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STUDIES ON THE CONSTITUTION
OF THE
SHELLAC COMPLEX

PART I
INTERACTION OF TOLYLIDOCHLORIDE WITH SHELLAC

By

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INTRODUCTION.

Several halogen reagents are in use for the determination of unsaturation in organic compounds.^{1,3,9} The behaviour of a new reagent, tolyiodochloride, with regard to the determination of unsaturation was studied, specially with a view to use this reagent in the determination of the so-called iodine value of shellac. The iodine value of shellac so far is an arbitrary number as with longer duration of contact and higher concentration of the halogen reagent, there is considerable increase in the quantity of iodine consumed. This reagent, tolyiodochloride, bears considerable analogy with Wijs' reagent, with the exception, however, that the additive compound is a chloro-derivative whilst in the case of Wijs' reagent, the additive compound is an iodochloroderivative. The direct application of chlorine to find unsaturation would be obviously too drastic, whilst with tolyiodochloride, the iodine being fixed to the aromatic nucleus the reagent would serve as the source of chlorine, the rapidity of the addition of which depending upon the nature of unsaturation. The velocity of chlorine addition on the unsaturation is also expected to be faster, and in analytical methods this property is of considerable practical importance, provided accurate and reproducible results were available. In the experiments detailed below, Wijs' figures have been taken as standard values, which no doubt are in the case of fats and oils. The constitution of shellac, however, is such that longer contacts of tolyiodochloride, or, in fact, of other halogen reagents with shellac give rise to variable figures for unsaturation, although with fats and oils, it gives accurate results. This is due to the fact that addition, substitution and oxidation simultaneously occur in

shellac with halogen solutions in different degrees. The latter takes place so readily that even an alcoholic solution of iodine begins from the very beginning to oxidise shellac, producing in the reaction mixture appreciable quantities of free acid. It would appear, therefore, that the mere estimation of the halogen removed due to contact with shellac is not the means of finding out the extent of unsaturation in shellac. An approximate approach to the true measure of unsaturation could be made by actually separating the halogenated shellac and determining the quantity of halogen actually present in it. This assumption, obviously is not free from flaw, as the whole of the shellac after contact with the halogen reagent can not be isolated as the halogenated compound. The diversity and the non-homogeneity of the shellac molecule are probably responsible for this, and as such it would be far more reasonable to attempt an assay of unsaturation in the shellac complex by direct hydrogenation of shellac in the presence of a catalyst. Here also one has to prove that the hydrogenation is complete, but as is obvious, reproducible results are more to be expected from hydrogen absorption than from interaction with halogen reagents, where the possibility of oxidative reactions and substitution cannot be ignored. Whilst investigations on the hydrogen absorption by shellac, soft lac, and pure lac resin (**a*-resin) are in progress and nearing completion, the use of tolyliodochloride as a general reagent for measuring unsaturation in oils, fats and resins is recorded in the present communication.

It is to be noted that whilst the behaviour of tolyliodochloride with shellac throws only light on the constitutional disposition of the latter, which is the main objective of the paper, its use as a reagent for the determination of unsaturation in more stable classes of compounds, can be safely recommended.

Among the several methods for estimating unsaturation by iodine, the notable ones are Wijs's⁹, Hübl's³ and Hanus's¹ which are most commonly used for determining this factor in all oils, fats and resins. Comparative merits and demerits of these with their modifications proposed by Waller⁸, Winkler¹⁰, etc., have been ably reviewed very recently by Schmitt⁷. Among the more recent methods, mention may be made of the use of two new reagents, namely, Pyridinesulphate-bromide and Toluene *p*-sulphondichloramide (Dichloramine T), developed by Rosenmond and Kuhnenn⁶, and Hunter and Hyde⁴ respectively.

* Sen, H. K. Jour. Soc. Chem. Ind., p. 257, 1938.

The application of the Pyridinesulphate-bromide method has been further examined by Hawley² for several oils, who reported that 'the figures obtained by the Pyridine sulphate bromide method can be duplicated and are independent of moderate variations as regards the time of contact or excess of the reagent, but they must be accepted with considerable caution when used for comparison with figures obtained by other methods'. Excepting Wijs' and Hübl's, practically none of the other methods has been used for finding the iodine value of resins.

EXPERIMENTAL.

Preparation of the Reagent.

p-Tolyliodochloride is prepared by passing dry chlorine at ice temperature into a solution of p-Iodotoluene dissolved in five times its weight of chloroform. When chlorine is no longer absorbed, the yellow needle-shaped crystals of the iodochloride are filtered off, washed with a little cold chloroform and finally with an excess of ether and dried on a porous plate.

