

## ON THE EXAMINATION OF VARNISH RESINS.

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*(Read at the Meeting, December 5, 1900.)*

I THINK it will be generally admitted that the analysis of varnishes is a *terra incognita*, if it is a question of determining by chemical means what gum has been used in the preparation of an oil varnish. In his despair the analyst will try to use the methods which have proved of such enormous advantage in fat analysis, and, as is well known, a number of determinations of the acid value, saponification value, and iodine values have been carried out, but their use for the diagnosis of gums in mixtures such as we have to deal with is almost infinitesimal.

It struck me that it has been generally overlooked that the determination of the so-called "constants" has been carried out on the original gums as obtained in the market, whilst the gums are, of course, subjected to a process of "running" or melting, which is accompanied in some cases by destructive distillation.

In the course of an examination of varnishes in my laboratory I had occasion to collect a few numbers representing the equivalent of what is termed in fat analysis "acid value," "saponification value," etc., and I have placed side by side with the numbers obtained with the most frequently used resins in the original state, those found after heating them to 300° C.

The result is very discouraging indeed, and I should certainly not have published the figures if I had not been asked to do so by a scientific varnish-maker, who thinks that these figures will be of value. So far, I cannot see that they will help in the analysis of varnishes, and the present paper must, therefore, be looked upon as merely putting on record some numbers such as anyone might get by a cursory examination.

I may add that the "acid value" was determined in the same manner as is done in fat analysis, with finely powdered material, regardless of whether the gum dissolved completely or not. If an excess of aqueous caustic potash is added, and back titration resorted to after some time, higher numbers are obtained, and it is possible to arrive at any figure for the acid value, provided one allows to stand long enough, and keeps adding fresh excess of alkali after neutralization, and again allows to stand. In some cases acid values were thus obtained which were far higher than the saponification value, a fact which would point to the gradual degradation of the constituents of the gums. The arbitrary fixing of a certain time during which an excess of alkali is allowed to act on the gum would therefore appear to lack scientific foundation.

As the bromine addition method was done in most cases in acid solution, the bromine substitution value was not determined throughout. This will be done in future.

I think I have made it sufficiently clear that I do not attach much value to the figures given in the tables for purposes of detecting the gums used in the preparation of an oil varnish, quite apart from the fact that commercial samples show the greatest possible divergencies. Perhaps other tests I have in hand may lead to

• Compare, however, R. Williams, ANALYST, 1898, 254.

more useful information (such as oxygen absorption, Twitchell's resin determination, Liebermann's starch colour reaction, and a few more that readily suggest themselves to the analyst).

I am indebted to my assistants, Messrs. C. D. Robertshaw and G. Warburton, for the figures in the following table :

	ORIGINAL GUMS.						GUMS AFTER HEATING TO 300° C.					
	Acid Value.	Sap. Value.	Unsap. %	Iodine Value.		Sol. in Alcohol, %	Acid Value.	Sap. Value.	Unsap. %	Iodine Value.		
				ICI.	Br.					ICI.	Br.	
Copal, Commercial ...	109.8	143.1	7.96	135.5	183.6	93.06	26.49	85.4	14.73	124.3	181.3	
Copal, Commercial ...	42.43	66.82	14.99	191.2	114.6	54.83	24.94	61.04	46.40	143.7	233.5	
Copal, Sierra Leone ...	72.83	119.03	18.81	105.7	96.05	—	12.89	114.9	17.22	125.5	173.6	
Copal, Manila ...	127.6	175.17	15.98	137.9	188.2	—	68.21	136.3	22.99	133.3	186.4	
Copal, Brazil ...	108.99	171.4	7.66	127.7	72.66	—	46.25	113.8	38.74	136.7	225.9	
Copal, Sierra Leone ...	65.7	110.5	16.27	94.55	117.0	—	15.32	123.8	22.31	95.23	135.4	
Cowrie ...	37.39	53.84	20.07	90.99	—	—	17.14	61.07	10.39	67.70	74.71	
Mastic ...	52.73	81.79	51.13	175.7	185.0	84.41	23.23	50.24	49.28	165.0	217.8	
Shellac, Dark ...	61.13	203.0	3.56	35.57	13.25	—	—	—	—	—	—	
Sandarac, Mogador ...	134.39	143.42	13.2	112.2	99.98	—	64.84	136.14	14.28	126.4	69.13	
Sandarac, Austral ...	131.15	134.32	17.44	125.4	63.83	—	106.6	137.26	9.93	—	—	
Animis No. 1 ...	18.69	73.15	6.3	105.3	182.7	—	9.25	58.73	—	106.1	207.4	
Animis No. 2 ...	30.22	93.5	6.85	96.21	95.85	—	—	—	—	—	—	
Dammar ...	35.22	32.73	75.96	127.5	169.4	—	10.85	60.44	86.57	127.0	196.8	
Amber ...	16.7	121.27	18.86	58.98	82.82	—	—	—	—	—	—	
Succinit* ...	11.24	113.68	7.06	55.05	73.4	—	10.60	99.19	16.25	74.34	147.8	
Colophony ...	—	—	—	—	—	—	146.46	153.01	15.94	133.7	302.1	

