

The results of this analysis do not indicate that this substance has any relation to the other proteids already described. Owing to its insolubility in neutral fluids no characteristic reactions could be obtained, and accordingly nothing more was learned respecting it.

The foregoing statements show that 100 grams of the yellow corn meal contained approximately :

| | | | | | | |
|--|------|--|---|-------|----------------|----------------|
| Proteid soluble in two-tenths per cent. potash.... | } | 3.15 grams containing 15.82 per cent. N. = 0.4983 gms. | | | | |
| Zein | | 5.00 | " | " | 16.13 | " " = 0.8065 " |
| Very soluble glob- ulin | 0.04 | " | " | 15.25 | " " = 0.0061 " | |
| Edestin | 0.10 | " | " | 18.10 | " " = 0.0181 " | |
| Maysin | 0.25 | " | " | 16.70 | " " = 0.0417 " | |
| Protease | 0.06 | " | " | 17.00 | " " = 0.0102 " | |
| | | | | | 1.3809 " | |
| Nitrogen undissolved by dilute potash water | | | | | 0.1645 " | |
| Total | | | | | 1.5454 " | |
| Nitrogen in meal by analysis..... | | | | | 1.5400 " | |
| Mean percentage of nitrogen in Maize Proteids | | | | | 16.057 | |

THE COMMERCIAL PREPARATION OF NITRONAPHTHALENES.

BY WILLIAM H. KRUG AND J. E. BLOMEN.

Received May 15, 1897.

THE manufacture of nitronaphthalenes has of recent years acquired considerable importance in the arts, and particularly in the explosive industry. In this industry it has been utilized in various ways and for different purposes. The late Nobel was the first to point out that the addition of nitronaphthalene to a nitroglycerol explosive, such as nitrogelatin, rendered this practically non-sensitive to concussion, and this property has been and is still widely applied to render the handling of nitroglycerol explosives more safe.

In the manufacture of nitro substitution powders, nitronaphthalene soon replaced the more expensive nitrobenzol as a basis, and a large number of patents were taken out for its use with oxidizing agents alone or with an admixture of sensitizing agents, such as nitroglycerol, picric acid, etc. A third use was found for nitronaphthalene when it was discovered that it seemingly ren-

dered dynamite "non-freezable." Even a small admixture of nitronaphthalene causes dynamite to remain soft to the touch at low temperatures, and it has therefore been extensively used for the manufacture of non-freezing dynamite. It has been proved that this advantage is only chimerical; the addition of nitronaphthalene in no wise changes the properties which are characteristic of nitroglycerol at low temperatures, but in fact adds a new element of danger, as it makes it impossible for the miner to determine whether the dynamite should be thawed before use.

Still another use of nitronaphthalene was taken advantage of in its property of rendering dynamite "fumeless," but this has not yet been definitely proved. In the manufacture of plastic dynamites it has always been difficult to obtain a nitrocellulose which gelatinizes perfectly in the nitroglycerol. An addition of nitronaphthalene will considerably increase the solvent action of nitroglycerol on nitrocellulose, *i. e.*, even higher nitration degrees than trinitrocellulose may be dissolved when nitronaphthalene is added to the nitroglycerol. The vast importance of this property will be realized by any manufacturer who has a large quantity of the expensive nitrocellulose rejected on account of its insolubility in nitroglycerol.

Almost every manufacturer of explosives has been confronted with the problem of preparing nitronaphthalene in a practical and economical way, but has found that very little of practical value has been published on this important subject.

In speaking of nitronaphthalene, a mixture of the nitronaphthalenes is always meant. When the nitronaphthalene is used in conjunction with nitroglycerol its melting-point is of minor importance, but it is desirable to have as high a degree of nitration as possible, since this will retard the momentum of the explosion to a less degree. When used with other sensitizing agents, such as picric acid, it is obvious that the melting-point must be below the decomposition-point of this agent. When it is desired to use a higher nitronaphthalene in this connection it may be accomplished by adding a small amount of mononitronaphthalene, as the latter acts as a solvent of the higher nitro derivatives, and they together will dissolve picric acid, nitrocellulose and the like.

The investigations, which form the basis of this paper, were

undertaken to determine under what conditions the largest yield of suitable nitronaphthalenes could be obtained. The nitro derivatives of naphthalene are generally obtained either by the action of nitric acid alone or mixtures of nitric and sulphuric acids on naphthalene, or for the highest nitro derivatives by renitration of the lower nitronaphthalenes. It has been suggested at different times to prepare the higher derivatives by the nitration of naphthalene-sulphonic acid similarly to the preparation of nitrophenols from phenolsulphonic acid. To ascertain the practicability of this proposition the following experiments were made :

α -Naphthalene-sulphonic acid was prepared by heating naphthalene to 100° C. for about eight hours with one, two, and three times the amount of sulphuric acid required by theory. A fourth preparation was made, using a large excess of sulphuric acid. This last preparation was the only one which appeared free from naphthalene, the substitution being practically complete. It had no odor, was free from naphthalene crystals and gave a clear solution with water.

