

although it might not be as close as it was in the dephlegmator, it was nearly the same, or at any rate the difference was inappreciable.

THE PRODUCTION OF FORMIC ACID BY THE ATMOSPHERIC OXIDATION OF TURPENTINE.

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There are a number of references in chemical literature, including those noted at foot,* to the alleged production of formic acid from oil of turpentine by its atmospheric oxidation. According to one of these, crystals of lead formate are sometimes formed when oil of turpentine is kept in lead vessels, and Laurent refers to granular crystals of zinc formate said to have been observed on the covers of zinc boxes in which oil of turpentine had been kept. In none of these references, however, so far as we have been able to ascertain, have any analytical figures been given satisfactorily establishing the identity of formic acid resulting as a direct product of the oxidation of turpentine.

Having observed a considerable formation of crystalline matter in galvanized iron tanks which were in use for the storage of air-oxidised Russian turpentine, we made an examination of it. The substance in question was of a dirty reddish brown colour, due to the association of oxide of iron and other impurities, from which it was purified by boiling with hot water. The crystalline matter readily dissolved, leaving the impurities behind. The white crystals resulting from some twelve successive recrystallisations, were analysed and found to consist of practically pure zinc formate, responding perfectly to all the well-known qualitative tests and furnishing upon analysis the appended figures.

The method of analysis was as follows: The zinc was estimated in the usual way, by precipitation with sodium carbonate and weighed as oxide. The formic acid was estimated in accordance with the method described by Franzen and Greve (*J. prak. Chem.*, 1909, 20, 308, 389; see also "Analyst," 1910, 29). This process depends upon the reduction of mercuric chloride to mercurous chloride by formic acid, the precipitated mercurous chloride being dried and weighed subject to the usual precautions.

In the earlier experiments, the determinations of formic acid were not as satisfactory as could be desired, and it was conjectured that this might possibly be due to some solvent action of the zinc chloride which is formed, upon the mercurous chloride. The zinc was therefore removed by precipitation with sodium carbonate and the filtrate containing the formic acid in the form of sodium formate was used for the determination. The results thus obtained were perfectly satisfactory and closely agreed with theoretical requirements, as shown below. The water was determined by drying in a water oven at 100° C.

Zinc formate has the composition $(\text{H.COO})_2\text{Zn}, 2\text{H}_2\text{O}$.

	Theory for $\text{ZnC}_2\text{O}_4 \cdot \text{H}_2\text{O}, 2\text{H}_2\text{O}$	Found	
		No. 1	No. 2
Zinc	34.15	34.18	34.19
HCO_2	47.03	46.95	46.89
H_2O	18.82	18.78	18.78
	100.00	99.91	99.86

The percentage of formic acid was also estimated by dissolving the crystals in water, acidulating with dilute sulphuric acid and distilling the mixture, the distillate being titrated with $N/10$ soda (using phenolphthalein as an indicator) with the following results:—

	Theory.	Found	
		No. 1	No. 2
HCO_2	47.03	47.10	47.01

* Watts' Dictionary of Chemistry, 1882, vol. II., p. 683, and 1877, vol. V., p. 921; Gmelin's Handbook of Chemistry, 1860, vol. XIV., pp. 245, 249; Journ. Chem. Soc., of June, 1873, p. 510 (C. T. Kingzett), and March, 1875, p. 6 (C. T. Kingzett); "Analyst," vol. 33, p. 225 (J. H. Coate).

As bearing upon the method of formation of the formic acid thus identified, it is apparently to be regarded as a cleavage product of some change that slowly occurs in the body of the air-oxidised oil. The oxidised oil in question consisted of some thousand gallons which had been prepared in the presence of water, so that any formic acid originally present in the turpentine or produced during the process of oxidation, would have passed into the watery solution, and it was after separation from the watery portion that the practically dry oil was placed in the storage tanks in which the zinc formate was produced.