#### DISCUSSION.

Mr. HEHNER agreed with Dr. Lewkowitsch that it was useless to examine the original gums, as they, on boiling, underwent considerable chemical change. The difficulty was rendered greater by the fact that the gums, as a rule, were not heated by themselves, but were mixed with oil. It was interesting to notice that a gum which, like mastic, had as much as 51—or of 49 after heating—of unsaponifiable matter, nevertheless had an iodine absorption of 175 before heating, or 165 after heating. This seemed strongly to suggest that the unsaponifiable matter itself had a high iodine absorption.

Mr. A. MARSHALL said that, in the determination of bromine absorption, working with carbon tetrachloride in the manner which he had described in a recent paper before the Society of Chemical Industry (*Journ. S. C. I.*, March, 1900), he had lately obtained some very interesting results; and he thought that possibly a similar process applied to some of these gums might yield results of value.

Dr. RIDEAL suggested that more might be learnt as to the changes which took

\* This is a species of amber.

place in these gums as the result of heating by taking one particular sample of gum and tracing the changes produced by heating it to different temperatures.

Mr. C. T. TYRER said that there were on the market so-called varnish gums which were practically manganese resins, containing considerable proportions of manganese; and probably in such cases the ordinary methods of analysis could not be successfully applied.

Mr. MITCHELL inquired whether the author had tried amyl alcohol as a solvent in the determination of the saponification value. Its use was said to produce values differing considerably from those obtained with ordinary alcohol.

Mr. MARSHALL said that in determining the acid value it was necessary, as nearly as possible, to dissolve the gum entirely, and some solvent, or mixture of solvents, should be used by means of which it was possible to effect this.

Dr. LEWKOWITSCH said that where only one gum was present the matter was comparatively easy to deal with, but when the gum consisted of a mixture of various copals, for instance, the question of identifying them was almost impossible to solve; for even among gums which were sold by the same name, trade samples varied so much that experts, judging by external indications, were frequently misled. In addition, information was in many cases not obtainable as to the treatment to which samples had been subjected, owing to the secrecy which prevailed in the trade. He was afraid that an investigation of the unsaponifiable matter would not prove of very much assistance. The figures were more or less accidental, depending mainly on the time of boiling with caustic potash. In some cases the figures were widely divergent, though in others—in the case of sandarac especially—they were more concordant. He was afraid that the adoption of Mr. Marshall's suggestion would not result in any improvement. As a matter of fact, the choice of an acetic acid solution in the bromine absorption determination in these particular cases had been due merely to a personal dislike of the use of carbon disulphide or tetrachloride; but the whole matter had been thoroughly investigated, and in some cases bromine addition values and bromine substitution values had been determined, although they were not given in the tables. He had not been able to spare sufficient time to go further into the matter and employ a menstruum which could completely dissolve the gums, and the question of time also had led him to adhere to one temperature, namely, that which was most commonly adopted in operations conducted on a large scale. He ought, perhaps, not to have referred to "varnish gums," but to "gums used in varnish-making." All these gums were of course added to oils which were afterwards boiled with certain proportions of manganese resin, or linolate, etc., and the metal was removed in the course of analysis. He had not tried amyl alcohol as a solvent, but he would be surprised if it were actually a fact that higher figures were obtained by its use, provided the saponification in alcoholic solution was carried out properly. The only explanation would seem to be that it was not pure.