The iodochloride thus obtained is hygroscopic and to prevent any deterioration or alteration in the composition, it is usually preserved in dark-brown, air-tight bottles in a cool place. When a solution of the iodochloride is required, it is made by dissolving it in a mixture of three parts of acetic acid and one part of chloroform. The use of chloroform is necessary, because it is not completely soluble in acetic acid alone. In the following experiments, the iodochloride solution was prepared as below:—

A quantity corresponding to 0.05 mol. of the iodochloride (14.45 gm.) was weighed and dissolved at first in 250 c.c. of chloroform and the solution was then made up to one litre with halogen stable glacial acetic acid. The solution is yellowish in colour and to minimise decomposition by light or temperature, it is stored at a low temperature in a dark-brown bottle. The

Note:—In the several methods of iodine value determinations mentioned above, the principle is the same, but the solutions differ in their composition according to the nature of the halogen employed. The time of contact and temperature of reaction are also different. It is recognised that chlorine is more reactive than iodine but less reactive than iodine monochloride as an additive reagent, as iodine monochloride itself acts as a catalyst. It has been found, however, that complete saturation of the double bonds without simultaneous substitution of halogen is not achieved by any of the methods. Nor is the rate of substitution equally alike, with the result that the iodine values estimated by various methods are not identical. (*c.f.* Hübl's figures for shellac which vary between 9 and 11, and Wijs' 13—15).

laboratory Frigidaire (0° — 5°C) is quite suitable for this purpose. The iodine or chlorine equivalent of the solution was determined in the usual way by estimating the iodine liberated by a known volume of the solution from an excess of aqueous potassium iodide. The reagent thus prepared usually has 19.0—19.4 c.c. of N/10 thiosulphate as the titre value for 20 c.c. of the solution. As the reagent deteriorates slightly on keeping, it is advisable not to store the solution for more than a week or better still to prepare just the sufficient quantity of the solution for the tests on hand.

The following table shows the change in the strength of the tolyl-iodochloride solution with time at $22^{\circ}\text{C} \pm 1^{\circ}$. For comparison the change in the strength of Wijs' solution is given.

TABLE I.

20 c.c. tolyliodochloride solution requires	18.65 c.c. of 0.1N thiosulphate.
" after $\frac{1}{2}$ hr.	18.65 "
" 1 hr.	18.65 "
" 4 hrs.	18.65 "
" 48 hrs.	18.30 "
" 7 days	17.30 "
" of Wijs' solution	41.6 "
" after $\frac{1}{2}$ hr.	41.6 "
" 1 hr.	41.6 "
" 4 hrs.	41.6 "
" 1 day	41.4 "
" 3 days	41.35 "
" 7 days	41.10 "

Procedure.

The method followed and the conditions of test are essentially the same as those of Wijs'.

Whenever it is desired to perform a series of experiments, on the same sample it is convenient to dissolve 4 grams of the substance of which the iodine value is required in a mixture of chloroform and acetic acid or acetic acid alone in a 200 c.c. graduated flask and the solution is allowed to attain the room temperature. 10 c.c. portions of this solution representing 0.2 g. of the substance are measured from a burette or an accurately graduated pipette. The general procedure was as follows: The exact weight of the substance of which the iodine value is desired was transferred to a 250 c.c. or 300 c.c. glass stoppered bottle and dissolved in 25 c.c. of halogen-stable acetic acid, 5 c.c. of chloroform were then added, followed by 20 c.c. of the iodochloride solution from an automatic pipette. The mixture was allowed

