

the melting-point, also increases with the amount of sulphuric acid present, but an excess has the opposite effect. The amount of nitric acid used in Set 1 has no advantage over the smaller amount used in Set 2, but it is not advisable to use still less acid, especially when higher nitration degrees are desired, since the product is apt to be attacked by the sulphuric acid.

To obtain nitro derivatives of naphthalene for commercial purposes, it is therefore best to nitrate the naphthalene with a mixture of nitric and sulphuric acids, using about three times as much  $36^{\circ}$  B. acid as naphthalene. The amount of sulphuric acid to be used will vary with the nitration degree desired and ranges from 4 : 1 (nitric : sulphuric) for low melting products, to 3 : 2 for the higher derivatives. Too large an excess must be avoided, as it chars the product, producing a tarry useless end-product.

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### SPONTANEOUS COMBUSTION OF MOLASSES.

BY J. T. CRAWLEY.

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EARLY in September of last year a sample of charred molasses was forwarded to the laboratory of the Hawaiian Experiment Station from the Hamakua Mill, Hawaii, but owing to stress of work it was not examined until quite recently. The following extracts are taken from the letter from Mr. William McQuaid, chemist at the Hamakua Mill, which accompanied the sample. "The molasses in question was boiled to what is known as "string proof," at a temperature of  $160^{\circ}$ - $165^{\circ}$  F., and run into an underground cistern from time to time until the molasses was within six or eight inches of the top of the cistern, when the walls cracked, and the molasses began to leak out. The molasses continued to leak for about one and a half months, during which time five or six feet of the molasses was thus lost. That which remained seemed to be in a perfect condition. Five days later, however, it was found flowing over the sides of the cistern in somewhat of a burnt state. The temperature at the point where the molasses flowed over was  $92^{\circ}$  C., but in the cistern, and especially where the crack was located, this boiling seemed to be more violent.

"This flowing continued for about twelve hours, but the molasses continued boiling within the cistern until there was left

nothing but a few feet of charred mass. The fumes given off affected the eyes very much, and coming in contact with the metal roof formed a salt."

The sample of char formed under the above conditions was tested with a view of establishing the probable degree of heat at which the changes took place, as also to find the origin of the heat. Parts of the sample were quite black, having somewhat a ropy feel and consistency; other parts were dry, brittle, vesicular masses, brownish in color, resembling very much vesicular lava, while still other portions were of a much lighter color, the decomposition having gone so far as to drive off almost all volatile products, leaving a residue of carbon, ash, etc.

Several hundred grams of the material were repeatedly macerated and digested with cold and hot water. A large portion dissolved, giving a very dark colored solution, resembling the solution of caramels. This dark colored substance was still dissolved in notable quantities even after five days' digestion. The water solution was quite acid; therefore a weighed quantity was taken, digested with water, and the filtrate distilled with phosphoric acid. The acid of the distillate proved to be acetic acid almost entirely, with a small quantity of formic acid. The total acid amounted to three and eight-tenths per cent. calculated as acetic acid.

*Sucrose.*—500 grams were extracted with water, sufficient alcohol added to bring the strength of the alcoholic solution to sixty per cent., and precipitated with strontium oxide. The very copious precipitate was filtered, washed, suspended in water, and saturated with carbon dioxide. The filtrate from this precipitate was clarified with lead acetate, the lead thrown out with hydrogen sulphide, and the clear filtrate evaporated. Not a trace of sucrose could be detected either by crystallization or by reduction of copper solution after hydrolysis. This negative result was to be expected, since the large content of free acid taken in connection with the high heat during combustion in the tank, would have broken up the sucrose very quickly.

The distillate, obtained by distilling a portion of the original matter with phenyl hydrazine, gave the characteristic furfural hydrazone, thereby proving the presence of furfural in the original material, but in minute quantities.

On evaporating the water solution of the char, and adding alcohol, a very dense precipitate was obtained, which on purification and hydrolyzing with hydrochloric acid, reduced Fehling's solution, showing the presence of glucose-yielding bodies, or mucilages in comparatively small quantities.

The original sample, on being distilled with hydrochloric acid, gave with phenyl hydrazine the test for furfural-yielding bodies, the gums, in extremely small quantities, thus showing that these bodies, the mucilages and gums, have been almost totally destroyed. In the so-called gums found in the sugar-cane Dr. Maxwell found 64.6 per cent. to be glucose-yielding bodies, or hexosans, and 3.6 per cent. furfural-yielding bodies, or pentosans.

