

Table I—Temperatures of Initial Plasticity, Maximum Pressure, and Coke Formation for Fresh and Oxidized Coals

| INITIAL PLASTICITY ° C. | MAX. PRESSURE Mm. | TEMP. MAX. PRESSURE ° C. | COKE FORMATION ° C. | COKE QUALITY | TIME OF OXIDATION ^a Hours |
|---|-------------------|--------------------------|---------------------|--------------|---|
| TAYLOR-ENGLISH, VERMILION COUNTY, ILL. | | | | | |
| 375 | 504 | 390 | 445 | Poor | Fresh coal |
| 382 | 430 | 432 | 480 | Weak | 1.5 |
| 383 | 324 | 418 | 470 | Very weak | 2 |
| 395 | 90 | 415 | 470 | Powder | 3 |
| 399 | 13 | 414 | 452 | Powder | 4 |
| ZIEGLER, FRANKLIN COUNTY, ILL. | | | | | |
| 378 | 998 | 465 | 512 | Poor | Fresh coal |
| 404 | 350 | 467 | 512 | Weak | 1.75 |
| 396 | 230 | 438 | 482 | Very poor | 3.5 |
| 376 | 74 | 426 | 477 | Powder | 7 |
| POCAHONTAS | | | | | |
| 418 | 1244 | 518 | 600 | Strong | Fresh coal |
| 432 | 1385 | 545 | 495 | Denser | 42 |
| 438 | 240 | 431 | 576 | Weak | 56 |
| 436 | 174 | 495 | 535 | Very poor | 90 |
| VINTON COLLIERY, MINE NO. 6, VINTON, PA. | | | | | |
| 403 | 1800 | 513 | 595 | Good | Fresh coal |
| 418 | 1289 | 535 | 590 | Denser | 56 |
| 405 | 1172 | 530 | 584 | Very dense | 90 |
| 453 | 473 | 556 | 600 | Medium | 104 |
| 417 | 246 | 478 | 540 | Very poor | 140 |
| ELKHORN, LATCHER COUNTY, KY. | | | | | |
| 385 | 755 | 431 | 480 | Very porous | Fresh coal |
| 388 | 510 | 434 | 490 | Denser | 15 |
| 395 | 324 | 438 | 483 | Weak | 20 |
| 398 | 23 | 430 | 453 | Powder | 300 |
| VERMILION COUNTY, ILL., FROM STORAGE PILE | | | | | |
| 373 | 219 | 413 | 481 | Weak | Outside of pile; storage 6 weeks Inside of pile; local heating |
| 375 | 86 | 417 | 469 | Powder | |

^a Temperature of oxidation, 110° C.

detrimental to its coking properties, while preheating may be carried on to higher temperatures in an inert atmosphere without affecting the nature of coke formed. In some cases preheating coal is beneficial to its coking properties. This should be indicative of the extent to which heating should be allowed to progress in storage.

Table II—Temperatures of Initial Plasticity, Maximum Pressure, and Coke Formation for Fresh and Preheated Coals

| INITIAL PLASTICITY ° C. | MAX. PRESSURE Mm. | TEMP. MAX. PRESSURE ° C. | COKE FORMATION ° C. | COKE QUALITY | PREHEATING TREATMENT Temp. ° C. | Medium |
|--|-------------------|--------------------------|---------------------|----------------------|---------------------------------|----------|
| JELLICO COUNTY, KY. | | | | | | |
| 372 | 754 | 420 | 491 | Good | Fresh coal | |
| 374 | 550 | 424 | 474 | Better than original | 150 | Air |
| 361 | 104 | 410 | 444 | Poor | 200 | Air |
| 368 | 94 | 390 | 420 | Very poor | 250 | Nitrogen |
| 377 | 780 | 439 | 473 | Good | 300 | Nitrogen |
| 375 | 480 | 452 | 490 | Fair | 350 | Nitrogen |
| O'GARA COAL CO., SALINE COUNTY, ILL. | | | | | | |
| 350 | 780 | 480 | 497 | Fair | Fresh coal | |
| 380 | 560 | 420 | 466 | Fair | 150 | Air |
| 380 | 386 | 407 | 470 | Weak | 200 | Air |
| 350 | 206 | 402 | 488 | Powder | 250 | Air |
| 367 | 12 | 394 | 510 | Powder | 350 | Air |
| 383 | 40 | 400 | 445 | Fair | 250 | Nitrogen |
| 396 | 40 | 415 | 458 | Powder | 350 | Nitrogen |
| UNITED ELECTRIC COAL CO., VERMILION COUNTY, ILL. | | | | | | |
| 349 | 911 | 442 | 491 | Fair | Fresh coal | |
| 349 | 530 | 404 | 451 | Good | 250 | Nitrogen |
| 390 | 17 | 413 | 434 | Powder | 350 | Nitrogen |
| HICKORY HILL, GALLATIN COUNTY, ILL. | | | | | | |
| 356 | 504 | 404 | 491 | Fair | Fresh coal | |
| 350 | 454 | 410 | 434 | Fair | 300 | Nitrogen |
| 345 | 314 | 396 | 435 | Poor | 350 | Nitrogen |