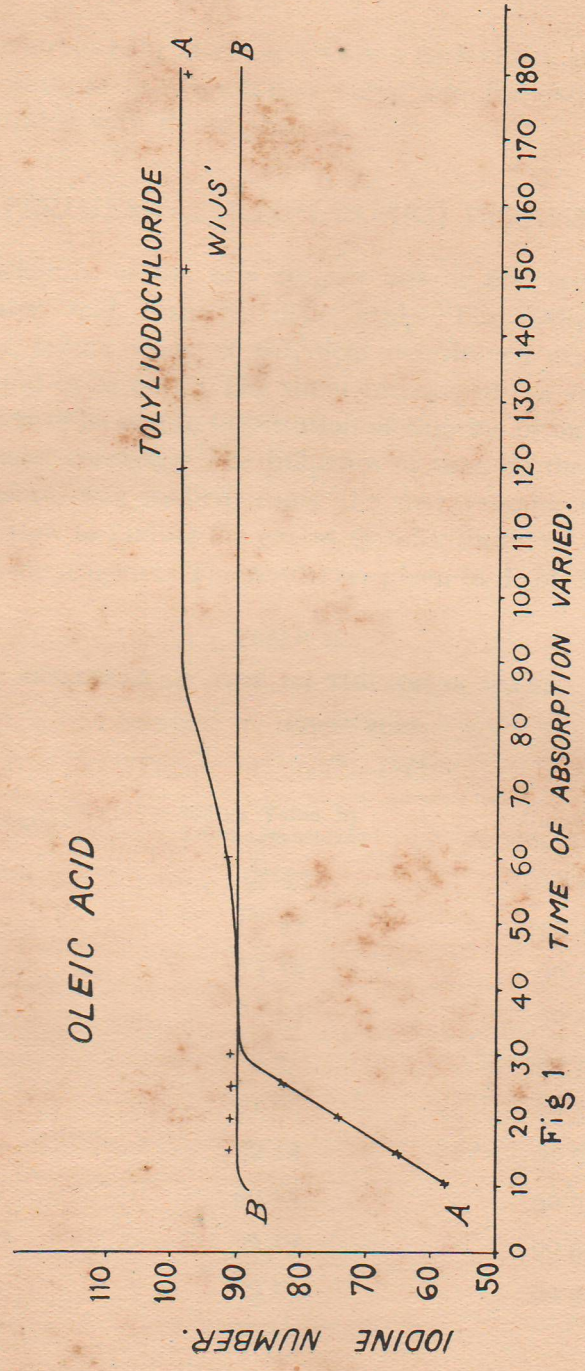


Fig 1
TIME OF ABSORPTION VARIED.

to stand exactly for an hour at $22^{\circ} \pm 1^{\circ}\text{C}$ in a dark closet, and then 10 c.c. of 10 per cent potassium iodide solution added and the excess of iodine was immediately titrated with thiosulphate.

EXPERIMENTAL RESULTS AND DISCUSSION.

The applicability of the new reagent was at first tested on a known unsaturated fatty acid, namely, oleic acid. The iodine value found was 91.8. The iodine value of this acid determined according to Wijs' method was found to be 90.1. The slight increase in the value obtained by the new reagent may be due to substitution of chlorine or oxidation as would appear from longer contacts. The influence of time on the iodine value of this acid, therefore, was studied, using the new reagent as well as Wijs' solution with a view to finding the extent of substitution or oxidation taking place with both the reagents. The results are given in Table II and Fig. 1:—

TABLE II.
INFLUENCE OF TIME ON THE IODINE VALUE.

Sample : Oleic acid.

Temp. $22^{\circ} \pm 1^{\circ}\text{C}$.

Time of reaction	Iodine Value by Tolyliodochloride	Iodine Value by Wijs' Reagent
10 min.	57.45	88.55
15 "	65.43	90.14
20 "	74.22	90.14
25 "	82.59	90.14
30 "	89.4	90.14
60 "	91.8	89.33
90 "	99.13	90.93
120 "	99.13	90.93
$2\frac{1}{2}$ hrs.	99.13	90.93
3 "	99.13	90.93
4 "	99.13	...

From the figures given in the table above, it will be obvious that with iodochloride, the iodine value at first increases rapidly with time and then

practically remains constant between the periods 30-60 minutes; thereafter, with further increase in time up to 90 minutes, the value rises to 99.13 at which figure it keeps constant for several hours. In the case of Wijs' reagent, the absorption is much quicker and the maximum iodine value is 90.93 against the theoretical iodine value of 89.95 which is practically reached in 15 minutes. With both the reagents, the corresponding maximum value is reached after 90 minutes, the value with iodo-chloride being about 9 units higher and with Wijs' reagent only one higher than the theoretical iodine value. It is evident that substitution or oxidation takes place with both the reagents, but it is only a question of degree. These observations are in agreement with those made by Meigen and Winogradoff⁵ who observed that unsaturated fatty acids like oleic acid absorb more chlorine than iodine from a mixture of the two halogens when more or less substitution of chlorine takes place. The influence of iodine on the reactivity of tolyliodochloride both as an additive and substituting reagent is very conspicuous. Thus, it is observed that if 10 c.c. of an iodine solution in acetic acid (0.05 mol/litre) is added to 90 c.c. of the tolyliodochloride solution, the time of absorption could be reduced from one hour to 15-20 minutes, whilst longer contacts caused rapid substitution. The results of some typical tests made with this modification on shellac and oleic acid are given in Table III.

TABLE III.
IODINE VALUE.

Time of reaction	(Palas Shellac)		(Oleic acid)	
	Tolyliodo-chloride	Tolyliodochloride+ 10% Iodine	Tolyliodo-chloride	Tolyliodo-chloride + 10% Iodine
10 min.	7.9	11.5	57.5	77.9
15 "	8.6	12.7	65.4	89.2
20 "	9.1	14.9	74.2	90.9
30 "	11.2	18.0	89.4	95.5
60 "	15.2	27.5	91.8	120.6

The theoretical iodine value if mono-substituted chlorooleic acid be assumed, would be 134.95; a contact of one hour shows already an iodine value of 120.6, which lends strength to the idea of substitution taking place, but oxidation is not also precluded.

The new reagent was next tested against some oils and the iodine values obtained were compared with those simultaneously carried out by Wijs' method. The results of tests are given in Table IV.

TABLE IV.
IODINE VALUE OF OILS.

