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ORPIMENT AND THE IODINE VALUE OF SHELLAC.

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Introduction.

Since the earliest days of shellac manufacture small quantities of orpiment, the naturally occuring sulphide of arsenic, As_2S_3, have been incorporated in certain grades of shellac. The object was to produce a lighter coloured material of increased market value. This practice is still quite extensive.

The influence of orpiment on the estimation of rosin in shellac by Langmuir's iodine value method was stated by Langmuir[1] to be small. Briggs[2] in 1925 pointed out that the effect might be quite appreciable. The nature and extent of the effect was not however indicated. It was felt desirable, therefore, that the matter should be investigated further.

Experimental.

Schneider[3] has pointed out that a solution of iodine in carbon disulphide reacts with pure As_2S_3 forming arsenious iodide and sulphur but that it is without action on natural orpiment. It might be expected that Wij's solution would be more reactive. The reaction of finely ground orpiment was accordingly investigated by determining its iodine value in the usual way. Table I gives the results obtained.

TABLE 1.

Amount of orpiment taken.	Iodine value.
0.0020	516
0.0041	694
0.0096	569
0.1500	587

It is obvious from the table that orpiment is appreciably attacked by Wij's solution. It was always observed, however, that small quantities still remained undissolved.

The reaction of pure As_2S_3 was next investigated with the following results:

TABLE II.

Amount of As_2S_3 taken.	Iodine value.
0.0364	440
0.0161	580
0.0140	595
0.0101	681
0.0051	755
0.0049	773
0.0020	1094

It will be noted that the results are somewhat variable. This would be explained by the incomplete reaction under the conditions of the experiment. A sample of very finely divided orpiment was prepared by air levitation of finely ground material. Table III gives results obtained.

TABLE III.

Amount of orpiment taken.	Iodine value.
0.0022	883
0.0050	1020
0.0099	822
0.0144	734

Comparing these results with Table I it is seen that higher values are given for the more finely divided material. The orpiment in commercial shellac is usually fairly finely divided and would therefore be expected to be quite reactive with Wij's solution.

A series of shellac samples containing varying amounts of commercial ground orpiment were manufactured by the native process. Control samples, free from orpiment, were prepared at the same time. To estimate the quantity of orpiment in the samples a modification of the Gooch Browing method was chosen. The following gives the details of the method:

Weigh 1-3 gms. (according to the orpiment content of the sample) of shellac ground to 30 mesh into a Kjeldahl digesting flask. Add 10 c. c. of pure sulphuric acid followed by 20-40 c. c. of pure nitric acid added in instalments. When the shellac is completely dissolved heat gently with further addition of nitric acid until the solution attains a light yellow colour. Complete oxidation is aided by the addition of a small quantity of sodium nitrate. Cool, add about 50 c. c. of water and heat again until all nitric acid fumes are expelled. Dilute again with water ; add 1 gm. potassium iodide and boil until nearly all the iodine is expelled. Cool, dilute again and completely remove iodine by careful addition of $\frac{N}{10}$ sodium thiosulphate solution. Partly neutralise with sodium hydroxide and finally treat with a fairly large excess of sodium bicarbonate. Titrate with $\frac{N}{10}$ standard iodine solution.

The method was found to combine ease and rapidity with a fair degree of accuracy, and has also the advantage that 4-6 determinations

can be run concurrently, which is not convenient with the U.S.S.I.A. method[4]

The percentage orpiment in the samples was determined together with the iodine value by Wij's method[5] care being taken to use only pure materials and to adhere strictly to stipulated conditions of time, temperature, etc. Table IV gives the results obtained.

TABLE IV.