Preparation and Properties of Diethyleneglycol Dinitrate^{1,2}

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DIETHYLENEGLYCOL dinitrate, $\text{CH}_2(\text{NO}_2)\text{CH}_2\text{OCH}_2\text{CH}_2(\text{NO}_2)$, not having as yet been described in the literature, a study of its synthesis and properties was undertaken as a part of a program dealing with the glycols and their nitric esters.

Preparation

Wurtz³ found that nitric acid reacts with diethyleneglycol to yield glycolic, oxalic, and another unnamed acid but did not try the effect of a mixture of nitric and sulfuric acids.

Nitrating mixtures containing varying percentages of water and of nitric and sulfuric acids were made up in the usual way. A measured quantity was cooled, and to this was added a weighed quantity of diethylene glycol, which was purified as described in a previous paper.⁴ It was added in small portions with continuous agitation of the mixture, care being taken to maintain the temperature between 5° and 10° C. The time required to complete the nitration was usually 30 minutes.

The results varied considerably with the strength of the acid employed. With the most concentrated acids the dini-

trate separated as an oily, upper layer, which decomposed vigorously when allowed to stand in contact with the spent acid at the same temperature for a short time, or when the temperature of the liquid was allowed to rise slightly during the course of separation. With the least concentrated nitrating acids no separation took place or there was formed an emulsion of the oily product in the spent acid which would not separate within 1.5 hours. In this case it was necessary to pour the mixture into ice and water and separate the dinitrate, which then settled out. Nitrating acids of composition intermediate between these extremes gave emulsions which separated into two layers within 1.5 hours.

The principal properties of the compound have been studied and recorded. Although comparatively insensitive, the compound is explosive when mixed with similar compounds. For this reason it will probably be of some interest in explosives practice, particularly because several of the other properties found add to the value of the compound from this viewpoint.

In either case the volume of the crude product was measured immediately after separation or precipitation. It was then washed one or more times with ice water, twice with a 2 per cent solution of potassium carbonate, and three more times with ice water; each washing was carried out in a separatory funnel and accompanied by agitation. The purified material was then placed in a sulfuric acid desiccator to remove traces of moisture and the weight of pure product determined. Table I summarizes the experiments.

The results indicate that the nitration should be carried out at a temperature not above 10° C., that the product is unstable in contact with spent acid containing free nitric

¹ Received March 30, 1927.

² Published with approval of the Director, U. S. Bureau of Mines.

³ *Ann. chim.*, [3], 69, 317 (1863).

⁴ Rinkenbach, *This Journal*, 19, 474 (1927).

acid, and that the best yields are obtained by using no excess of a nitrating acid containing 25 per cent nitric acid and from 5 to 10 per cent of water. It would appear that the best procedure is to add the glycol to such a nitrating acid, keep the temperature at or below 10° C., pour the resulting emulsion into three times its weight of ice and water and purify the oily precipitate in the manner previously described.

