine in free resin (B+D)
		(A) Halogenated resin.	(B) Free resin.	(C) Halogenated resin	(D) Free resin.	
24 hrs.	40.50	3.77	4.10	4.37	4.76	8.86
48 "	48.23	2.56	2.77	5.06	5.48	8.25
168 "	58.56	1.70	1.83	5.27	5.67	7.50

(2) Sample—Ether Soluble Resin (Wax free)

24 "	40.96	—	—	—	—	—
48 "	47.38	7.65	8.79	5.34	6.14	14.93
168 "	58.60	7.95	9.60	9.22	11.13	20.73

(3) Sample—Pure Lac Resin

1 hr.	12.90	2.65	2.80	2.75	2.91	5.71
3 hrs.	28.42	6.25	7.11	5.82	6.62	13.73
24 "	43.92	7.86	9.15	6.24	7.26	16.41
48 "	48.39	8.42	10.04	7.82	9.34	19.34
168 "	58.30	7.06	8.17	6.49	7.51	15.78

An explanation may be sought for this non-equivalence of the two halogens by assuming that in course of the isolation of the halogenated shellac after contact with Wijs' reagent, a portion of the halogen is disengaged due to the hydrolytic action of water. Further, the probability of substitution cannot be altogether excluded. It would appear, therefore, that to estimate any unsaturation in shellac by Wijs' reagent an essential condition would be that the isolated shellac, after reaction, should have both chlorine and iodine in equivalent proportions. From the tables above, this would appear not to be the case, and as such the determination of unsaturation in shellac by Wijs' method is of doubtful value. Obviously, the difference between the total halogen consumed and the halogen actually present in the isolated lac would correspond to the halogen used up in oxidising the shellac, but even then there is no proof

