

# Diazodinitrophenol, a Detonating Explosive

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THE 4,6-dinitrobenzene-2-diazo-1-oxide, more commonly known as diazodinitrophenol, and hereafter referred to as DDNP, is a detonating compound, the manufacture and use of which for charges in percussion caps and in detonators has been the subject of several patents (2, 5, 6, 12-14) issued in the United States, Germany, and Great Britain.

The so-called diazophenols, to which DDNP belongs, are in reality internal diazooxides, formed from the true diazophenols by a process of dehydration. The diazooxides are of great historical interest inasmuch as the preparation of one member (DDNP) of the class from picramic acid in 1858 by Griess (9, 10) led him to undertake his classical researches on the diazo compounds.

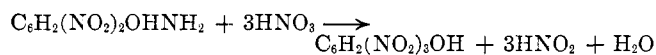
More recently these compounds have acquired considerable industrial importance because the *o*-diazooxides furnish numerous azo dyes which form valuable lakes with suitable acid mordants (24).

## PREPARATION OF DDNP

The epochal discovery of the diazo reaction was made by Griess (9) when he prepared 4,6-dinitrobenzene-2-diazo-1-oxide (DDNP) by passing nitrous acid as a gas into an alcoholic solution of picramic acid. He also obtained DDNP from both ether and aqueous nitric acid solutions, but found that the product from nitric acid solutions was contaminated with picric acid and other by-products. The best results were obtained when working with alcoholic solutions.

Schmitt (22), Knoevenagel (16), and Hantzsch and Davidson (11) recommended the addition of amyl nitrite to an acidified anhydrous solution of picramic acid in absolute alcohol, and thus the generation of the nitrous acid *in situ*.

Stenhouse (25) prepared DDNP by pouring boiling nitric acid on picramic acid. According to Cain (3) the preparation of diazo compounds may also be accomplished by causing fuming nitric acid to act directly on an amine. In either case the required nitrous acid is produced *in statu nascendi* by the reducing action of the picramic acid according to the equation:



At least 25 per cent of the picramic acid is lost through oxidation to picric acid when DDNP is prepared in this manner.

Dehn (6) developed a method for preparing DDNP wherein the use of organic solvents and gaseous nitrous acid is avoided. Dehn's significant contribution lay in the addition of reducing agents such as methyl or ethyl alcohol, or carbohydrates, to replace and conserve the picramic acid previously lost by oxidation. Dehn also introduced the use of a floating layer of a high-boiling paraffin oil, which serves (1) to reduce the liability of spontaneous surface combustion,

(2) to aid in the retention of oxides of nitrogen, and (3) to eliminate the hazard of explosion of the charge, particularly during the later stages of the process.

This process does not appear to be one that can find ready application to commercial use, largely because of the extreme precaution which must be exercised to complete a run satisfactorily. Moreover, the unused nitric acid cannot be recovered and therefore constitutes an appreciable loss. Several attempts by the author to prepare DDNP by this method met with only mediocre success; hence, it was abandoned in favor of methods to be described later.

Some of the numerous and interesting means available for the preparation of some of the other diazooxides are as follows: Morgan and Porter (19) obtained 2-nitrobenzene-4-diazo-1-oxide in quantitative yield by hydrolysis in acid solution of 4-chloro-3-nitrobenzenediazonium chloride. This diazooxide was produced by a similar method by Meldola and Stevens (17), and by Klemenec (15) from 4-methoxy-3-nitrobenzenediazonium chloride, by which means the formation of a diazooxide by the demethylation of a nitroanisidine derivative is brought about. Morgan and Porter (19) prepared 2-nitrobenzene-4-diazo-1-oxide from the 3-nitrophenylazoimide of Friedländer and Zeitlin (7) by converting the azoimide into 2-nitro-4-aminophenol sulfate and treating this compound in ice-cold, dilute sulfuric acid solution with sodium nitrite. The 3-nitrobenzene-4-diazo-1-oxide was obtained by Morgan and Porter (19) by the action of ethyl nitrite on 3-nitro-4-aminophenol in acetic acid solution.

Likewise, the compound was obtained by the action of nitrous acid gas on the aminophenol. The last two methods are similar to those of Griess, Schmitt, Knoevenagel, and Hantzsch and Davidson. The 2-nitrobenzene-4-diazo-1-oxide may also be prepared by diazotization of 4-chloro-3-nitraniline, with subsequent diminution of the acidity, complete neutralization, or addition of sodium acetate to the diazo solution.<sup>1</sup>

Patent literature shows that dye manufacturers prior to 1899 were making DDNP in a very different way from the above methods, preparing it as an intermediate by diazotizing picramic acid with sodium nitrite in a manner similar to that used in the preparation of the diazonium compounds.

Abel (1) stated that picramic acid may be diazotized by the addition of 6.9 kg. of sodium nitrite to 22.1 kg. of picramic acid in 20 kg. of hydrochloric acid (sp. gr. 1.16). In 1899 Newdon (21) referred to a similar method as "the known manner" of preparing DDNP. This method of preparation is of distinct advantage to dyers because DDNP is soluble in hydrochloric acid of sp. gr. 1.16, and may be run directly to the coupling tanks.