Table I—Preparation of Diethyleneglycol Dinitrate

| NITRATING MIXTURE | | | HNO ₂ EX- CESS OVER THEO- | CRUDE PER 100 GLYCOL | WASHED OIL PER 100 GLYCOL | YIELD | |
|-------------------|------------------|--------------------------------|--|-------------------------------|------------------------------------|-------|--------|
| H ₂ O | HNO ₃ | H ₂ SO ₄ | RETI- CAL | GRAMS | GRAMS | Crude | Washed |
| % | % | % | % | Cc. | Grams | % | % |
| 1.3 | 38.7 | 60.0 | 20 | 78 | a | 59 | |
| 1.3 | 38.7 | 60.0 | 10 | b | b | | |
| 8.0 | 30.0 | 62.0 | 0 | 34+ | c | 26+ | |
| 15.5 | 27.8 | 56.7 | 10 | 90 | 98.5 | 68 | 53 |
| 15.5 | 27.8 | 56.7 | 5 | 93 | 104 | 70 | 56 |
| 25.0 | 25.0 | 50.0 | 10 | d | 18 | | 10 |
| 10.7 | 25.0 | 64.3 | 0 | e | 113 | | 61 |
| 8.0 | 25.0 | 67.0 | 0 | f | 116.5 | | 63 |
| 5.0 | 25.0 | 70.0 | 31.5 | 92g | 84.6 | 69 | 46 |
| 5.0 | 25.0 | 70.0 | 0 | 92h | 112.6 | 69 | 61 |

^a During transference to funnel temperature rose slightly and violent decomposition ensued; complete separation had taken place.

^b Carried out at 22° C.; violent decomposition took place before all the glycol could be added.

^c Standing at 5° C., decomposition took place 15 minutes after completion of nitration, when some product had separated.

^d Emulsion formed; poured into ice and water after 2 hours' standing at 5° C.

^e Emulsion formed; only partial separation; poured into ice and water.

^f Emulsion formed; no separation; poured into ice and water.

^g Emulsion formed; no separation; poured into ice and water; volume of oil, 92 cc.

^h Emulsion formed; no separation; poured into ice and water; volume of oil, 92 cc.

Properties

The diethyleneglycol dinitrate prepared by this method was allowed to stand in a sulfuric acid desiccator for 2 months to remove all trace of moisture or other volatile impurities. During part of this period the pressure was reduced to 1 cm. of mercury. Analysis by means of the nitrometer at the end of this time showed a nitrogen content of 14.12 per cent as compared with a theoretical content of 14.29 per cent. This material was used for the purpose of studying the properties of the compound.

Diethyleneglycol dinitrate is a clear, colorless liquid that has no apparent odor.

SPECIFIC GRAVITY—Nineteen determinations of the specific gravity of diethyleneglycol dinitrate at temperatures ranging from 1.1° to 29.7° C. were made by means of the Westphal balance, using a calibrated thermometer and immersing the container in a water bath. The values obtained, when plotted, gave a straight line, and from this the values in Table II were read off at regular temperature intervals.

Table II—Specific Gravity Determinations

| TEMPERATURE | SP. GR. | TEMPERATURE | SP. GR. |
|-------------|-----------------------------|-------------|-----------------------------|
| ° C. | $\alpha/15^\circ \text{C.}$ | ° C. | $\alpha/15^\circ \text{C.}$ |
| 0.0 | 1.4092 | 20.0 | 1.3846 |
| 5.0 | 1.4030 | 25.0 | 1.3785 |
| 10.0 | 1.3969 | 30.0 | 1.3724 |
| 15.0 | 1.3908 | | |

FREEZING POINT—By means of a calibrated mercury thermometer, a transparent Dewar flask of 50 cc. capacity and having a long neck, an acetone bath chilled to from -40° to -20° C., and using about 20 grams of material, it was found that when stirred during cooling, diethyleneglycol dinitrate freezes after some supercooling. In one case the liquid supercooled to -35° C. Freezing point values of -11.4°, -11.2°, -11.2°, and -11.4° C. (average -11.3° C.) were obtained in this way. On warming, the crystals melt at about this temperature, but the liquid-solid mixture does not maintain an absolutely constant temperature until all the solid has melted; a slow rise is apparent in spite of vigorous stirring.