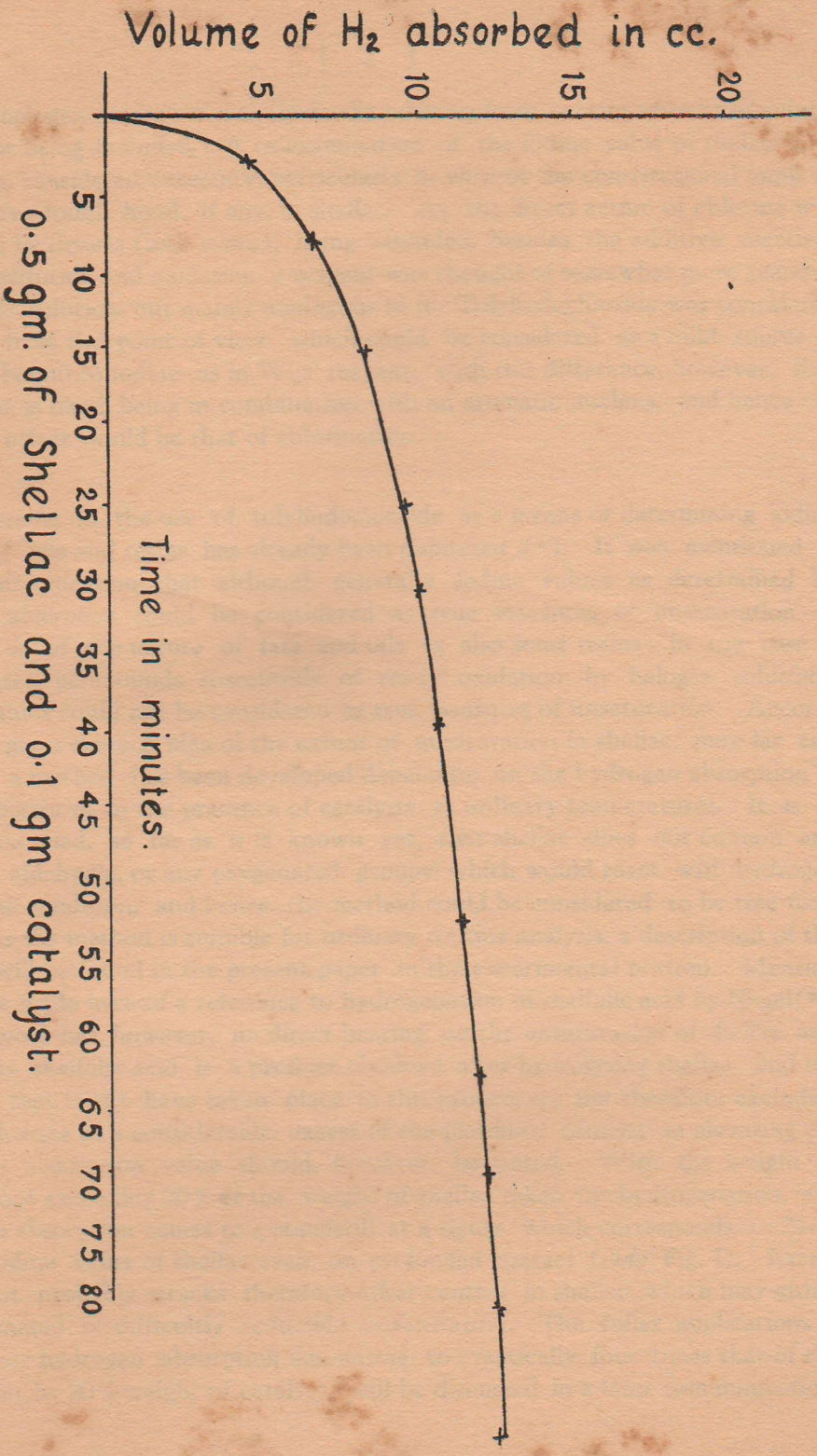


FIG. 1.

that the halogen present is entirely in the additive form, certain amount of substitution not being excluded. A re-examination of the iodine value of shellac was, therefore, considered necessary, particularly in view of the constitutional implications of the double bond, if any, in shellac. As the direct action of chlorine was found to be drastic (*vide supra*), being attended, besides the additive reaction, with substitution and oxidation, a reagent was thought of somewhat more reactive than Wijs' solution, but mainly analogous to it. Tolyiodochloride was considered suitable from this point of view, which could be considered as a mild source of chlorine bound to iodine as in Wijs' reagent, with this difference, however, that the iodine is fixed, being in combination with an aromatic nucleus, and hence the ultimate effect would be that of chlorination.

A report on the use of tolyiodochloride as a means of determining iodine values of oils and resins has already been published (1). It was mentioned in that communication that although generally iodine values as determined by halogen *absorption* could be considered as true measures of unsaturation in compounds of the nature of fats and oils as also some resins; in the case of complicated compounds susceptible of ready oxidation by halogen solutions, iodine values could not be considered as true measures of unsaturation. Accordingly, to get a correct idea of the extent of unsaturation in shellac, pure lac and soft lac, a method has been developed depending on the hydrogen absorption of these substances in the presence of catalysts at ordinary temperatures. It is of course assumed, so far as it is known yet, that shellac does not contain any ketonic, aldehydic, or any oxygenated groups which would react with hydrogen under the condition, and hence the method could be considered to be free from flaw. As the method is suitable for ordinary routine analysis, a description of the process will be found in the present paper in the experimental portion. Mention should be made here of a reference to hydrogenation of shellolic acid by Nagel(2). Nagel's work has, however, no direct bearing on the unsaturation of shellac as a whole, as shellolic acid is a product obtained after hydrolysing shellac, and the changes that might have taken place in this process are not therefore excluded. The influence of a considerable excess of the platinum catalyst in elevating the hydrogen absorption value should, however, be noted. With the weight of catalyst not exceeding 20% of the weight of shellac taken for hydrogenation, the hydrogen absorption comes to a standstill at a figure which corresponds to 24-25 as the iodine value of shellac even on prolonged contact (*vide* Fig. I). Excess of catalyst probably attacks therefore other centres in shellac, which may either be oxygenated or difficultly reducible unsaturation. The fuller implications of this higher hydrogen absorption amounting to practically four times that of the absorption by 20% weight of catalyst, will be discussed in a later communication