Preliminary tests showed that diazotization may also be effected in hydrochloric acid of 5 to 10 per cent strength

<sup>1</sup> The diazooxides so far discussed are either of the ortho or the para configuration. Morgan and Porter, *J. Chem. Soc.*, 107, 645 (1915), have demonstrated the nonexistence of a *m*-diazooxide.

in which case the DDNP is obtained as a solid which is only slightly soluble in the acid medium and may be filtered and washed in the usual manner. The obvious advantages of this procedure led to its use in the preparation of DDNP

pressure of 3400 pounds per square inch (239 kg. per sq. cm.), it has an apparent density of 0.86.

**SOLUBILITY.** DDNP is soluble in most of the more common organic solvents (Table I).

TABLE I. SOLUBILITY OF DDNP IN ORGANIC SOLVENTS

SOLVENT	SOLY. IN 100 GRAMS SOLVENT AT 50° C.		SOLVENT	SOLY. IN 100 GRAMS SOLVENT AT 50° C.	
	Grams			Grams	
Ethyl acetate	2.45		Benzene	0.23	
Methyl alcohol	1.25		Toluene	0.15	
Ethyl alcohol	2.43		Petroleum ether	Insol. (20° C.)	
Ethylene chloride	0.79		Ethyl ether	0.08 (30° C.)	
Carbon tetrachloride	Trace		Carbon disulfide	Trace (30° C.)	
Chloroform	0.11				

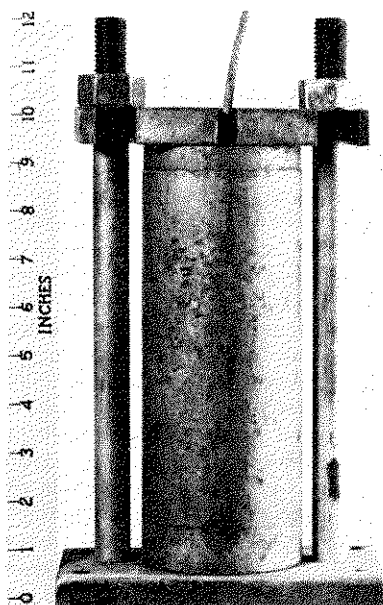


FIGURE 1. NO. 2 SAND-TEST BOMB ASSEMBLED

used in this investigation. Two modifications of the procedure were employed.

**METHOD A.** The DDNP is prepared by diazotizing one part of sodium picramate in 14 parts of 5 per cent hydrochloric acid. The product obtained is a dark brown, granular, free-flowing powder. If the small brown granules are finely pulverized, the resulting yellow powder is tinged with brown. DDNP prepared by this method was designated sample A and was used in one of the series of physical tests.

**METHOD B.** One part of sodium picramate (100 per cent) is rapidly agitated in 12.5 parts of 5.5 per cent hydrochloric acid at a temperature of 15° C. A slight excess of sodium nitrite dissolved in 150 to 200 cc. of water is added all at once. At this stage the temperature rises to 18° or 20° C. The color changes rapidly from the characteristic brown of sodium picramate solutions to a bright yellow which is slightly masked by a tinge of brown. Agitation is continued for one hour at a temperature of 15° C., after which time the product is filtered and thoroughly washed with distilled water saturated with DDNP. This washing largely removes the brownish shade. The DDNP so prepared has been designated sample B. It may be further purified by quickly adding a large volume of ice water to a rapidly agitated hot acetone solution of the DDNP. The product obtained is in an amorphous state and has a brilliant yellow color.

Preliminary test in the No. 2 sand-test bomb (27) (Figure 1) showed that this additional purification did not enhance the explosive power of DDNP. Method B offers little difficulty to the operator, and has the advantage of producing a consistently uniform product which is substantially pure. Sample B has been used in all tests herein reported unless otherwise stated.

#### PHYSICAL PROPERTIES OF DDNP

**DENSITY.** DDNP prepared according to method B, is in the form of bright yellow, microscopic, needlelike crystals which are odorless, and which readily agglomerate into lumps. Its true density at 25°/4° is 1.63, yet its apparent density after being placed in a tube and tapped is only 0.27. When compressed in a detonator shell at a

Dehn (5) reports DDNP to be soluble in nitrobenzene, acetone, aniline, pyridine, acetic acid, strong hydrochloric acid, acetyl chloride, and glyceryl trinitrate at room temperature. He says that DDNP is stable in cold mineral acids but is decomposed by hot concentrated sulfuric acid and by cold alkali solutions.

Recrystallization may be made from nitrobenzene or from acetone solution by addition of the solution to cold ether. DDNP may be purified by addition of ice water in considerable excess to a rapidly agitated hot acetone solution. This treatment produces a brilliant yellow amorphous powder.

#### EXPLOSIVE CHARACTERISTICS OF DDNP

**SENSITIVENESS TO IMPACT AND FRICTION.** DDNP detonates when struck a sharp blow, but, when ignited (unconfined) by fuse, it flashes like nitrocellulose, even in quantities of several grams.