Calibration of the thermometer used makes possible a correction of the value given⁵ for the freezing point of the homologous compound, ethyleneglycol dinitrate. On applying the necessary correction, this is found to be -22.75° C. instead of the given value (average) of -22.3° C.

VISCOSITY—The viscosities of diethyleneglycol dinitrate and nitroglycerin were determined by means of a viscometer of the pipet type, which was calibrated at definite temperatures by means of liquids having known viscosities. (Table III)

Table III—Viscosity Determinations

| TEMPERATURE ° C. | DIETHYLENEGLYCOL DINITRATE | | NITROGLYCERIN | |
|---------------------|-------------------------------|---------------------|-------------------------|---------------------|
| | Time of flow Seconds | Viscosity Poises | Time of flow Seconds | Viscosity Poises |
| 15.0 | 50.3 | 0.099 | 105.9 | 0.511 |
| 17.5 | 48.9 | 0.085 | 93.0 | 0.423 |
| 20.0 | 47.8 | 0.078 | 84.0 | 0.355 |
| 22.5 | 46.8 | 0.073 | 77.0 | 0.303 |
| 25.0 | 45.9 | 0.070 | 71.8 | 0.283 |
| 27.0 | 45.1 | 0.066 | 68.0 | 0.258 |

REFRACTIVE INDEX—The refractive index of diethyleneglycol dinitrate was observed at twenty-one points between 2.55° and 43.2° C. by means of a Zeiss refractometer equipped with a water jacket and a calibrated thermometer and employing sodium light. The values were plotted against temperature readings and found to represent a straight-line function. From this the values in Table IV were read off at regular temperature intervals.

Table IV—Determinations of Refractive Index

| TEMPERATURE ° C. | REFRACTIVE INDEX | TEMPERATURE ° C. | REFRACTIVE INDEX |
|---------------------|---------------------|---------------------|---------------------|
| 0.0 | 1.4593 | 20.0 | 1.4517 |
| 5.0 | 1.4574 | 25.0 | 1.4498 |
| 10.0 | 1.4555 | 30.0 | 1.4479 |
| 15.0 | 1.4536 | 35.0 | 1.4460 |

HEAT OF COMBUSTION—Calorimetric determinations of the heat of combustion of diethyleneglycol dinitrate gave the values in Table V.

Table V—Determinations of Heat of Combustion

| HEAT OF COMBUSTION | AT CONSTANT | AT CONSTANT |
|-------------------------------------|-------------|-------------|
| | VOLUME | PRESSURE |
| Calories per gram | 2798 | 2792 |
| Kilogram calories per gram molecule | 548.7 | 547.5 |

HEAT OF FORMATION—Using the values 94,400 and 67,500 calories per gram molecule as the heats of formation of carbon dioxide and liquid water, respectively, the data (Table V) for heat of combustion gave the values in Table VI.

Table VI—Heat of Formation

| HEAT OF FORMATION | AT CONSTANT | AT CONSTANT |
|----------------------------|-------------|-------------|
| | VOLUME | PRESSURE |
| Calories per gram | 505.35 | 510.25 |
| Calories per gram molecule | 99,100 | 100,060 |

SOLUBILITY EFFECTS—At ordinary temperatures diethyleneglycol dinitrate is completely miscible with nitroglycerin, ethyleneglycol dinitrate, ether, acetone, methanol, chloroform, benzene, toluene, aniline, nitrobenzene, glacial acetic acid, and glycol diacetate. It is immiscible or slightly soluble in ethanol, carbon tetrachloride, and carbon disulfide. Its solubility in water was found to be 4.1 grams per liter of water at 24° C.

HYGROSCOPICITY—Diethyleneglycol dinitrate is slightly hygroscopic. Samples kept in air spaces saturated with water vapor at room temperature (20° to 30° C.) and weighed regularly during periods of from 7 to 15 days showed maximum gains in weight within 48 hours. These were 0.34 and 0.44 per cent of the weight of the samples.