Sample	Tolyiodo- chloride	Average	Wijs'	Average
Linseed oil	...	173.2	180.1	
		174.4	183.2	
		177.2		
		173.2	174.5	181.7
Cod Liver oil (Norwegian)	...	153.7	150.0	
		152.2	155.7	152.9
Castor oil	83.1	85.1	
		88.9	86.8	
		90.9		
		90.4	88.3	86.0
Olive oil	83.1	83.4	
		86.9	83.2	
		86.1	85.4	83.7
Sesame oil (Local)	...	94.1	93.4	
		94.5	93.0	
		94.6	94.4	93.2
Almond oil	94.1	94.2	
		96.9	95.5	94.3

From the figures given in the table above, it will be seen that within the limits of experimental error, the two methods give practically agreeing results. The slight increased figures given by the new reagent in the case of some oils may be due to the effect of substitution or oxidation as explained before. Curiously, however, linseed oil gave a somewhat reduced iodine value.

In Tables V and VI the iodine values of some samples of shellac, rosin and waxes are given. From the figures given in the Table V, it would appear that the results obtained with the new reagent agree very closely with those of Wijs' when a correction of 1.4 for substitution is applied for one hour's contact. The remarks of Schmitt in this connection are instructive. While

discussing the comparative merits of the different methods of determining the iodine value, he remarks that though Wijs' solution is often recommended owing to the speed of working and trustworthy values obtained, nevertheless, hydroxyl compounds undergo substitution. Since shellac is known to be composed mostly of hydroxyl compounds, the chances of substitution or oxidation even with Wijs' method are therefore not excluded even when great care and precaution are taken with regard to conditions of temperature, time of absorption, etc.

TABLE V.

Sample	Tolyliodo- chloride	Average	Corrected value after allowing for substi- tution (1.4)	Wijs'	Average
Ber Shellac (July 1936 crop)	14.5 14.7	14.6	13.2	13.5 13.3	13.4
Palas Shellac (July 1936 crop)	16.2 15.9	16.05	14.65	14.3 14.8	14.05
Khair Shellac	15.5 15.9	15.7	14.3	13.6 13.7	13.7
Kusum Shellac	14.2 14.3	14.3	12.9	13.1 13.0	13.1
Kusum Shellac (Burma)	16.4 16.3	16.4	15.0	15.1 15.2	15.2
Bleached lac	8.9			10.8	
Ether soluble Resin from Shellac	20.2 20.7	20.5	19.1	17.9 19.1	18.5
Shellac Wax	9.2 9.1 8.5	8.9		7.1 7.9	7.5
Rosin	203.5 204.8 204.8	204.4		206.8 206.1 206.8	206.9

IODINE NUMBER.

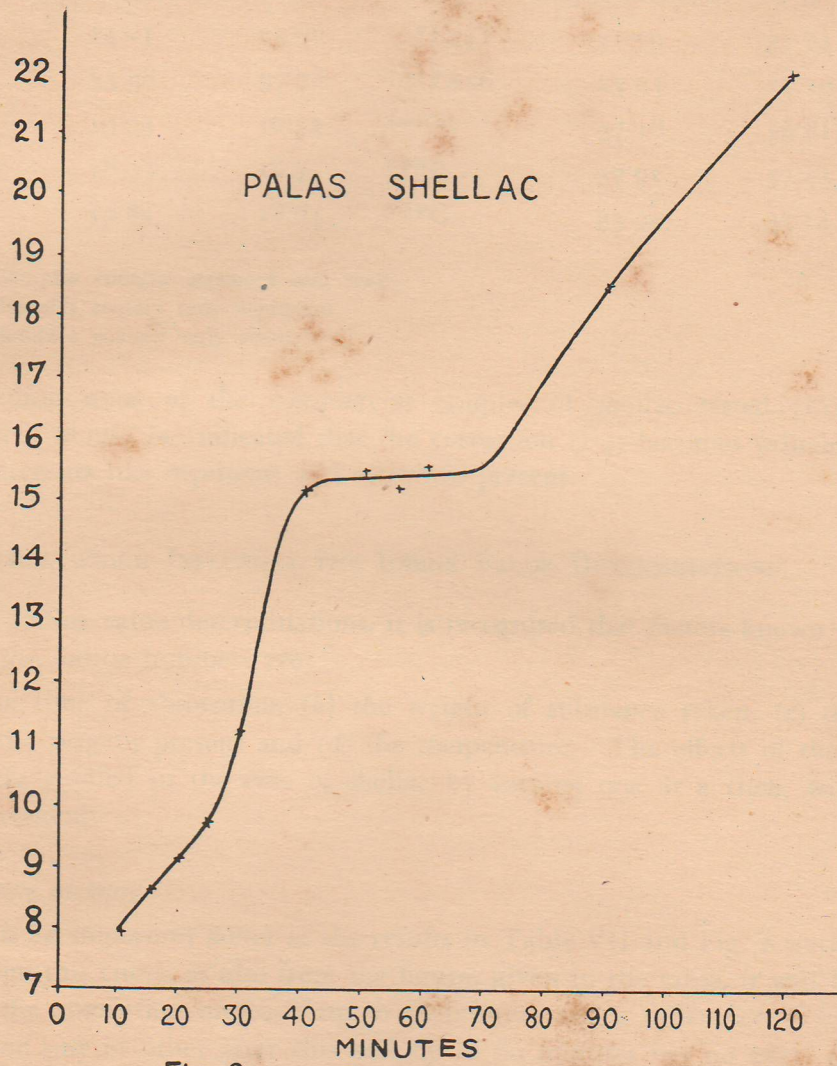


Fig 2. TIME OF ABSORPTION VARIED.

