chemical manufacturers for the purpose of introducing the process into the plants on a commercial scale. Some months later all of the coöperation that could be handled advantageously was effected and the constantly increasing pressure of war problems employing the laboratories and personnel made it advisable to withdraw the offer, which was done on November 1, 1917.¹ Shortly after the signing of the armistice it was decided to reopen the offer of coöperation and an announcement to that effect was issued on March 17, 1919.² The reasons for this action were several.

First—The work upon war problems was practically over and men and funds were again available for the work for which this laboratory was planned.

Second—Several manufacturers stated that they could not enter into the coöperative agreement when first announced because at that time their entire staff was devoted to work on hand, but that now their resources were larger, war work was over, parts of the plant were idle, and they would like to be put in position to utilize the information originally given to other coöperators and upon the same terms.

Third—Publications of the completed work will not be ready for an indefinite period, since the scope of the investigations is undergoing great expansion, and it is considered desirable that the manufacturing process first be firmly established in this country. In the interim coöperators are furnished immediate reports on the latest developments.

Fourth—It seems desirable that a number of plants work upon the same problem in order that the best commercial installation be ultimately obtained.

Although the development was delayed somewhat by war conditions, the large-scale manufacture of phthalic anhydride is now proceeding in a satisfactory manner, and it is believed that eventually the details of the factory units will be so worked out that this process will be the most economical and practicable known for making phthalic anhydride. In fact, phthalic anhydride may become one of the cheapest organic compounds.

It is interesting to note that the phthalic anhydride produced by this process is of a remarkable degree of purity. Naturally it is free from chlorine or sulfur compounds, common impurities in phthalic anhydride as formerly found on the market.

Many data on the work have accumulated and new facts are continually being discovered. A series of papers descriptive of the work is now in preparation and will appear at intervals when the status of this and other investigations will permit.

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HYGROSCOPIC PROPERTIES OF BLACK POWDER³

By G. B. TAYLOR
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Among the questions referred to the Bureau of Mines by the military authorities during the war was

that of whether black powder in which a small part of the potassium nitrate had been replaced by potassium perchlorate was less resistant to moisture than straight black powder. This led to a brief study of the conditions under which black powder absorbed atmospheric moisture, the results of which are presented in this report. The fact that powder is more effective in the moisture-free condition is embodied in the old admonition to "keep your powder dry."

The methods followed were those of a previous investigation on moisture absorption by detonators.¹ The rate of moisture absorption in a saturated atmosphere was determined at 25° C. by exposing the material in shallow flat-bottom crucibles. Ordinary quart jars closing with glass tops and spring clamps were filled about an inch deep with distilled water; in each jar was placed a copper wire tripod for supporting one crucible. The jars were then closed and submerged completely in a large water thermostat electrically heated and stirred, and controlled by a toluene thermoregulator within $\pm 0.01^\circ$ of 25° C.

Two grams of the material whose rate of moisture absorption was to be determined were spread evenly over the bottom of the crucible (3.7 cm. in diameter), the crucible brought to 25°, and placed in one of the jars. After a certain number of hours the crucible was removed, placed in a weighing bottle, and weighed. Each result was obtained from a separate crucible, as it was found unsatisfactory to return the same crucible to the jar, on account of change in temperature of the crucible during weighing and slight losses in moisture while handling.

It was found in the previous investigation² that the moisture absorbed in a given time by pure salts under the conditions above outlined was independent of the weight of salt taken within certain limits (0.5 to 2.0 g.) and also independent of the degree of fineness to which the salt was ground. The relative rates of moisture absorption of different salts were found to be proportional to the difference between the vapor pressures of their saturated solutions and the partial pressure of water vapor in the surrounding atmosphere. It follows that when this difference is zero or when the partial pressure of water vapor in the surrounding atmosphere is less than the vapor pressure of the saturated solution of the salt no moisture will be absorbed. In the latter case a moist salt would dry out.

In American practice black powder is a mixture of 75 per cent potassium or sodium nitrate, 10 per cent sulfur, and 15 per cent charcoal. Moisture absorption is largely due to the nitrate or soluble constituents. Charcoal plays a small part.

EXPERIMENTAL

Two samples of black powder were submitted by the Ordnance Department for test. These were given the laboratory numbers M-2332 and M-2333. The size of grain appeared to be F. For comparison, the

¹ G. B. Taylor and W. C. Cope, "Hygroscopic Properties of Sodium, Potassium, and Ammonium Nitrates, Potassium Chlorate, and Mercury Fulminate," *Mel. & Chem. Eng.*, **15** (1916), 140.

² *Loc. cit.*

¹ THIS JOURNAL, **9** (1917), 1148.

² *Ibid.*, **11** (1919), 489.

³ Published by permission of Director, U. S. Bureau of Mines.