When American or Russian turpentine is oxidised in the presence of water, the aqueous solution reveals an increasing acidity during the process and as the result of a further examination of this matter we find that the acidity results from the presence of acetic and formic acids in admixture. In the case of one such aqueous solution resulting from the oxidation of Russian turpentine, 100 c.c. took 6 c.c. of normal soda to neutralise. Two litres were made alkaline with sodium carbonate and evaporated to about 200 c.c.; this was then filtered to free from separated oily matter, the clear filtrate made acid with sulphuric acid and then distilled. The distillate exhibited the characteristic reactions of formic and acetic acids, the presence of formic acid being demonstrated by the silver nitrate reduction test and by the reduction of mercuric chloride to mercurous chloride. The presence of acetic acid was proved by first removing the formic acid by boiling with mercuric oxide until the reaction was complete (according to the equation $\text{HgO} + \text{HCOOH} = \text{Hg} + \text{CO}_2 + \text{H}_2\text{O}$), and it was found that the filtrate gave the characteristic reactions of acetic acid.

In order to obtain some quantitative appreciation of the relative quantities of acetic and formic acids present in the aqueous solution above referred to, a further quantity was taken of which it was noted that 100 c.c. required 5.2 c.c. of normal soda; $1\frac{1}{2}$ litres of this fluid was acidulated with sulphuric acid and then distilled, and the distillate made up to $1\frac{1}{2}$ litres again; 250 c.c. of this being then taken and treated with mercuric chloride to determine the formic acid present by taking the weight of the precipitated mercurous chloride. Four experiments gave the following results:—1,420, 1,388, 1,290, and 1,303 grms. shewing an average of 1,349 grms., equal to 0.0527 gm. of formic acid in 100 c.c. Now, as this amount of formic acid would neutralise 1.14 c.c. of normal soda, whereas 100 c.c. of the liquid took 5.2 c.c. the difference may be regarded as representing the acetic acid present, namely, 0.2436 gm. per 100 c.c. The formic and acetic acids thus shewn to be present to an appreciable amount in the aqueous solution resulting from the oxidation of Russian turpentine in the presence of water, are no doubt the immediate results of the oxidation process, as was further evidenced by an examination of the Russian turpentine yielding the oxidised oil.

In order to ascertain to what possible extent the formic acid could have been derived from the original Russian turpentine, 150 c.c. of the latter was washed with an equal bulk of warm water, with constant agitation, during a period of half an hour, when the total acidity of the water was found to be 0.075 normal soda. The turpentine on being washed a second time with its own bulk of water during a further half-hour, gave a washing, the total acidity of which required 0.15 normal soda. Similar results were obtained upon an examination of another batch of Russian turpentine, and a batch of Swedish turpentine examined on the same lines gave a washing the total acidity of which amounted to 0.3 c.c. of normal soda.

In order to ascertain whether turpentine vapour acts upon zinc, portions of zinc foil were suspended above turpentine in covered test-glasses. Samples of good quality of commercial American, Swedish, and Russian turpentines respectively were employed, and after a period of nine weeks it was found that practically no action had taken place. Similar experiments were then made in the presence of aqueous vapour, the turpentine being placed in small beakers, surrounded with water in test glasses,

zinc foil being suspended above the liquids and the glasses being covered as before. Using American or Swedish turpentine, in four weeks there was a decided action, and in the case of Russian turpentine, a piece of foil 12×3 cm. increased in weight by 0.011 grm. This foil was covered with a thin white incrustation which, upon microscopical examination, shewed to be a mass of minute crystals: these were tested qualitatively and found to be zinc formate.

We hope to carry the investigation further, and in the meantime desire to express our acknowledgements to Mr. W. G. Carey, F.C.S., A.I.C., for the assistance he has given us in conducting the analytical work involved in this investigation.

DISCUSSION.

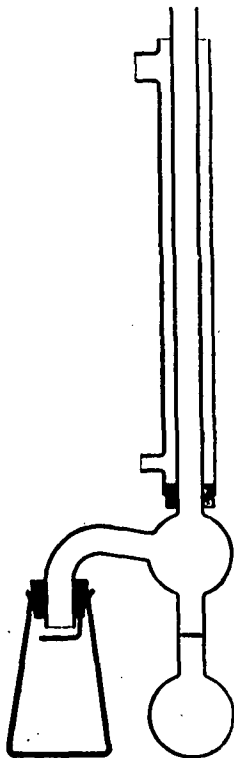
Mr. J. H. COSTE said that he had found formic acid to be present in turpentine which had been allowed to stand without being protected from the action of the atmosphere. He had been asked what would be a suitable varnish for protecting tanks in which turpentine was kept. Could the author suggest a suitable material?