TABLE VI.

IODINE VALUE OF SOME COMMERCIAL SHELLACS.

Sample.	Tolyliodochloride.	Wijs'.	Sample.	Tolyliodochloride.	Wijs'.
*L225	24.21	23.68	*L241	31.59	34.64
*L226	35.98	37.78	**L256	23.54	22.19
L228	19.73	16.52	*A	37.18	36.81
L229	18.97	16.71	*B	37.92	37.44
L230	19.84	18.64	*C	33.94	33.14

N.B.—* Samples contain orpiment and rosin.

** Samples contain only orpiment.

*** Samples contain only rosin.

Regarding some of the commercial samples of shellac tested (*Vide* Table VI), it should be indicated that the correction (1.4) becomes valueless when adulterants like orpiment and rosin are present.

FACTORS WHICH INFLUENCE THE IODINE VALUE DETERMINATIONS.

In all iodine value determinations, it is recognised that factors known to influence the iodine numbers are:

(a) the time of absorption, (b) the weight of substance taken, (c) the excess of the reagent present and (d) the temperature. The effects of these factors were studied in the case of shellac by varying one at a time, with this new reagent.

(a) Influence of time.

This is an important factor as the results in Table VII and Fig. 2 would show. From this curve, as also from the figures given in the table, it will be seen that the absorption increases up to 40 minutes and a difference of few minutes one way or other after this and up to 60 minutes has no effect on the iodine value. Any period between 40 and 60 minutes should therefore prove satisfactory for iodine value determination. In all our experiments we have reckoned 60 minutes as the maximum period of absorption. The study of the time of absorption up to one week was undertaken with a view to determine the maximum effect of the reagent on the iodine value of shellac. This investigation has shown that the iodine value of shellac does

not keep constant after one hour but gradually increases up to 61 for a period of 24 hours, thereafter, for the next 144 hours, it increases rather slowly, up to a maximum of about 69 per cent. This increase in the iodine value is to be traced to substitution or oxidation or both. Comparative results obtained with Wijs' solution are recorded in Table VIII.

TABLE VII.

Palas Shellac.—Time of absorption varied.

Temperature.— $22^{\circ} \pm 1^{\circ}\text{C.}$; 0.2 g. of shellac.

Tolyliodochloride solution—20 c.c.

Time.	Tolyliodochloride.	Average.	Time.	Tolyliodochloride.	Average.
10 min.	7.9		30 "	11.2	
10 "	7.9	7.9	30 "	11.5	11.2
15 "	8.6		40 "	15.3	
15 "	8.6	8.6	40 "	15.0	15.2
20 "	8.9		45 "	15.0	
20 "	9.2	9.1	45 "	15.1	15.1
25 "	9.8		50 "	15.6	
25 "	9.6	9.7	50 "	15.4	15.5
55 "	15.0		8 "	42.3	
55 "	15.3	15.2	8 "	42.5	42.4
60 "	15.6		12 "	49.7	
60 "	15.6	15.6	12 "	50.0	49.9
90 "	18.8		24 "	60.8	
90 "	18.5	18.6	24 "	61.3	61.1
2 hrs.	22.0		48 "	64.9	64.9
2 "	22.2	22.1	72 "	64.9	
3 "	27.3		72 "	65.4	65.2
3 "	27.0	27.2	96 "	66.6	66.6
4 "	30.5		168 " (1 week)	69.4	
4 "	30.7	30.6	168 " "	69.4	69.4