Several samples of DDNP were tested for sensitiveness to impact on the Bureau of Mines small impact device (20) (Figures 2 and 3), and for sensitiveness to friction on its type B pendulum friction device (20) (Figure 4). It was found that DDNP requires the drop of a 500-gram weight through 22.5 cm. to produce detonation. Table II shows the results of impact tests on DDNP, compared with similar tests on mercury fulminate, lead azide, and lead styphnate.

TABLE II. SENSITIVENESS TO IMPACT\*

EXPLOSIVE	MAX. HEIGHT OF DROP OF 500-GRAM WEIGHT FOR "NO EXPLOSIONS" IN 5 TRIALS	
	Cm.	
DDNP	22.5	
Lead azide	17.5	
Mercury fulminate	15	
Lead styphnate	20	

\* 0.02-gram sample used for each test.

Results of tests with the type B pendulum friction device are shown in Table III.

TABLE III. SENSITIVENESS TO FRICTION\*

EXPLOSIVE	HEIGHT OF FALL OF PENDULUM	MAX. ADDED WEIGHT FOR "NO EXPLOSIONS" IN 10 SUCCESSIVE TRIALS		SWINGS OF PENDULUM IN EACH TRIAL
		Cm.	Grams	
DDNP	50	>5000		28-32
Lead azide	50	1000		13-15
Mercury fulminate	50	25		8
Lead styphnate	50	>5000		30-33

\* 0.02-gram sample used for each test.

The results of these tests show that the samples of DDNP prepared according to method B are no more sensitive to impact than the other detonants tested, and are markedly less sensitive to friction than either the lead azide or mercury fulminate. Numerous attempts to detonate DDNP under water with No. 8 electric detonators met with failure.

**EFFECT OF PRESSURE ON EXPLOSIBILITY.** DDNP, either loose or when compressed under high pressures, is easily ignited by the spit of a fuse. Under the first condition it merely puffs off like nitrocellulose; under the second condition it may burn with explosive violence or detonate, but can

be depended upon to detonate with certainty only when confined by a reinforcing capsule. Accordingly, a reinforcing capsule was used in making up all the experimental detonators. Several attempts were made to dead-press DDNP. Pressures up to 100,000 pounds per square inch (7030 kg. per sq. cm.) failed to prevent detonation when ignition was by fuse. Two attempts were made to use greater pressures. In the first case, explosion occurred in the press at 116,000 and in the second at 130,000 pounds per square inch (8155 and 9139 kg. per sq. cm.).

**STRENGTH TESTS.** In 1910 Snelling (23) devised a direct method for testing the strength of detonators. This method depends upon the extent to which a hard brittle substance, such as quartz sand, is pulverized by firing a detonator embedded in it. To carry out this test, a container later known as the Bureau of Mines sand-test bomb No. 1 was designed. Specifications for this bomb, methods for its use, and specifications for the quartz sand have been discussed in detail by Storm and Cope (26). Taylor and Munroe (27) made a further study of this method and recommended the use of a bomb of larger diameter, known as the Bureau of Mines sand-test bomb No. 2, which differentiates more exactly between the different grades of detonators in commercial use.

**PROCEDURE.** Eighty grams of sand, weighed on a prescription balance, are placed in the bottom of the bomb which is jarred to level the surface of the sand. The detonator is rested on the center of this, 120 grams more of the sand are poured around it, and the bomb is rocked or tapped to level the surface. The cover is placed and the detonator fired. The weight of sand crushed finer than 30 mesh is taken as a measure of the strength of the detonator. This method of testing, using the No. 2 sand-test bomb, was followed throughout this investigation. Dehn (4) studied the effect of greater confinement of the sand by placing a weight on it, and stated that "The mass of metal superimposed on the sand \* \* \* can be increased with accompanying increase in the weight of sand crushed." Taylor and Munroe (27) showed that the results obtained by this method are more erratic than when the sand is simply "settled" in the bomb by jarring.

TABLE IV. EFFECT OF COMPRESSION ON STRENGTH OF DDNP

EXPT.	PRESSURE		WEIGHT OF SAND CRUSHED FINER THAN 30 MESH	
	Lb./sq. in. (kg./sq. cm.)		Grams	
1	1160	(81.5)	43.1	
2	1750	(123.0)	46.5	
3	2320	(163.1)	45.9	
4	3490	(239.0)	45.6	
5	4000	(281.2)	47.8	
6	4640	(326.2)	43.5	
7	5260	(369.8)	45.3	
8	5830	(409.8)	44.9	
9	6380	(448.5)	43.7	

Average 45.14

Preliminary tests in the No. 2 sand-test bomb to determine the strength of DDNP indicated that it had a greater sand-crushing strength, gram for gram, than mercury fulminate when both were tested under the same conditions.

To test the effect of compression on the strength of DDNP, 0.50-gram charges were placed in No. 8 detonator shells, pressed under reinforcing capsules at various pressures, and fired in the No. 2 sand-test bomb by means of a fuse (Table IV).