In the present paper attempt has been made to reconcile, as far as possible, the values of hydrogenation with those of halogen absorption. By the interaction of Wijs' and Margosche's reagents on shellac, after contacts up to *one week*, the actual halogen contents obtained fall far short of the theoretical iodine value of 25.4 due, no doubt, to the very fast oxidative reaction of halogen solutions on the free hydroxyl groups (³). The iodine values by Margosche's method for different periods of contact are given in Table II.

TABLE II.

MARGOSCHE'S IODINE VALUES AND HALOGEN CONTENTS.

Time of contact	Iodine value	Iodine equivalent of acid produced	Percentage of Iodine in	
			(A) Halogenated resin	(B) Free resin
(1) Sample—Kusum Shellac				
24 hrs.	51.77	46.74	5.29	5.59
48 "	61.39	50.74	7.01	7.54
168 "	80.44	67.25	13.08	15.04
(2) Sample—Pure Lac Resin				
24 "	49.83	40.78	4.35	4.55
48 "	56.66	49.55	6.15	6.55
168 "	78.02	60.39	11.56	13.07

It is clear from the above tables that to spot down the extent of unsaturation in shellac, the use of halogen solution is at best unsuitable, and a better indication of the unsaturation would be available from hydrogen absorption. As a matter of fact, the theoretical figure for the iodine value of shellac would be 25.4, if it is assumed that the molecular weight is 1,000 and that it contains only one double bond in the molecule. This value has been confirmed by the hydrogen absorption and important indications of the nature of the individual components of shellac have been obtained by estimating the hydrogen absorption values of the several components, *e. g.*, pure lac (the portion insoluble in ether), soft lac and shellac wax. The hydrogen absorption of the individual components was determined, and on making proper allowance for the hydrogen values according to their percentage composition in shellac, the value was identical with that for normal shellac. It is noteworthy also that there is a closer correspondence between the halogen content of pure lac after long contact with Margosche's reagent and hydrogen absorption values thereof. The agreement between chlorine and iodine equivalents with Wijs' reagent is fairly satisfactory in the case of pure lac resin although the hydrogen equivalent is slightly less.