A quantity of each of these preparations corresponding to ten grams naphthalin, was weighed into flasks and treated in one series with forty grams 36° B. nitric acid, and in another series with thirty grams of the same acid. This strength acid was chosen because it most nearly represents the waste acid recovered in the regaining works of nitroglycerol plants. The stronger acid, 1.42 sp. gr., is so much more expensive that its use is practically out of the question in the commercial preparation of nitronaphthalenes. The action is furthermore so violent when it is used that there is considerable loss of naphthalene through sublimation, and the gain in yield is not proportionally higher. Dilution below 36° B. offers no advantages, as we will show, and is therefore not necessary.

The nitrations were made on a water-bath and were considered complete some time after the red fumes ceased to come off. The resulting mass was melted under water and washed in this state until acid-free. It was then carefully dried on watch-glasses and weighed. When the nitronaphthalenes are used with nitroglycerol or nitrocellulose, it is very important that it should be neutral, and it may even be slightly alkaline. We have

found that this cannot be done with a weak solution of alkali, as it decomposes the product, giving a deep yellow solution. It may, however, be done with a weak solution of sodium carbonate.

The results were :

SERIES I.—FORTY GRAMS 36° B. NITRIC ACID.

| No. | Weight of product. | Color. | Odor. | Melting-point. | Remarks. |
|------|--------------------|----------------|--------|----------------|------------------------|
| 1 | 13.3661 | yellow | strong | 49.0° | crystalline mass, soft |
| 1A | 12.8342 | " | " | 50.0° | " " " |
| Mean | 13.1002 | | | | |
| 2 | 7.6504 | yellow | strong | 50.0° | crystalline mass, soft |
| 2A | 7.0289 | " | " | 52.0° | " " " |
| Mean | 7.3397 | | | | |
| 3 | 1.0022 | greyish-yellow | slight | 152.0° | fine silky crystals |
| 3A | 0.8288 | yellow | " | | " " " |
| Mean | 0.9155 | | | | |
| 4 | 0.0514 | brown-yellow | none | | solid crystalline mass |
| 5 | 0.4830 | pale yellow | none | 150.0° | fine crystals |
| 5A | 1.3017 | " " | " | | " " |
| Mean | 0.8923 | | | | |

SERIES II.—THIRTY GRAMS 36° B. ACID.

| No. | Weight of product. | Color. | Odor. | Melting-point. | Remarks. |
|------|--------------------|----------------|--------|----------------|---------------------------|
| 1 | 10.6374 | orange | strong | 54.0° | crystalline mass, soft |
| 2 | 9.6721 | yellow | strong | 57.0° | crystalline mass, soft |
| 2A | 13.6125 | orange-yellow | " | 52.0° | " " " |
| Mean | 11.6423 | | | | |
| 3 | 0.7623 | greyish-yellow | slight | 163.0° | bulky fine crystals |
| 3A | 0.4714 | yellow | " | | " " " |
| Mean | 0.6169 | | | | |
| 4 | 0.0227 | brown | none | | slightly crystalline mass |
| 5 | 0.8708 | almost white | none | 165.0° | crystals |
| 5A | 0.3020 | pale yellow | " | | " |
| Mean | 0.5864 | | | | |

No. 1. Pure naphthalene.

No. 2. Naphthalene treated with the theoretical amount of sulphuric acid.

No. 3. Naphthalene treated with twice the theoretical amount of sulphuric acid.

No. 4. Naphthalene treated with three times the theoretical amount of sulphuric acid.

No. 5. Naphthalene treated with excess sulphuric acid.

It will be seen that the two series correspond quite closely

in every respect, and that the yield decreases proportionately with the extent of sulphonation. It is therefore impossible under these conditions to prepare nitronaphthalenes from α -naphthalene-sulphonic acid although a higher nitration degree is obtained than with pure naphthalene. The products obtained with the latter seem to be practically mononitronaphthalene, and previous sulphonation in the other tests was so incomplete that the advantage to be gained by it is not apparent.

We next turned our attention to the preparation of the nitronaphthalenes from naphthalene direct with a view of determining the mixture of nitric and sulphuric acids which would give the best results. Ten grams of naphthalene were used in each experiment. The sulphuric acid was mixed with the nitric acid before adding it to the naphthalene and the amount used corresponded to that present in the tests of the first series.