Bureau of Mines secured a sample of straight black powder, M-2334, size FF. The analyses follow:

	TABLE I M-2332	M-2333	M-2334
KNO ₃	70.56	68.79	74.37
Sulfur.....	10.43	10.45	10.28
KClO ₄	2.91	4.80	
Charcoal.....	15.78	15.44	15.08
Moisture.....	0.32	0.52	0.27
	100.00	100.00	100.00

The rate of moisture absorption was determined on all these samples in a saturated atmosphere at 25° both as received and after crushing the grains to about 40 mesh. The results are given in Table II. Two-gram samples were weighed out in crucibles and desiccated over sulfuric acid several days previous to the tests.

TABLE II—RATE OF MOISTURE ABSORPTION IN A SATURATED ATMOSPHERE AT 25° C.

MATERIAL	HOURS	Moisture Absorbed Gram
M-2332, crushed grains (2.91 per cent KClO ₄).....	17 1/2	0.1665
	30 1/2	0.2354
	48 1/4	0.3803
M-2333, crushed grains (4.80 per cent KClO ₄).....	17 1/2	0.1649
	30	0.2482
	48	0.3844
M-2334, crushed grains.....	17 3/4	0.1420
	29 1/2	0.2174
	47 1/2	0.3595
M-2332, as received (2.91 per cent KClO ₄).....	7	0.0670
	16 1/2	0.1311
	30 1/2	0.2386
M-2333, as received (4.80 per cent KClO ₄).....	7	0.0607
	16 1/2	0.1248
	30 1/2	0.2173
M-2334, as received.....	7	0.0587
	16 1/2	0.1158
	30 1/2	0.2186
Potassium perchlorate.....	17	0.0070
	41 1/8	0.0191
	65	0.0238
Potassium perchlorate, 5 per cent } { 6 1/2		0.0429
Potassium nitrate, 95 per cent. } { 23 3/8		0.1582
	{ 47 1/2	0.3012

For purposes of comparison the rates of moisture absorption of pure potassium perchlorate and a mixture of 5 per cent of this salt with 95 per cent pure potassium nitrate were determined. The results obtained are plotted in Fig. 1. When the increase in weight due to absorbed moisture is plotted against time, the points for pure salts lie on straight lines. In the figure the potassium chlorate, potassium nitrate, and sodium nitrate lines are taken from a former Bureau of Mines investigation.¹ To make sure that the conditions of experiment were the same, two points on the potassium nitrate line and one on the potassium chlorate were repeated. The new and old data were found to be in agreement.

Inspection of the figure shows that potassium perchlorate takes up moisture slowly from a saturated atmosphere, as might have been expected from its slight solubility. Calculation from its rate of moisture absorption shows that this salt is not hygroscopic unless the relative humidity exceeds 99 per cent at 25° C. Potassium nitrate absorbs moisture when the relative humidity exceeds 93 per cent, so that it was not to be expected that perchlorate would greatly influence the hygroscopicity of nitrate. The experimental results show that a mixture of 95 per cent potassium nitrate and 5 per cent potassium per-

chlorate absorbs moisture at practically the same rate as pure nitrate. It may be interesting to point out, however, that a mixture of 95 per cent perchlorate and 5 per cent chlorate absorbs moisture during the first 48 hrs. as fast as pure chlorate.

FIG. 1

The fact that a mixture of 5 per cent perchlorate with nitrate absorbs moisture at practically the same rate as pure nitrate would seem to indicate that the replacement of part of the nitrate in black powder by perchlorate does not increase its sensitiveness towards atmospheric moisture. Charcoal also absorbs moisture, which accounts for the deviation of black powder from the potassium nitrate line. In order to determine the order of magnitude of this effect, the soluble constituents of the powders were carefully washed out with water and the resulting charcoal-sulfur mixture dried and then exposed to a saturated atmosphere at 25° until equilibrium was reached. The results follow:

Weight of charcoal and sulfur mixture Gram	TABLE III GRAM OF MOISTURE ABSORBED AT EQUILIBRIUM AT 25° C.		
	M-2332	M-2333	M-2334
0.100	0.0190	0.0133	0.0153
0.250	0.0310	0.0252	0.0393

Equilibrium occurs in about 24 hrs. The results of the table were obtained from 48 hrs. exposure and it is seen that the moisture absorbed in proportion to weight within the experimental error. Two-gram samples containing 0.5 g. of charcoal-sulfur can absorb about 0.06 g. of water due to this mixture, which is about the maximum deviation of the powder samples from the potassium nitrate line.

The slightly greater affinity for atmospheric moisture of the samples containing perchlorate over the sample of straight black powder is of no practical im-

¹ Taylor and Cope, *Loc. cit.*

portance and may be accounted for by variations in structure or minor impurities. None of the samples gave a positive flame test for sodium.

SUMMARY

1—The relative rates of moisture absorption of three samples of black powder in a saturated atmosphere at 25° have been determined.

2—The presence of potassium perchlorate up to 5 per cent in mixtures with potassium nitrate has been shown to have only slight effect on the rate of moisture absorption.