Shellac Sample No.	Orpiment content as % As_2S_3	Iodine Value % Duplicates	Mean.	Rise in iodine value.	Calculated iodine value of As_2S_3 present.
1	nil	12.67; 13.11;	12.87	—	—
	0.25	15.80; 15.10;	15.45	2.58	1032
2	nil	14.53; 13.99;	14.26	—	—
	0.67	20.00; 19.35;	19.68	5.42	816
	1.15	22.65; 23.27;	22.96	8.70	757
	1.57	27.23; 27.79;	27.51	13.25	844
3	nil	14.55; 14.40;	14.48	—	—
	2.71	34.75; 33.24;	34.00	19.51	720
4	nil	14.87; 14.38;	14.62	—	—
	0.30	16.58; 17.22;	16.90	1.28	427
	0.15	15.23; 15.00;	15.11	0.49	327

The 'rise in iodine value' is calculated from the mean results of iodine value determinations. It will be observed that this rise is greater with increasing orpiment content. The 'calculated iodine values of the arsenic sulphide' indicate that the magnitude of the effect of the orpiment is somewhat variable. These figures are calculated from the 'rise in iodine value' and the As_2S_3 content assuming that the increase is entirely due to the presence of the orpiment *per se* and not to any chemical effect of orpiment on the unsaturation of the shellac during the process of incorporating. To justify this assumption samples of shellac containing orpiment were dissolved in 90% alcohol and filtered hot to remove insolubles. The filtrates were poured on to clean glass plates and the films allowed to dry at room temperature, peeled off, dried at a temperature of about 38°C—43°C and the iodine value determined in the usual way. Table V gives results obtained.

TABLE V.

Sample.	% As_2S_3	Iodine value of original.	Iodine value of insolubles free Shellac Duplicates.		Mean.
2	nil	—	13.89	13.31	13.60
	0.67	19.68	13.82	14.01	13.91
	1.15	22.96	12.59	13.14	13.37
	1.57	27.51	13.92	13.63	13.78
3	nil	—	14.53	14.59	14.56
	2.71	34.00	14.54	I4.65	14.60

These figures indicate that after removal of orpiment the shellac gives the same iodine value as its control sample. This method of removal of orpiment and subsequent determinations of iodine value gives a means of avoiding the effect of orpiment on the estimation of rosin in shellac. A somewhat more convenient method is as follows :—

About 1.0 gm. of shellac is weighed into a small beaker and dissolved in a few c. c. of pure glacial acetic acid (M. P. 14.8° as is used in Wij's method). When the shellac has dissolved the solution is filtered through a fairly close texture filter paper, washing the beaker and filter with warm acetic acid. The filtrate is then made up to 100 c. c. and 20 c. c. (containing approximately the equivalent of 0.2 grms. of original shellac) are removed and the iodine value determined in the usual way. This method was found to give results about 1 unit lower than those determined in the normal way.

Discussion.

The orpiment in commercial shellacs is not always uniformly distributed throughout the material nor is the particle size of the orpiment very uniform. It would be expected, therefore, that the extent of the effect of orpiment on the iodine value would be somewhat variable. Undoubtedly, however, the effect may often be sufficiently large to affect seriously the determination of rosin by the iodine value method. The accepted value of 18 for the iodine value of pure rosin free shellac was established at a time when the effect of orpiment was not recognised. Undoubtedly some of the higher iodine values obtained for rosin free shellacs were due to this orpiment content. It is suggested that the figure 18 is too high for pure shellacs free from both orpiment and rosin. Certainly if the tentative modified method of iodine value determination suggested above be adopted then this figure must be revised.

Summary.

Orpiment and pure As_2S_3 are both attacked by Wij's reagent. The iodine value of orpiment determined by the method used for shellac varies from about 450 to 1000. The effect of the presence of small quantities of orpiment in shellac on the iodine value was shown to be considerable. A tentative method for avoiding this effect is given. It is suggested that the figure 18 accepted as standard for pure rosin free shellac should be modified.

Literature cited.

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3. R. Schneider: J. pr. Chem. 1888 2, *36*, 498.
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5. Proc. Am. Soc. Test. Mats. 1929, *29*, 659

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