VAPOR PRESSURE—Using the air-bubbling method, in

⁵ Rinkenbach, THIS JOURNAL, 18, 1195 (1926).

which 19 liters of thoroughly dried air were passed through pure material at a fixed temperature and the loss in weight was determined, the vapor pressure of diethyleneglycol dinitrate at 22.4° C. was found to be 0.0098, 0.0079, and 0.0044 (average 0.007) mm. of mercury.

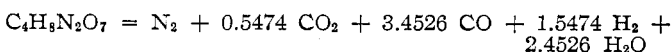
When a drop of the material, contained in a melting point tube, was heated in an oil bath, ebullition began at 161° C. No decomposition was apparent, so this may be taken as the boiling point of the compound.

An effort to determine the boiling point at reduced pressure showed that when a larger quantity was slowly heated to the boiling point the compound underwent a partial decomposition that resulted in variable values and sometimes culminated in the explosion of the material. It was therefore impracticable to derive a vapor-pressure curve for the pure substance.

INFLAMMABILITY—Diethyleneglycol dinitrate could be ignited only with difficulty; it was necessary to heat it to a point above that of the temperature of the air. When ignited it burned quietly with a yellow, luminous flame.

When small quantities held in the tip of capillary tubes were thrust into a gas flame, no explosion took place in five trials. Some of the material was ejected as a vapor which burned readily and quietly at the mouth of the tube.

EXPLOSIBILITY—The constitution of diethyleneglycol dinitrate would lead to the assumption that, like similar compounds, it is of an explosive nature. Calculation of explosives constants for this substance and for nitroglycerin and glycol dinitrate for purposes of comparison are given in Table VII. For this purpose the equation of decomposition



was derived by the use of data for the water-gas equilibrium. Extrapolated values of those given by Partington and Shilling⁶ for the specific heats of the various products of explosion were used for calculating the heat capacities of the mixture at various temperatures. From these the temperature of explosion was found by the diagrammatic method.

Table VII—Comparison of Explosives Constants

| COMPOUND | TEMP. OF EXPLOSION ° C. | GAS PRODUCED FROM 1 KG. AT 760 MM. AND: | | PRESSURE IN 1 LITER Kg./sq. cm. | ENERGY DEVELOPED ON EXPLODING 1 KG. MATERIAL Meter-kg. |
|----------------------------|-------------------------|---|--------|---------------------------------|--|
| | | LITERS | LITERS | | |
| | | | | | |
| Diethyleneglycol dinitrate | 2810 | 1,028.58 | 11,615 | 11,999 | 410.7 × 10 ⁶ |
| Glycol dinitrate | 4209 | 736.93 | 12,099 | 12,498 | 695.7 × 10 ⁶ |
| Nitroglycerin | 4177 | 715.53 | 11,663 | 12,048 | 647.8 × 10 ⁶ |

Table VIII—Sand Bomb Tests

| CHARGE OF MIXTURE | EXPLOSIVE IN CHARGE | SAND CRUSHED BY 0.300 GRAM MERCURY FULMINATE AND: | | | | |
|-------------------|---------------------|---|---------------------|------------------------|---------------------------------|--------------------------------|
| | | Di-ethyleneglycol dinitrate Grams | Nitroglycerin Grams | Glycol dinitrate Grams | 50% Nitroglycerin, 50% diethyl- | 50% Glycol dinitrate, 50% di- |
| | | | | | enylglycol dinitrate Grams | ethyleneglycol dinitrate Grams |
| 0.150 | 0.090 | 14.6 | 20.15 | 20.1 | 19.6 | 19.0 |
| 0.250 | 0.150 | 17.8 ^a | 26.85 | 27.7 | 25.35 | 26.15 |
| 0.333 | 0.200 | 2.9 ^a | 33.9 | 34.9 | 31.1 | 30.8 |
| 0.500 | 0.300 | 2.2 ^a | 44.25 | 47.3 | 43.0 | 41.6 |
| 0.833 | 0.500 | 1.9 ^a | 68.0 | 70.3 | 60.3 | 62.9 |

^a Incomplete detonation.