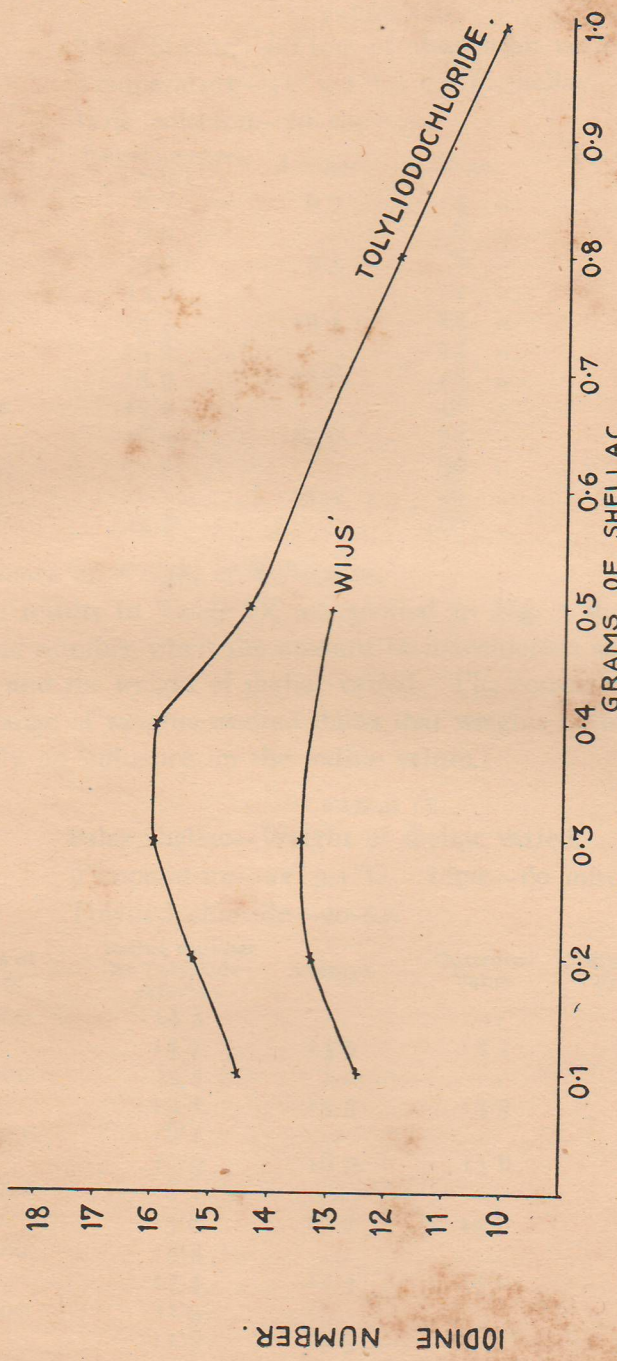


Fig 3. WEIGHT OF SHELLAC VARIED.

TABLE VIII.

Palas Shellac:—Time of absorption varied.
 Temperature— $22^{\circ} \pm 1^{\circ}\text{C.}$, 0.2 g. shellac.
 Wijs' solution—20 c.c.

Time.	Iodine number (Wijs')	Average.	Time.	Iodine number (Wijs')	Average.
15 min.	6.7	6.7	4 "	23.0	22.9
30 "	9.5		8 "	27.8	
30 "	9.0	9.3	8 "	27.8	27.8
60 "	13.1		12 "	30.7	30.7
60 "	13.7	13.4	24 "	37.0	
90 "	15.6		24 "	37.0	37.0
90 "	15.9	15.8	48 "	44.1	
2 hrs.	17.2		48 "	44.3	44.2
2 "	18.5	17.9	72 "	49.1	49.1
3 "	21.7		96 "	51.3	
3 "	21.1	21.4	96 "	52.0	51.7
4 "	22.8		168 "	58.3	58.3

(b) *Influence of Weight of Substance.*

The results in Table IX are plotted in Fig. 3 showing the change in the iodine number when the amount of iodochloride solution added is kept constant and the weight of shellac varied. The constancy of figures obtained for the range of weights studied shows that weights between 0.2–0.4 g. have practically no influence on the iodine values.

TABLE IX.

Palas Shellac—Weight of shellac varied.
 Temperature— $22^{\circ} \pm 1^{\circ}\text{C.}$ Time—60 min.
 Tolyliodochloride—20 c.c.

Grams of Shellac.	Iodine number by Tolyliodo- chloride.	Average.	Corrected Value.	Iodine number by Wijs'.	Average.
0.1000	14.3	12.6	...
	14.7	14.5	13.1	12.3	12.5
0.2000	15.4	13.4	...
	15.2	15.3	13.9	13.2	13.3
0.3000	16.1	13.4	...
	15.9	16.0	14.6	13.5	13.5
0.4000	16.2		
	15.8	16.0	14.6		
0.5000	14.3	13.0	...
	14.4	14.4	13.0	12.9	13.0
0.8000	11.9	...			
	11.8	11.9			
1.0000	10.2	...			
	10.1	10.2			

(c) *Influence of excess of Reagent.*

Table X and Fig. 4 show that 20 c.c. of the reagent is sufficient to give the correct range of results.

TABLE X.

Palas Shellac—Amount of Tolyliodochloride solution varied.
Temperature— $22^{\circ} \pm 1^{\circ}\text{C}$. Shellac 0.2 g. Time—60 min.

cc. of Tolyliodochloride solution.	Iodine number (Average).	cc. of Tolyliodochloride solution.	Iodine number (Average).
5	7.3	30	16.8*
10	12.4	40	18.4
15	14.3	50	20.4
20	16.2*	80	27.7
25	16.8*		

(d) *The Effect of Temperature.*

Other factors remaining unchanged, the temperature was varied. The results are shown in Table XI and Fig. 5.

TABLE XI.

Palas Shellac—Time and Temperature varied.
Tolyliodochloride 20 c.c.

Time in minutes	10°C	22°C	32°C
10	—	7.9	8.9
15	5.5	8.6	10.2
30	7.6	11.2	16.6
45	8.9	15.1	20.7
60	9.9	15.6	25.2
120	15.3	22.1	—

The rate of reaction of p-tolyliodochloride with shellac, additive or substitutive, is very slow at 0° — 3°C , whether in the presence of 10% iodine solution (*vide* page 6) or without, as would be seen from the table below:—

TABLE XII.