Mr. KINGZETT said he had not observed that there was any particular corrosive action on the tanks in which turpentine was stored, except at the line of contact where there was exposure to the air and aqueous vapour, and even that was very insignificant. Some little further action was liable to take place at the bottom of the tank, where sometimes a little water accumulated. He did not know of any protective coating which could be relied upon, for the simple reason that all such mixtures were practically soluble in turpentine.

PROPOSED METHOD FOR THE ESTIMATION OF BUTTER AND COCOANUT FAT IN MARGARINE.

BY S. H. BLICHFELDT.

The recent introduction of palm kernel oil and coconut oil as materials for the manufacture of margarine, has necessitated the devising of some method by which these



substances may be estimated in presence of other fats occurring in margarine, which may possibly include

butter fat as a constituent. The methods hitherto available for the analysis of margarine and butter fat, though not altogether useless, have proved incapable of furnishing reliable results in dealing with such mixtures; the present communication includes an account of experiments undertaken in the Monsted Laboratory, Southall, with a view to improving these methods, and a detailed description of a method designed with a view to solving the problem under consideration.

One defect in Polenske's method is that appreciable quantities of the insoluble acids settle in the tube connecting the distilling flask with the condenser. The washing out of the condenser tube, receiving flask, and filter with water is not only a tedious process, but may also involve considerable experimental errors, as it often happens that an appreciable quantity of sparingly soluble acids are dissolved by the water and thus lost.

To overcome these difficulties, the condensing apparatus shown in the accompanying diagram was designed.* The side tube, the condenser tube and receiver are all in one piece. The whole of the distillate consisting of water and fatty acids at a temperature of 60° — 70° C. collects in the lower bulb. After removing the condenser jacket, an excess of *N*/10 sodium hydroxide is added to the distillate, the warm alkaline liquid is shaken up in the receiver and condenser tube to dissolve all volatile acids, and transferred to a 200 c.c. graduated flask. The apparatus is then rinsed with warm water and the rinsings are added to the main portion. The total volatile acids, soluble and insoluble, may be determined by titrating the excess of alkali by means of sulphuric acid, using phenolphthalein as indicator. The proportion between the soluble and insoluble acids may be determined as follows:—The volatile acids are liberated from their sodium salts by the addition of an equivalent quantity of sulphuric acid, the liquid is made up to 200 c.c. with water and set aside to cool in order that the insoluble acids may separate. It is then filtered clear and the soluble acids are determined in 150 c.c. of the filtrate by titration. The insoluble acids are determined by difference. The following values were thus obtained:—

	Total volatile acids.	Soluble.	Insoluble.
Butter	32	28	4
Cocoanut oil	22	8	14
Palm kernel oil	15	5	10

A large number of analyses was made by this method; the results though more trustworthy than those obtained by the Polenske method, were nevertheless, far from satisfactory.

In dealing with mixtures containing small percentages of cocoanut oil or palm kernel oil, great difficulty was experienced in obtaining clear filtrates containing the soluble acids. A further defect appeared in the fact that when the percentage of cocoanut or palm kernel oil present in the mixture was small, a larger proportion of the sparingly soluble acids passed into solution than when higher percentages of these oils were present. This defect was aggravated by the dilution of the distillate to 200 c.c. The accompanying curves illustrate this point; had the ratio of the insoluble to the soluble acids produced by the same cocoanut oil in different mixtures been constant, these curves would have appeared as straight lines, whereas in reality, the ratio is seen to vary with the quantity of volatile acids produced by the fatty mixtures.

In order to obtain a clear filtrate and also, if possible, to get a more constant ratio, it was decided to try the method of precipitating silver salts from the neutral solution. The silver salts filter easily, giving a perfectly clear filtrate, but what is still more important is that the ratio between the volatile acids giving soluble and those giving insoluble silver salts affords a much better means of characterising the fats dealt with.

* The complete apparatus is made by F. E. Becker & Co., 17-27, Hatton Wall, E.C.