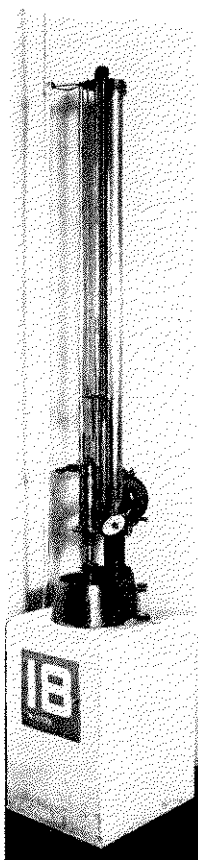


FIGURE 2. SMALL IMPACT DEVICE

The average weight of the sand crushed in these nine experiments was but 2.4 grams more than the lowest result in experiment 1, and 2.66 grams less than the highest result in experiment 5. It is fair to assume that DDNP is not affected in its development of energy by any static pressure to which it has been subjected.

Under the same conditions with a 0.50-gram charge of mercury fulminate previously subjected to a pressure of 3400 pounds per square inch, 25 grams of sand were crushed; with an equal weight of lead azide exposed to similar pressure, 20 grams of sand were crushed; DDNP under 3400 pounds pressure crushed 45.6 grams.

By these tests it would appear that the sand-crushing strength of DDNP is nearly twice that of mercury fulminate and more than twice that of lead azide. To ascertain whether the strength of DDNP is enhanced by the use of a priming charge of mercury fulminate, tests were made in the No. 2 sand-test bomb with detonators containing 0.50 gram of DDNP as the base charge. The fulminate in the priming charges varied from 0.15 to 0.30 gram. A reinforcing capsule was superimposed on the priming charge, and the base and priming charges were then compressed under the capsule at pressures varying from 500 to 4000 pounds per square inch (Table V).

The results indicate that an increase in the weight of fulminate at a given pressure does not increase the sand crushing strength of DDNP, whereas for a given weight of priming charge the strength increases somewhat with increasing pressure.

No efforts were made to ascertain the effect on DDNP of using a priming charge of lead azide. The mixing of lead azide with DDNP is definitely to be avoided because such a mixture decomposes promptly and destroys the properties of both explosives. Moreover, sensitiveness to impact of the mixture is greater than that of either of the constituents. Using a mixture of equal weights of DDNP and lead azide, the maximum height of drop of a 500-gram weight for "no explosion" in five trials is 7.5 cm. Values for lead azide and DDNP alone are 17.5 and 22.5 cm., respectively.

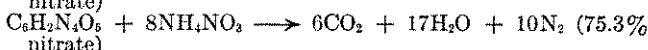
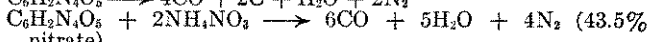
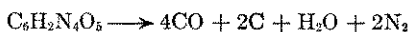
TABLE V. SAND TESTS OF 0.50-GRAM CHARGE OF DDNP PRIMED WITH MERCURY FULMINATE

PRESSURE Lb./sq. in. (kg./sq. cm.)	WEIGHT OF SAND CRUSHED FINER THAN 30 MESH BY DDNP ALONE <sup>a</sup>				
	0.0	0.15	0.20	0.25	0.30
	gram M. F. <sup>b</sup>	gram M. F. <sup>b</sup>	gram M. F. <sup>b</sup>	gram M. F. <sup>b</sup>	gram M. F. <sup>b</sup>
500 (35.2)	45.4	45.4	43.1	45.9	45.9
1160 (81.5)	43.1	45.2	46.7	48.4	44.5
1750 (123.0)	46.5	48.2	50.9	49.3	49.6
2320 (163.1)	44.9	53.8	48.9	52.1	49.6
3400 (239.0)	45.6	51.9	51.1	52.2	50.8
4000 (281.2)	47.8	52.0	54.1	51.7	54.5

<sup>a</sup> Obtained by subtracting weight of sand crushed by fulminate from that crushed by whole charge.

<sup>b</sup> Mercury fulminate.

Dehn's patent (5) states that a great advantage in the use of DDNP lies in its ability, in explosive compositions containing oxidants, to utilize the available oxygen and thus add to its own power. This patent gives the following equations for the decomposition of DDNP alone and also when mixed with an oxidant such as ammonium nitrate:



To compare the strength of DDNP with mixtures of DDNP and oxidants by the sand tests, mixtures in various proportions of DDNP with potassium chlorate or with potassium perchlorate were prepared. A 0.50-gram charge of the mixture was weighed into a No. 8 detonator shell, a 0.2-gram priming charge of fulminate added, a reënforcing capsule superimposed on the fulminate, and the whole system subjected to a pressure of 3400 pounds per square inch. This method of loading was first used by Wöhler and Matter (28). The detonators so made were fired in the No. 2 sand-test bomb (Table VI).