Temperature: 0° — 3°C .

Time in hours	p-tolyliodochloride reagent	p-tolyliodochloride + 10% iodine
4	4.08	5.96
5	5.96	6.59
	6.27	6.27
6	7.21	6.59
	7.21	6.90
9	7.53	8.15
	7.83	8.15

* With the correction of 1.4, these figures would be 14.8, 15.4 and 15.4. Further corrections may be necessary as the quantity of the reagent is increased.

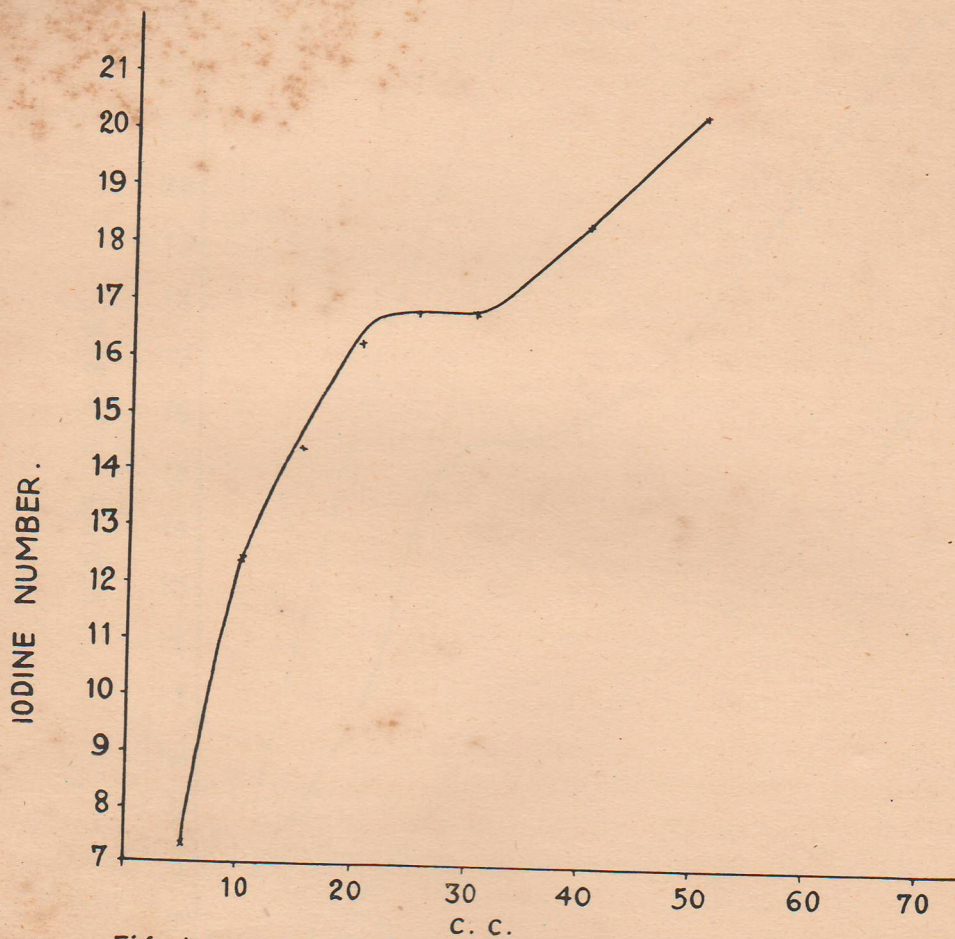


Fig 4. AMOUNT OF TOLYLIDOCHLORIDE SOLUTION VARIED.