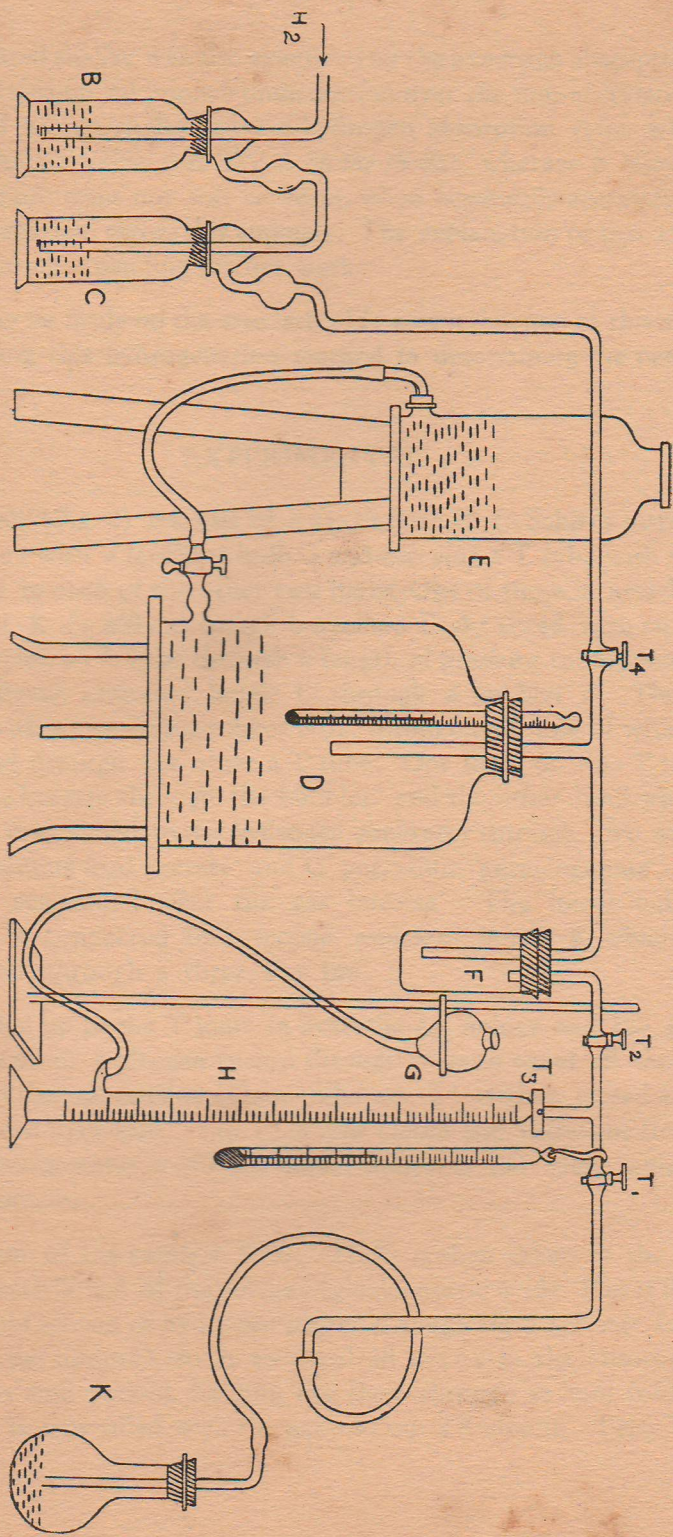


Fig. 2.

Fully acetylated shellac was also examined by the hydrogen absorption process when it revealed certain additional unsaturation over the non-acetylated product. Thus, acetylated kusum shellac gave a hydrogen absorption value which, when converted into iodine value was 37.2% *on the shellac*, whereas it should only be 25.4%. Neither pure resin nor soft lac resin, when separately acetylated and subjected to hydrogenation, shows this anomaly. The explanation of this anomaly can now be only a surmise, pending further work.

Mention may be made on the strength of few experiments, at this stage, of the possibility of using this hydrogenation method in determining the percentage of rosin in shellac.

EXPERIMENTAL

The apparatus (Fig. 2) consists of a gas burette H (a Schiff's nitrometer will serve the purpose) with a levelling bulb G and carrying a T tube with stop cocks T^1 and T^2 , one in each of the other two limbs. One of these is attached to the absorption vessel K (a 250 c.c. round bottomed flask) fitted with an one-holed rubber cork carrying an L tube through a length of pressure tubing, and the other to a large (10 litres) aspirator bottle D through a bubbler F. The aspirator bottle is fitted with a two-holed rubber cork, through one hole of which passes a thermometer and through the other a T tube. One limb of this T tube is connected to the gas burette through the bubbler, and the other limb which carries a stop cock T^4 is attached to the hydrogen generator through two wash-bottles B and C, B containing lead acetate and C potassium permanganate. A second thermometer is suspended near the gas burette. The lower outlet of the aspirator bottle is connected to a second aspirator bottle E which serves as the pressure head, through a three-way tap.

Water is filled up to the T joint in both the gas holder and the gas burette and a steady stream of hydrogen passed through so as to expel all the air in the wash-bottles and the connecting tubes. The tap T^1 is then closed and the gas holder is filled with hydrogen. Tap T^4 is now closed and sufficient time is allowed so that the thermometer in the gas holder indicates the same temperature as the other thermometer.