TABLE VI. SAND TEST WITH DDNP-OXIDANT MIXTURES

COMPOSITION OF DDNP %	BASE CHARGE OXIDANT %	WEIGHT OF SAND CRUSHED FINER THAN 30 MESH	
		By total charge <sup>a</sup> Grams	By DDNP-oxidant Grams
WITH POTASSIUM CHLORATE			
100	0	58.7	52.2
95	5	57.6	51.1
90	10	58.8	52.3
85	15	57.3	50.8
80	20	57.7	51.2
65	35	54.1	47.6
50	50	51.1	44.6
35	65	47.6	41.0
20	80	30.2	23.7
WITH POTASSIUM PERCHLORATE			
100	0	58.7	52.2
95	5	55.2	48.7
90	10	54.8	48.3
85	15	55.9	49.4
80	20	54.9	48.4
65	35	54.3	47.8
45	55	49.9	43.4
30	70	41.9	35.4
15	85	25.0	18.5

<sup>a</sup> Total charge consisting of base charge of 0.50 gram of DDNP-oxidant mixture plus a 0.2-gram priming charge of mercury fulminate.

It has been stated that method A produces DDNP in the form of a free-flowing granular powder. Inasmuch as these physical characteristics are those which make a material most easily adaptable in detonator loading, sample A was tested in the No. 2 sand-test bomb in a series of tests similar to the above, in order to compare the explosive properties of samples A and B. Tests were made to determine (1) the relative strength of sample A and of mixtures of it with oxidants, and (2) whether the strength of these mixtures of sample A with oxidants is enhanced by the use of a mercury fulminate priming charge (Table VII).

TABLE VII. SAND TEST OF DDNP (SAMPLE A)

COMPOSITION OF DDNP %	BASE CHARGE KClO <sub>3</sub> %	WEIGHT OF SAND CRUSHED FINER THAN 30 MESH		
		By total charge <sup>a</sup> Grams	By DDNP-KClO <sub>3</sub> Grams	FIRIED WITHOUT PRIMING CHARGE Grams
100	0	56.1	49.6	44.6
90	10	54.9	48.4	44.4
80	20	55.5	49.0	44.5
60	40	55.5	49.0	44.3
50	50	57.2	50.7	29.6

<sup>a</sup> Total charge consisting of base charge of 0.50 gram of DDNP-KClO<sub>3</sub> mixture plus 0.2-gram priming charge of mercury fulminate.

These tests show no appreciable difference in the strength developed by the bright yellow, amorphous DDNP and the brown, granular, free-flowing modification. Comparing Tables IV and VII (where no fulminate priming charge was used) with Tables V and VI (where a priming was used), it is apparent that, weight for weight, the strength of mixtures of DDNP with oxidants is of the same order as DDNP alone. Hence the addition of oxidizing salts would seem of considerable value from the economic viewpoint. The strength of mixtures of DDNP with potassium chlorate or potassium perchlorate is increased to the same slight extent as that of DDNP alone by the use of a 0.2-gram priming charge of fulminate.

In the last column of Table VII a marked decrease in the strength of DDNP-potassium chlorate mixtures containing more than 40 per cent of potassium perchlorate is noted when no fulminate priming charge is used.

To compare further the strength of DDNP with mercury fulminate and lead azide, various weights of the explosive to be tested were put in No. 8 detonator shells, pressed under a reënforcing capsule at 3400 pounds per square inch, and fired in the No. 2 sand-test bomb (Table VIII).

TABLE VIII. COMPARISON OF SAND TESTS USING DDNP, MERCURY FULMINATE, AND LEAD AZIDE

WEIGHT OF CHARGE Grams	WEIGHT OF SAND CRUSHED FINER THAN 30 MESH		
	DDNP Grams	Mercury fulminate Grams	Lead azide Grams
0.10	9.1	3.1	3.5
0.20	19.3	6.5	7.2
0.40	36.2	17.0	14.2
0.60	54.3	27.5	21.5
0.80	72.1	38.0	28.7
1.00	90.6	48.4	36.0

Results show that DDNP is much more powerful than either mercury fulminate or lead azide.

Additional tests were made in the No. 2 sand-test bomb to compare the strength of DDNP with other nitroaromatic explosives. In the preparation of the charges, 0.50 gram of the nitroaromatic explosive to be tested was placed in a No. 8 detonator shell, a priming charge of 0.3 gram of mercury fulminate added, a reënforcing capsule superimposed on the fulminate, and the whole system compressed at a pressure of 3400 pounds per square inch (Table IX).

TABLE IX. COMPARISON OF SAND TESTS USING DDNP AND OTHER NITROAROMATIC EXPLOSIVES

EXPLOSIVE	WEIGHT OF SAND CRUSHED FINER THAN 30 MESH	
	By total charge <sup>a</sup> Grams	By nitroaromatic explosive Grams
DDNP <sup>b</sup>	63.9	52.2
Trinitrotoluene	55.3	43.6
Picric acid	57.0	45.3
Trinitroresorcin	52.9	41.2
Tetranitraniline	56.3	44.6
Hexanitrodiphenylamine	60.2	49.5
Trinitrobenzaldehyde	62.8	51.1
Tetryl	65.9	54.2

<sup>a</sup> Using 0.3-gram mercury fulminate primer.