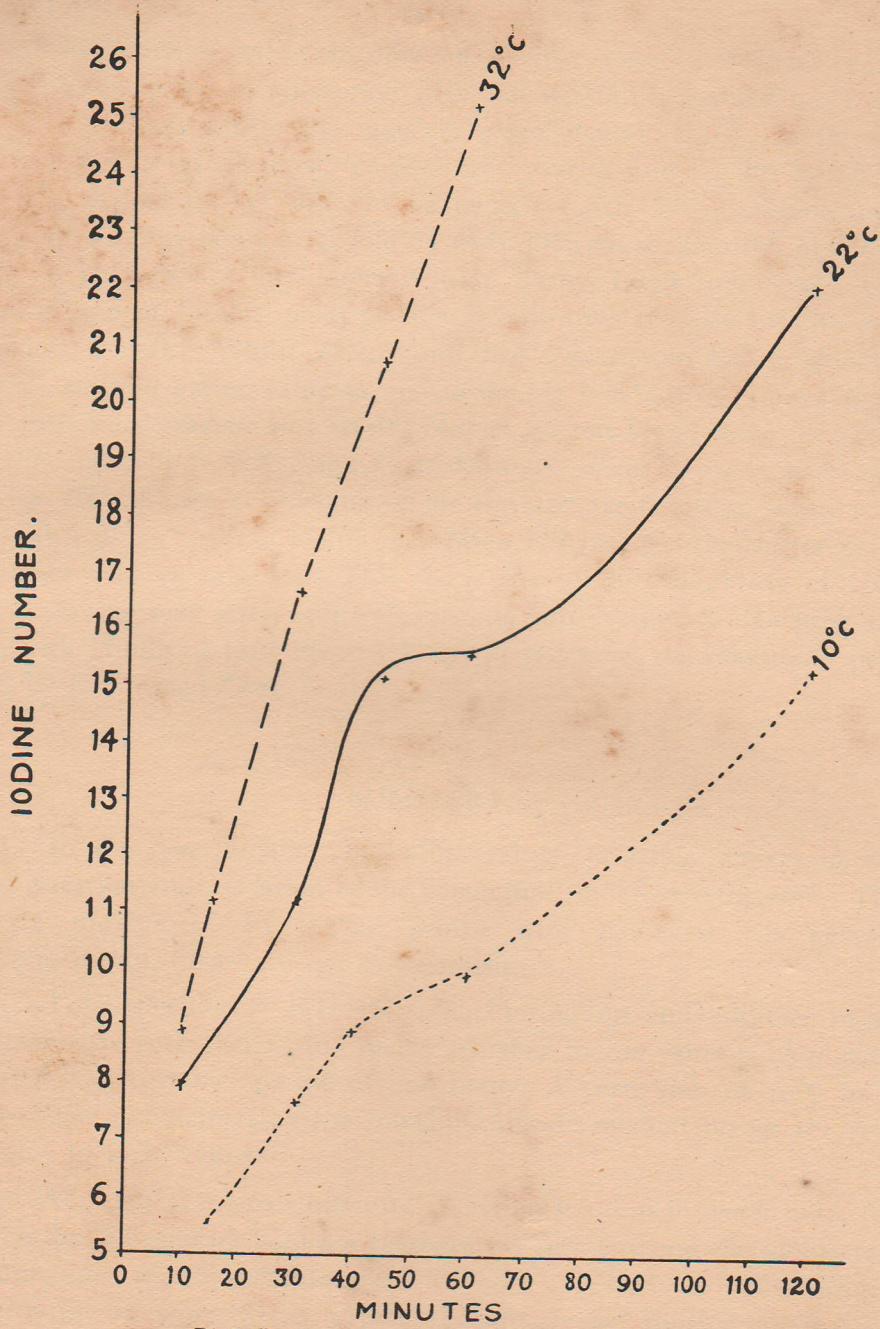


Fig 5. TEMPERATURE VARIED.

It would appear that at this low temperature, except for longer contacts, the difference in iodine absorption with and without added iodine, is small and in some cases within the range of experimental error. On the other extreme, that is at elevated temperatures, Karim and Cook¹¹ found that refluxing shellac for 30 minutes at 92-93°C with Wijs' reagent, iodine absorption ranging between 55 and 63 with different shellacs was obtainable. They do not attempt any interpretation of this interesting result, which from the present authors' point of view is indicative of rapid substitution or oxidation or both. Whilst Karim and Cook's maximum iodine *absorption* (as distinct from iodine value to denote double bond) is 63, in the present work with Wijs' reagent on a week's contact, 58 was found to be the percent of iodine used up. Karim and Cook however, seems to have made out a case for Hübl's reagent working at an elevated temperature, when a constant value of 11.7 as the iodine absorption is found for shellac for periods of contact over 20 minutes. This shows the specific suitability of Hübl's reagent, as one may safely conclude that no substitution or oxidation takes place with Hübl's at least up to 2 hours of reflexing, the maximum period tested by Karim and Cook.

SUMMARY.

1. In the determination of iodine values, probable sources of error are substitution and oxidation of the compound under investigation. These two are pronounced in shellac, whilst with fats and oils generally encountered with, these are not so prominent.
2. Tolyiodochloride behaves as a chlorinating and additive reagent simultaneously with shellac and hence a higher iodine value is obtained by following Wijs' contact period of one hour. A correction of 10% in the iodine value as obtained by the tolyiodochloride method brings the result very close to Wijs' values.
3. Addition of a small quantity of iodine solution in acetic acid, (*e.g.*, 10%) to the iodochloride solution catalyses the reaction, and the iodine value determinations can be completed in as short a period as 15—20 minutes which must be regarded as a great advantage for routine analysis. In practice, this modification is recommended.
4. Several factors, such as influence of time of absorption, the variation in the weight of substance taken, the variation in the amount of excess of

the reagent, the effect of changes in temperature have all been studied in connection with shellac.

5. The effect of orpiment and rosin adulterations on shellac in raising the iodine values are clearly indicated by the new reagent as by Wijs'.

The study has indicated that tolyliodochloride could be employed as a fairly useful reagent for determining the degree of unsaturation in fatty and resinous substances. With oils and fats, however, this reagent gives accurate values for unsaturation.

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