In order to test the actual explosibility of diethyleneglycol dinitrate and give a direct comparison, the following procedure was carried out:

Mixtures of exactly 40 per cent of kieselguhr and 60 per cent of liquid explosive by weight were made up, diluted with ether, and stirred until all the ether had been evaporated and an even mixture remained. Weighed charges of each of these mixtures were pressed into No. 8 detonator shells (0.300 gram of mercury

fulminate was added in each case), the whole was surmounted by a reënforcing cap, and after being subjected to a pressure of 50 pounds (91,700 grams per sq. cm.) the detonator so constructed was fired in the No. 2 standard sand test bomb.⁷ The amount of sand crushed was found by sieving and weighing. Table VIII gives the results.

These results indicate that diethyleneglycol dinitrate is so insensitive that its explosive is not sufficiently strong to produce continuous propagation under conditions which permit nitroglycerin or glycol dinitrate to produce this effect. In admixture with either of these other compounds, however, diethyleneglycol dinitrate can be completely detonated and shows an explosive effect but little less than that of either of the other compounds. From the values given, by taking into account the amount of crushing due to the fulminate, it is possible to calculate the crushing effects of different weights of diethyleneglycol dinitrate when completely detonated, as well as those of the other compounds (Table IX). For purposes of comparison, the values found for mercury fulminate are added.

Table IX—Crushing Effects of Diethyleneglycol Dinitrate

| EXPLOSIVE Gram | SAND CRUSHED BY: | | | |
|----------------|----------------------------------|------------------------|---------------------|-------------------------|
| | Diethyleneglycol dinitrate Grams | Glycol dinitrate Grams | Nitroglycerin Grams | Mercury fulminate Grams |
| 0.05 | 5.5 | 6.7 | 7.4 | |
| 0.10 | 9.9 | 13.4 | 13.3 | |
| 0.20 | 18.7 | 27.1 | 25.0 | 4.0 |
| 0.30 | 27.6 | 39.5 | 36.8 | 7.8 |
| 0.50 | 45.0 | 62.5 | 60.2 | 16.5 |

These comparative values agree quite well with those calculated from theoretical considerations.

SENSITIVITY TO IMPACT—From the foregoing facts concerning inflammability and propagation of detonation, it would appear that diethyleneglycol dinitrate is a comparatively insensitive compound. Tests made on the small impact machine⁸ on drops of the pure substance showed that it would not detonate when subjected to the blow of a 500-gram weight falling a distance of 110 cm., whereas glycol dinitrate and nitroglycerin detonated when the weight fell distances of 110 cm. and 70 cm., respectively.

SAPONIFICATION—Diethyleneglycol dinitrate is not easily saponified. No decomposition ensued when dissolved in 3 per cent alcoholic potash; the unchanged ester was recovered on evaporation of the solution at air temperature. This indicates a high degree of stability at ordinary temperatures.

TOXICITY AND ANIMAL POISONING—A dilute solution of diethyleneglycol dinitrate in water was injected intramuscularly into guinea pigs. A dosage of 0.000006 gram of the ester per 100 grams of the animal weight is proportional to the standard dosage prescribed for the injection of nitroglycerin with human beings. Although in some cases double this dosage was used, none of the guinea pigs showed untoward symptoms. It is probable, therefore, that diethyleneglycol dinitrate is no more toxic than nitroglycerin.

In order to determine if diethyleneglycol dinitrate would, when absorbed through the skin, cause increase in the blood pressure and consequent headache, a drop of the pure substance was placed on the forearm of each of three subjects, spread, and allowed to absorb. In one case this was expedited by the addition of several drops of ether. In no case were any unusual symptoms apparent, although each of the three persons was definitely sensitive to nitroglycerin poisoning and similar applications of pure nitroglycerin produced violent headaches. It is to be concluded that if diethyleneglycol dinitrate has any of the effects of nitroglycerin on the human system, these are much less marked than are those of the latter.

⁷ Storm and Cope, *Bur. Mines, Tech. Paper 125* (1916).

⁸ Hall, Snelling, and Howell, *Bur. Mines, Bull. 15*, p. 101.

⁶ "The Specific Heats of Gases," Ernest Benn, Ltd., 1924.