<sup>b</sup> Weight of sand crushed by DDNP when no priming charge was used = 45.7 grams.

STRENGTH IN SMALL TRAUZL BLOCK. A 1.00-gram charge of DDNP, mercury fulminate, or lead azide was weighed into a No. 8 detonator shell, compressed under a reënforcing capsule at a pressure of 3400 pounds per square inch, and fired in the small Trauzl block by means of a fuse (Table X).

TABLE X. COMPARISON OF TESTS IN SMALL TRAUZL BLOCK

EXPLOSIVE	EXPANSION OF LEAD BLOCK	
	Cc.	
DDNP	25.0	
Mercury fulminate	8.1	
Lead azide	7.2	

INITIATING POWER OF DDNP. The initiating power of a detonant is expressed in terms of the minimum weight which will cause maximum detonation as shown by no further increase of sand crushed with an increased weight of initiator, except that resulting from the additional weight of initiator.

To compare the value of DDNP with mercury fulminate or lead azide as an initiator of detonation of various nitroaromatic explosives, a 0.50-gram charge of the explosive to be tested was weighed into a No. 8 detonator shell, and a desired weight of the priming charge was placed as a top layer. The charge was then compressed under a reënforcing capsule at a pressure of 3400 pounds per square inch. The detonator was fired in the No. 2 sand-test bomb, and the weight of sand crushed noted (Table XI).

TABLE XI. INITIATING POWER OF DDNP COMPARED WITH MERCURY FULMINATE AND LEAD AZIDE

EXPLOSIVE	MINIMUM DETONATING CHARGE		
	Fulminate	DDNP	Lead azide
	Gram	Gram	Gram
Picric acid	0.225	0.115	0.12
Trinitrotoluene	0.240	0.163	0.16
Tetryl	0.165	0.075	0.03
Trinitroresorcin	0.225	0.110	0.075
Trinitrobenzaldehyde	0.165	0.075	0.05
Tetranitraniline	0.175	0.085	0.05
Hexanitrodiphenylamine	0.165	0.075	0.05

Results show that approximately only one-half as much DDNP as mercury fulminate is required to cause the complete detonation of the explosives in the left-hand column of Table XI. DDNP is, however, shown to be a slightly less effective initiator of detonation than is lead azide.

**EFFECT OF LIGHT ON DDNP.** The true diazo compounds are readily affected by light. Those containing negative groups such as OH, NO<sub>2</sub>, COOH, etc., in the para position are more sensitive than those containing similarly situated positive groups; the influence of the nitro group is greatest. Ortho-substituted groups behave in the same manner as similar para-substituted groups. The sensitizing effect is greatest for a meta group (19). Meldola, Woolcott, and Wray (18) found that the diazo oxide, 3-bromo-5-nitrobenzene-1-diazo-2-oxide, is more stable to light than the true diazo compounds, the stability being due in all probability to its peculiar diazo oxide ring structure.

In the case of DDNP it seemed possible that the sensitizing effect of the two *m*-nitro groups might more than overshadow the stabilizing effect of the diazo oxide ring structure. DDNP has been found to be stable for long periods of time in diffused light. Samples standing in the laboratory and protected from direct sunlight have shown no signs of discoloration after 6 months. In direct sunlight, however, DDNP darkens rapidly, eventually acquiring a dark brown color.

To determine the effect of direct sunlight on its explosive strength, DDNP was exposed for various periods of time. A 0.50-gram portion of the exposed material was then placed in a No. 8 detonator shell and compressed under a reinforcing capsule at 3400 pounds per square inch. The detonators so prepared were fired in the No. 2 sand-test bomb, and the weight of sand crushed was noted (Table XII).

TABLE XII. SAND TESTS WITH DDNP AFTER EXPOSURE TO DIRECT SUNLIGHT

TIME OF EXPOSURE	WEIGHT OF SAND CRUSHED FINER THAN 30 MESH	TIME OF EXPOSURE	WEIGHT OF SAND CRUSHED FINER THAN 30 MESH
Hours	Grams	Hours	Grams
0	45.1	5	42.8
1	45.3	10	38.8
2	43.9	15	36.3
3	41.8	20	35.3

TABLE XIII. SAND TESTS ON DDNP AFTER HEATING AT 60° C.