3—Charcoal has been shown to contribute to the hygroscopic property of black powder but in much smaller degree than nitrate.

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THE COLOR CHANGES OF SUGAR-CANE JUICE AND THE NATURE OF CANE TANNIN¹

By F. W. ZERBAN

Received May 2, 1919

A former article on this subject² dealt with the rôle of oxidases and of iron in the color changes of sugar-cane juice. The third factor known to be involved in the reactions is a water-soluble polyphenol which gives a green coloration with ferric salts. The previous literature regarding the whole subject was discussed in the paper referred to, but since its publication there has been noticed a very interesting and valuable contribution, overlooked before, on the oxidases of the sugar cane, by Ramji Narain.³ His studies were made more particularly from the standpoint of the plant physiologist, the principal object being the discovery of possible connections between oxidase activity and the formation of carbohydrates in the plant. He obtained positive reactions for a laccase and for peroxidase, but did not find tyrosinase, evidently because he did not employ the specific reagent consisting of *p*-cresol and glyocoll. Narain also reports some observations regarding the thermostability of cane oxidase. He found that his oxidase preparations could be boiled vigorously for 15 min. without the permanent loss of their effect. Their activity was found to be greatly impaired directly after boiling, but it reappeared almost undiminished after cooling. The boiling for 15 min. could even be repeated with the same effect as before. Like observations were made by him upon treating the oxidase preparations with hydrogen sulfide. Similar results had been previously obtained, by Euler and Bolin, and by others, but it appears that the action of heat on oxidases depends largely on their state of purity. Narain draws the conclusion that oxidases can no longer be classed as enzymes, because they do not show the characteristic thermolability of these substances. Neither Browne nor Raciborski report the return of the activity of cane oxidase after boiling, and our own experiments did not confirm

Narain's results. But even if the oxidases were not permanently inactivated by boiling, the matter of their classification still depends entirely on the definition of "enzymes." Schmidt,¹ Gramenitzki,² Mellanby and Woolley,³ report that under certain conditions, trypsin, taka-diaxase, and other enzymes can be boiled, and trypsin be heated in glycerol to 292°, without permanently losing their activity, and yet nobody has ceased to classify them as enzymes. If we accept the definition of Bayliss,⁴ who says that "Enzymes are merely a particular class of catalysts, considered for convenience apart, owing to the fact that they are produced by living organisms and are, for the most part, of unknown chemical constitution," then the resistance to heat is not a sure criterion for classification. It is true that oxidases differ from other enzymes also in not being specific, but even this is no reason for separate classification under Bayliss's definition.

Narain in the same paper also publishes some observations on the polyphenol of the cane. He states that on account of its behavior with lime water it must belong to the oak tannin group and not to the gallotannic acid group, but that some of its reactions resemble those of pyrogallol. He was unable to isolate pyrocatechin from the cane. This polyphenol, according to Miss Wheldale,⁵ is the cause of the guaiac reaction given by a number of plants. The author's experiments fully confirm Narain's claims on this point. Miss Wheldale's supposed pyrocatechin was most probably some other substance, because she reports finding it after treatment of the plant extract with chloroform, in which solvent pyrocatechin is appreciably soluble. Dekker⁶ also expresses serious doubts concerning the alleged occurrence of pyrocatechin in plants. The absence in sugar cane of pyrocatechin was proven by us by digesting sliced cane tops, which give a strong reaction with ferric salts, with benzene in a glass-stoppered bottle. The benzene extract was evaporated, the residue treated with water, filtered, and the filtrate tested for pyrocatechin. It did not even give the iron reaction.

In our further investigations on the nature of the cane polyphenol, we first tried to prepare extracts rich in this substance by dropping sliced cane tops, and eyes cut from the cane, into alcohol. This was done during the grinding season, and we hoped to work up these extracts after the end of the campaign. But it was found that, in spite of the high percentage of alcohol which was used to weaken enzyme activity, the extracts darkened very much while being kept, and we concluded that a large part of the polyphenol originally present must have been oxidized. After a number of unsuccessful attempts to prevent this oxidation, we finally adopted the method of slicing cane tops directly into boiling water, continuing the boiling for 5 to 10 min., and then pressing the juice out rapidly

¹ *Z. physiol. Chem.*, **67**, 314.

² *Ibid.*, **69**, 286.

³ Bayliss, "The Nature of Enzyme Action," 3rd Ed., p. 97.

⁴ *Loc. cit.*, pp. 11, 139.

⁵ *Proc. Roy. Soc.*, **84B** (1911), 121.

⁶ "De Looistoffen," **1**, p. 209.

¹ Presented at the 56th Meeting of the American Chemical Society, Cleveland, Ohio, September 9 to 13, 1918.

² *This Journal*, **10** (1918), 814.

³ *Ag. J. India*, **1918**. Science Congress Number, 47.