The water-soluble bodies present in the original char were separated by alcohol of different strength into bodies having melting-points varying from 130° C. to 275° C., while others decompose without melting.

The following bodies were detected, the per cent. being given where that was estimated :

Organic acid distilled	3.80 per cent. calculated as acetic acid.
Furfural .....	minute quantities
Furfural-yielding bodies .....	“ “
Glucose-yielding bodies .....	small “
Caramels .....	large “
	Per cent.
Reducing sugars .....	11.20
Nitrogen .....	0.87
Phosphoric acid .....	0.30
Potash .....	2.27
Insoluble in water .....	38.20
Moisture .....	15.00

The moisture fumes given off from the burning mass came in contact with a metal roof and formed a salt, a sample of which also was forwarded to this office. The salt was almost pure zinc acetate with a little formate. The formic acid was separated from acetic by digesting their lead salts with alcohol, breaking up the insoluble lead formate with hydrogen sulphide and proving the presence of formic acid by its reducing action on silver and mercury salts.

Taking the original molasses from which this char resulted as having the probable composition,

	Per cent.
Water .....	20
Sucrose.....	45
Glucose.....	10

we see (1) that fully eighty per cent. of the sugars present have been destroyed, with a large part of the gums and mucilages; (2) that they have yielded, among other bodies, formic and acetic acid, the latter in large quantities, furfurol and caramels of varying degrees of solubility and melting-points; and (3) that a residue of insoluble caramels and unburnt carbon largely, to the amount of fully one-third the weight of the char is left behind.

As to the degree of heat at which these changes took place, we must conclude that at least a temperature of 200° C. was maintained for some time during which the caramel was formed, while a very much higher degree was reached toward the end of the action.

The phenomenon can have been nothing else than spontaneous combustion, the acid products being oxidation products, and therefore having lower thermal values than the original sugars. The successive stages of oxidation and decomposition furnished the heat necessary to carry the whole mass to the next stage.

As to the initial cause of the rise in temperature, little can be said; the high water content and known fluidity of molasses would tend to retard decomposition by oxidation. It is a fact well known among practical sugar-house men, that if a molasses of low grade be boiled at a high temperature and run into coolers it is very apt to froth and foam, and run over the sides of the containers. It is also known that running successive charges of hot molasses into the same container will often result in a burning of the product and foaming over the sides of the container.

The cause of this foaming and frothing is not positively known. Fermentation often proceeds in a very thick molasses, in fact at a much higher density than is generally known, and the escaping carbon dioxide would tend to cause the mass to rise up. I am inclined to believe, however, that in the majority of

cases this frothing is due to decomposition of the non-sugars. This is a subject that will be looked into.

Whatever may have been the initial cause of heat, whether fermentation or decomposition due to the treatment, there can be no doubt that there was a violent manifestation of heat most destructive in its effects.

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## THE FERROCYANIDES OF ZINC AND MANGANESE.<sup>1</sup>

BY G. C. STONE AND D. A. VAN INGEN.

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OUR work on ferrocyanides was undertaken more to try to reconcile the very discordant statements that have been made about its value as a means for the volumetric determination of zinc than to determine the exact composition of the salts. We therefore have merely tried to determine the influence of temperature and acidity on the composition of the precipitates formed when potassium ferrocyanide is added to the solution of a salt of zinc or manganese. The simplest method for this is to add to a known amount of a zinc solution an excess of a ferrocyanide solution, the strength of which has been accurately determined by titration with permanganate and to determine the excess of ferrocyanide not precipitated by the zinc by titration with permanganate. We found that it was practically impossible to filter the ferrocyanides of either zinc or manganese, but by diluting to a known volume, allowing the precipitate to settle and titrating an aliquot portion, we obtained results that agreed with each other, provided the excess of ferrocyanide remained the same; but with varying excesses the ratio of zinc to ferrocyanogen in the precipitate fell irregularly as the excess of ferrocyanide increased. With manganese this method also failed, as we found that the ferrocyanides of manganese were somewhat soluble in water, rather more so in potassium ferrocyanide and entirely soluble in strongly acid solutions.

We next tried precipitating zinc and manganese in neutral, strongly acid solutions, both hot and cold, and in cold slightly acid ones. The precipitates were washed by decantation. Most of them settled very slowly, especially when nearly washed. We found that they settled much more rapidly if some other salt

<sup>1</sup> Read at the meeting of the New York Section, May 7, 1897.