DURATION OF HEATING	WEIGHT OF SAND CRUSHED FINER THAN 30 MESH	DURATION OF HEATING	WEIGHT OF SAND CRUSHED FINER THAN 30 MESH
Days	Grams	Days	Grams
0	45.8	7	44.2
2	44.8	14	45.4
4	45.5	28	45.2

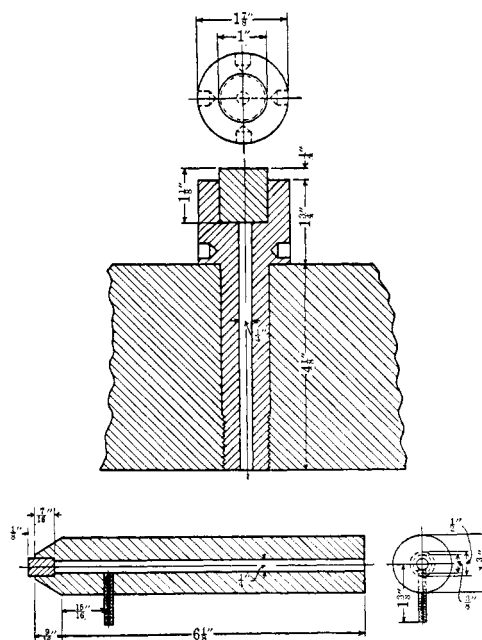
These results show that DDNP undergoes no loss of strength on exposure of one hour to direct sunlight and shows no marked decrease even after 3 to 5 hours, despite a marked darkening in color.

**EFFECT OF HEAT ON DDNP.** The DDNP was subjected to a temperature of 60° C., which is higher than is usually encountered under storage conditions; 0.5-gram charges of the test sample were weighed into No. 8 detonator shells, compressed under a reinforcing capsule with a pressure of

3400 pounds per square inch, and fired in the No. 2 sand-test bomb. Results are shown in Table XIII.

DDNP was also subjected to a temperature of 75° C. for 48 hours with a loss of only 0.3 per cent in weight. After this period of heating, 0.50 gram of the test sample crushed 45.60 grams of sand, whereas the original sample crushed 45.80 grams.

A similar sample of DDNP, heated at 100° C. for 96 hours, lost only 1.25 per cent in weight. It is interesting to note that diazobenzene nitrate, a true diazo compound, explodes violently when heated to 90° C.

FIGURE 3. DETAILS OF SMALL IMPACT DEVICE  
Above, impact block; below, plunger and plunger tip.

**EFFECT OF DRY AND WET STORAGE ON DDNP.** A 0.50-gram charge of freshly made DDNP crushed 45.80 grams of sand. This weight of DDNP preserved dry in a dark bottle for 5 months crushed 45.00 grams of sand. The difference is within experimental error. A similar sample preserved in a moist state over the same period of time showed no loss in strength as indicated by the sand test. Neither sample developed any discoloration during storage.

To verify further the impassivity of DDNP to moisture, a quantity was stored under distilled water at room temperature. After chosen periods of time, 0.50-gram samples were withdrawn, dried, compressed in No. 8 detonator shells under a reinforcing capsule at a pressure of 3400 pounds per square inch, and tested in the No. 2 sand-test bomb (Table XIV).

TABLE XIV. SAND TEST ON DDNP AFTER UNDERWATER STORAGE

STORAGE PERIOD	WEIGHT OF SAND CRUSHED FINER THAN 30 MESH	STORAGE PERIOD	WEIGHT OF SAND CRUSHED FINER THAN 30 MESH
Days	Grams	Days	Grams
0	45.6	28	45.8
7	45.4	36	46.4
14	44.2	50	44.0
21	45.5		

Results show that the sand-crushing strength of DDNP is not affected by storage under water for a 50-day period.

As it seemed possible that DDNP might undergo very slow decomposition when immersed in water and to so

limited an extent as to be undetectable by the sand test, a sample was placed under water at room temperature, and means were provided to collect any gases resulting from its decomposition; however, none was liberated during a 45-day period.

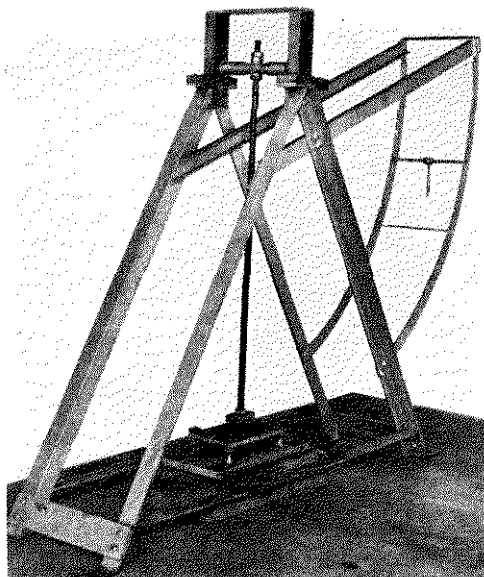


FIGURE 4. TYPE B PENDULUM FRICTION DEVICE

**PROPAGATION TESTS.** A modified gap test was used by Gawthrop (8) and others to determine the relative ability of the disturbance sent out by the explosion of a shielded detonator to transfer detonation over an air gap to a receiving charge of explosive. For these tests a 0.50-gram charge of DDNP was placed in a No. 8 detonator shell and pressed under a reinforcing capsule at 3400 pounds per square inch. In a similar manner detonators were prepared containing 0.50- and 1.00-gram charges of mercury fulminate.

The test detonator was placed centrally in a cylindrical oaken shield, with its long axis parallel to and coinciding with the long axis of the shield and with its base flush with the end of the shield. The shield containing the detonator under test and the cartridge of receiving explosive with its cut end facing the detonator were then wrapped in three turns of heavy paper. The maximum gap over which detonation would be transferred with certainty from the detonator to the cartridge of explosive was determined by four trials. Results of these tests compared with tests on commercial detonators made by Gawthrop are shown in Table XV.