SET 1.—30.23 GRAMS NITRIC ACID USED CORRESPONDING TO FORTY GRAMS 36° B. ACID.

| No. | Weight H ₂ SO ₄ . | Weight of product. | Color. | Odor. | Melting-point. | Remarks. |
|-----|---|--------------------|--------------|--------|----------------|---------------------------|
| I | 8.0 | 14.3470 | orange | strong | 86.0° | crystalline mass, soft |
| IA | 8.0 | 14.2646 | " | " | 99.0° | " " " |
| | | Mean 14.3058 | | | | |
| 2 | 16.0 | 14.5964 | orange | strong | 116.0° | crystalline mass, hard |
| 2A | 16.0 | 14.6278 | " | " | 124.0° | " " " |
| | | Mean 14.6121 | | | | |
| 3 | 24.0 | 15.2593 | yellow | none | 136.0° | no visible crystals, hard |
| 3A | 24.0 | 14.8473 | " | " | 139.0° | " " " " |
| | | Mean 15.0533 | | | | |
| 4 | 52.4 | 16.9195 | light yellow | none | 112.5° | no visible crystals, hard |
| 4A | 52.4 | 17.2489 | " | " | 109.0° | " " " " |
| | | Mean 17.0847 | | | | |

SET 2.—22.67 GRAMS NITRIC ACID USED CORRESPONDING TO THIRTY GRAMS 36° B. ACID.

| No. | Weight H ₂ SO ₄ . | Weight of product. | Color. | Odor. | Melting-point. | Remarks. |
|-----|---|--------------------|--------------|--------|----------------|------------------------|
| I | 8.0 | 14.2030 | orange | strong | 72.0° | semi-crystalline, soft |
| IA | 8.0 | 14.3260 | " | " | 80.0° | " " " |
| | | Mean 14.2645 | | | | |
| 2 | 16.0 | 13.7764 | orange-brown | strong | 100.0° | semi-crystalline, soft |
| 2A | 16.0 | 13.4370 | deep orange | " | 108.0° | " " " |
| | | Mean 13.6067 | | | | |

| No. | Weight H ₂ SO ₄ . | Weight of product. | Color. | Odor. | Melting-point. | Remarks. |
|-----|---|--------------------|--------------|--------|----------------|---------------------------|
| 3 | 24.0 | 15.0656 | yellow | slight | 129.5° | slightly crystal'e, hard |
| 3A | 24.0 | 15.7075 | " | none | 136.0° | " " " |
| | | Mean 15.3866 | | | | |
| 4 | 52.4 | 17.7699 | light yellow | none | 108.0° | no visible crystals, hard |
| 4A | 52.4 | 16.9200 | " | " | 110.0° | " " " " |
| | | Mean 17.3449 | | | | |

SET 3.—27.87 GRAMS OF NITRIC ACID USED CORRESPONDING TO FORTY GRAMS 34° B. ACID.

| No. | Weight H ₂ SO ₄ . | Weight of product. | Color. | Odor. | Melting-point. | Remarks. |
|-----|---|--------------------|---------------|--------|----------------|------------------------|
| I | 8.0 | 13.4895 | orange | strong | 84.0° | crystalline mass, soft |
| IA | 8.0 | 14.2570 | " | " | 80.0° | " " " |
| | | Mean 13.8733 | | | | |
| 2 | 16.0 | 14.7964 | deep orange | slight | 97.0° | crystalline mass, soft |
| 2A | 16.0 | 15.0230 | " " | " | 94.0° | " " " |
| | | Mean 14.9097 | | | | |
| 3 | 24.0 | 16.2178 | orange-yellow | none | 133.0° | slight'y cryst'l, hard |
| 4 | 52.4 | 16.3830 | brown-yellow | none | 126.0° | slight'y cryst'l, hard |
| 4A | 52.4 | 16.7150 | light brown | " | 126.0° | " " " |
| | | Mean 16.5490 | | | | |

SET 4.—20.90 GRAMS OF NITRIC ACID USED CORRESPONDING TO THIRTY GRAMS 34° B. ACID.

| No. | Weight H ₂ SO ₄ . | Weight of product. | Color. | Odor. | Melting-point. | Remarks. |
|-----|---|--------------------|--------------|--------|----------------|-------------------------------------|
| I | 8.0 | 13.6220 | orange | strong | 99.0° | crystalline mass, soft |
| IA | 8.0 | 13.6460 | " | " | 85.0° | " " " |
| | | Mean 13.6340 | | | | |
| 2 | 16.0 | 13.7861 | yellow | none | 122.0° | slightly crystalline, somewhat soft |
| 2A | 16.0 | 14.2410 | " | " | | slightly crystalline, hard. |
| | | Mean 14.0136 | | | | |
| 3 | 24.0 | 14.4400 | choc'l-brown | none | 106.0° | no visible crystals, hard |
| 3A | 24.0 | 14.9230 | " " " | " | 108.0° | " " " " |
| | | Mean 14.6815 | | | | |
| 4 | 52.4 | charred | | | | tarry, semi-liquid |
| 4A | 52.5 | charred | | | | " " |

The highest yield was therefore obtained in every set except No. 4, when an excess of sulphuric acid was used. In No. 4 so little nitric acid was present that the product was decomposed by the sulphuric acid. The degree of nitration, as characterized by

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° 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.

WASHINGTON, D. C., MAY 13, 1897.

SPONTANEOUS COMBUSTION OF MOLASSES.

BY J. T. CRAWLEY.

Received April 3, 1897.

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° - 165° 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° 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