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THE IODINE VALUE OF SHELLAC.

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This value has been a subject of considerable investigation. Schmidt & Erban (1) in 1889 gave values 6·0 & 8·3 for specimens of brown shellac, and Williams (2) gave figures varying from 17·5 to 28·7 for various other types of shellac. Results of greater importance were obtained by Parry (3) in 1903 who made efforts to obtain pure rosin-free shellacs. His figures obtained by the Hubl method varied from 7·5 to 11·0 with an average of 9·0. On this latter figure and a value of 160 for rosin, was based a method of estimating the amount of rosin in shellac. Langmuir (4) in 1905 introduced Wijs method and gave reasons why he considered it superior. His figures for pure shellac varied from 13·5 to 18·0. The latter figure was given as the maximum for pure shellacs and was adopted in 1907 by the American Sub-Committee on shellac analysis (5) for use in calculating the percentage rosin from the iodine value of a shellac. The specification has been subjected to a certain amount of adverse criticism. McLean & Thomas (6) had found that Wijs solution caused considerable substitution and for this reason Bayly Parker (7) suggested that Hubl's, being a slower and truly additive reaction was more reliable. Pecuraru (8) confirmed the substitution effect of Wij's reagent and pointed out the need for extreme care in preparing the solution. That difficulties are associated with the method was illustrated in the report (9) of the Sub-Committee on Shellac Analysis in 1924 when nine chemists gave results for the analysis of the same sample of pure Orange shellac varying from 16·1 to 17·83.

Further iodine values have been given by Hooper (10) who gave an average of 11·4 for various sticklacs and by Puran Singh (11) who gave 8·2—9·6 for certain lacs and shellacs determined by Hubl's method.

The necessity for extreme care in controlling the conditions under which the determination is carried out has been often illustrated (12, 13, 14,) and cannot be too strongly emphasised. For this reason uncertainty must be attached to many of the published results because of the omission of details of the method used. In all cases there is considerable doubt as to the absolute purity of the samples. It is extremely difficult to obtain shellac from India which is absolutely pure. Most commercial samples contain traces of either rosin, orpiment or both. Materials used by some investigators may have been rosin free but no mention is made of their orpiment content. That presence of orpiment raises the iodine value of shellac was pointed out by Briggs (15) in 1925 although Langmuir (4) in 1905 had stated that it had no effect. The extent of the effect of orpiment has been investigated by Rangaswami and Aldis (16), and shown to be quite appreciable.

In view of this uncertainty which must be attached to all previous figures it was felt desirable to investigate further the iodine values of pure shellacs by a strictly controlled method.

Experimental.

Fresh sticklacs were collected from various reliable sources. Many samples were taken from the experimental plantation attached to the Indian Lac Research Institute; others were sent by members of the Indian Forest Service and by reliable dealers. These samples comprised sticklacs from different host trees grown in different seasons, in different localities and collected in different stages of maturity. Samples which had been stored for known periods were also obtained. These sticklacs were manufactured into shellac under the author's supervision, by the native process in an experimental factory attached to the Institute.

The method of estimation was that given by the A.S.T.M's tentative method for shellac analysis for 1929 (14). Particular care was taken in the choice of reagents, in the preparation of the Wij's solution, and in control of time and temperature of the reaction. Results reproducible to about 3% could be readily obtained. Over seventy samples were investigated. Results are given in the following table.

TABLE I.

Type of lac.	Iodine value. Min.	Max.
Kusum	12·8	15·0
Palas	12·8	15·5
Ber	12·6	15·0
Khair (from Kusum brood) ...	12·8	14·2
Shorea talura (South India) ...	14·0	15·0
Assam lacs (dark)	15·5	16·8
Assam lacs (light)	14·0	15·0
Burma lacs	14·0	16·8

* For a description of the localities & trees producing the lacs mentioned, reference may be made to Glover's "Manual of lac cultivation (17).

THE STATE OF MATURITY OF THE CROP.

Certain sticklac samples were collected 'ari' *i.e.* about a month before the swarming time of the insect. Shellac from this material was compared with that from lac cut phunki *i.e.*, after swarming was completed; no appreciable difference in the iodine value was noticed.

EFFECT OF AGING.

Samples of shellac were prepared from sticklacs which had been stored for about 2 years. No change in iodine value was noticed in spite of the aging of the lac as regards other properties, such as fluidity, solubility etc. This agrees with Langmuir's (12) observation.

EFFECT OF HEAT TREATMENT.

Samples were prepared by heat treating shellac. The table gives iodine values for this material. The figures for viscosity are those determined by means of the Metropolitan Vickers apparatus at 125°C.

TABLE II.

Sample.	Heat treatment.	Viscosity.	Iodine value.
1	Original sample	42 secs.	14·04
2	½ hr. at 100-110°C	160 „	14·49
3	2 hrs. „ 100-110°C	369 „	15·12
4	3 hrs. „ 100-110°C	746 „	15·13

Apparently no appreciable change in iodine value is produced by heat treatment

DISCUSSION.

It will be seen from Table I that, with the exception of certain lacs from Assam and Burma, all iodine values lie below 15·5. Assam and Burma contribute less than 10% of the world's shellac. It appears, therefore, that the accepted maximum figure of 18·0 for the iodine value of pure shellacs is too high. A figure of 16·0 would be quite safe for over 90% of shellac manufactured. A figure of 17·0 would be quite safe for *all* lacs. Orpiment, which often existed up to about 1·0% in so-called Pure Orange Shellac was probably the cause of the higher values obtained for pure rosin free shellacs of previous investigators.

It is further demonstrated that the iodine value is not effected by such storage or heating as are met with in ordinary commercial treatment of lac and shellac. Commercial shellacs with values higher than those indicated in this paper are undoubtedly impure.

An orpiment free shellac containing rosin with an iodine value of 24 has a calculated rosin content of 2·86% based on the present accepted formula. This shellac has a calculated rosin content of 3·77% based on the assumption that pure shellac has iodine value 16·0. An excess of rosin of almost 1% over the accepted 3% standard for U.S.S. T.N. may, therefore, be passed undetected by the present accepted formula.

Summary.

Results of previous determination of iodine values of shellac are reviewed. The effect of orpiment in raising the iodine value was not realised by previous workers and detracts from the value of their results. Results of over seventy determinations of iodine value are summarised and indicate that the present accepted value 18 for pure shellac is too high and should be revised.

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