About 0.1 gm. of the catalyst (PtO_2 , H_2O) is then taken in the absorption vessel together with 50 c.c. of the solvent (glacial acetic acid). This is then loosely corked and a rapid stream of hydrogen passed through for 5 minutes (at the rate of about 200 c.c. per minute), so as to expel all the air in the absorption vessel. The flask is then well corked, holding the flask through several folds of cloth. The gas burette is now filled with the gas and tap T^2 closed. Taps T^1 and T^3

are now fully opened and the volume of hydrogen read off at atmospheric pressure. (Throughout the experiment the tip of the inlet tube should be just above the surface of the liquid and should never actually dip into the solvent.) The absorption flask is now fixed to the shaking machine and the shaking continued till there is no more absorption. (0.1 gm. of the catalyst usually takes about 35-45 minutes.) The volume is then read off and the difference gives the volume of hydrogen absorbed.

The tap T₁ is closed, the flask opened and 0.5-1 gm. of the substance accurately weighed into it or a solution containing a known weight introduced. Hydrogen is again passed for five minutes and the process continued as before. The temperature at the start and end of the experiment is noted and a correction applied, if necessary. The absorption is usually complete in 1-1½ hours and seldom exceeds two hours. From the volume of hydrogen absorbed and knowing the temperature and pressure, the iodine value is calculated.

IODINE VALUES OF SHELLAC BY HYDROGEN ABSORPTION

Solvent used : glacial acetic acid.

TABLE III

Shellac used	Weight taken	Vol. of H ₂ absorbed ² at 22-24°C.	Iodine value	Average
Ber	0.5 gm.	12.5 cc.	23.32	23.9
"	0.709 gm.	19.1 cc.	25.0	
"	0.5 gm.	12 cc.	22.8	
"	1 gm.	26.6 cc.	25.2	
Palas	1 gm.	25.7 cc.	24.35	
Kusum	1 gm.	25.1 cc.	23.79	18.54
Angelo's dewaxed blonde	1 gm.	18.7 cc.	17.76	
"	1 gm.	19.4 cc.	18.53	
"	1.172 gm.	24.1 cc.	19.34	

TABLE IV

Pure lac Resin	1 gm.	14.2 cc.	13.26	14.43
"	1 gm.	16.8 cc.	15.6	
Soft lac resin	0.406 gm.	24.3 cc.	55.9	53.15
"	0.728 gm.	13.1 cc.	50.4	
Shellac wax	0.50.	9.7 cc.	18.1	18.1

TABLE V

Shellac used	Weight taken	Vol. of H ₂ absorbed at 22-24°C	Iodine value
Acetylated shellac	0.5 gm.	16.3 cc.	30.4
Acetylated dewaxed blonde	0.486 gm.	16.2 cc.	31.1
Acetylated pure resin	1.052 gm.	13.8 cc.	12.25
Acetylated soft resin including wax	0.558 gm.	20.5 cc.	34.3

SUMMARY

The iodine values of shellac as determined by Wijs' reagent vary so considerably with the time of contact and quantity of reagent, that no definite values could be fixed for the unsaturation. On keeping shellac and Wijs' reagent in contact for 168 hours, the total iodine *absorption* was found to be 58.6%. On isolating the lac from this solution, however, it was found that the total halogen content was only 7.5% and that there was no equivalence between the chlorine and iodine contents. The non-equivalence between the two halogens points either to substitution or partial disengagement of the halogens during isolation.

The iodine value of shellac by hydrogen absorption, with 20% or less of platinum catalyst, has been found to be 24.2% which fairly agrees with the theoretical value of 25.4% assuming 1,000 as the molecular weight of the shellac complex and that it contains one double bond.

The individual components of shellac, namely, pure lac resin, soft lac resin and wax, were also hydrogenated and the value of 23-24 for total shellac was confirmed from the hydrogenation values of individual components. With a quantity of platinum catalyst exceeding 20% of the weight of shellac taken for hydrogenation, increased hydrogen absorption values were obtained. The implication of this will form the subject matter of a future communication. The hydrogen absorption method is fully described in the body of the paper so that it could be included as an ordinary routine test. It has been found possible to estimate moderate amounts of rosin adulteration by the *hydrogen* absorption method.

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