TABLE XV. PROPAGATION TESTS ON DDNP EXPERIMENTAL DETONATOR COMPARED WITH COMMERCIAL ELECTRIC DETONATORS

GRADE	CLASSIFICATION OF DETONATOR ACCORDING TO BASE CHARGE	WEIGHT OF CHARGE	MAX. DISTANCE OVER WHICH DETONATION OF 40% STRAIGHT DYNAMITE OCCURS
		Grams	Cm.
-	DDNP	0.50	350
-	Mercury fulminate	0.50	150
-	Mercury fulminate	1.00	300
6	Tetryl primed with lead azide	0.66	400 <sup>a</sup>
6	Picric acid primed with mercury fulminate	1.25	300 <sup>a</sup>
8	80:20 mercury fulminate-KClO <sub>3</sub>	2.12	90 <sup>a</sup>
6	80:20 mercury fulminate-KClO <sub>3</sub>	1.05	100 <sup>a</sup>
7	Lead styphnate	1.74	50 <sup>a</sup>
8	Nitromannitol-mercury fulminate	1.16	90 <sup>a</sup>

<sup>a</sup> Data by Gawthrop from commercial detonators.

These results show that the effectiveness of the disturbance set up by a 0.50-gram charge of DDNP (in a reinforced detonator) in propagation of detonation across an air gap is greater than that of any of the commercial detonators tested except tetryl.

**IGNITION TEMPERATURE.** Ignition temperature of DDNP was determined by dropping 0.02-gram charges of DDNP on a molten metal bath and noting the interval between the moment of contact of the explosive with the hot molten mass, and the moment of explosion (Table XVI).

TABLE XVI. IGNITION TEMPERATURE OF DDNP

TEMP. OF BATH ° C.	TIME INTERVAL Seconds	TEMP. OF BATH ° C.	TIME INTERVAL Seconds
230	0.5	190	2.5
220	0.5	185	5.0
210	0.5	180	10.0
200	1.0	177	Decomposed without explosion

### SUMMARY

A study of the method of preparation, and of the explosive and certain of the chemical characteristics of diazodinitrophenol has shown the following:

1. The methods found in patent literature may be modified to give a more satisfactory method of preparing DDNP.
2. DDNP, prepared according to method B, is a bright yellow amorphous powder having a true density of 1.63 ( $d_4^{25}$ ), an apparent density of 0.27, and a density of 0.86 when pressed in a detonator shell at 3400 pounds per square inch (239 kg. per sq. cm.). A modification of the method of preparation produces a brown, granular, free-flowing product.
3. DDNP is soluble in most of the common organic solvents and also in glyceryl trinitrate.
4. The sensitiveness of DDNP to impact is less than either mercury fulminate or lead azide, and the sensitiveness to friction is much less than that of mercury fulminate and similar to that of lead azide.
5. Pressure does not affect the strength of DDNP when it is fired without a priming charge of mercury fulminate. When a priming charge was used, an increase in the weight of primer at a given pressure appeared to have no beneficial effect on strength. However, for a given weight of primer, the strength increased somewhat with increasing pressure.
6. DDNP cannot be detonated under water with a No. 8 electric detonator.
7. DDNP is not dead-pressed even by pressures up to 130,000 pounds per square inch (9139 kg. per sq. cm.).
8. The strength of mixtures of DDNP with oxidants is similar to that of DDNP itself; hence, the addition of oxidants is of value from the economic viewpoint.
9. The strength of DDNP, interpreted in terms of the weight of sand crushed in the sand test bomb, is about twice that of mercury fulminate or lead azide. By the same criterion, the strength of DDNP is of the same order as other nitro aromatic explosives, such as tetryl and trinitrobenzaldehyde, and is somewhat stronger than TNT, picric acid, trinitroresorcin, tetranitraniline, or hexanitrodiphenylamine.
10. The strength of DDNP tested in the small Trauzl-block is approximately three times that of mercury fulminate or lead azide.
11. The initiating power of DDNP is greater than that of mercury fulminate and similar to that of lead azide.
12. DDNP is stable for long periods of time in diffused light but rapidly loses its strength when exposed to direct sunlight.
13. The strength of DDNP is not appreciably affected by heat up to 100° C.; there is no appreciable loss in weight when heated at 75° C. for 48 hours, and a loss of only 1.25 per cent at 100° C. for 96 hours.
14. The strength of DDNP is not affected by storage under water for 50 days.
15. The effect of the disturbance set up by a detonator containing 0.50 gram of DDNP is greater, as shown by propagation tests, than that of any of the commercial detonators tested except those containing tetryl as a base charge.
16. DDNP explodes when heated to a temperature of 180° C.

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## Gelation of Frozen Egg Magma

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**I**N ADDITION to the cold storage of hens' eggs in the shell, millions of pounds of hens' eggs are commercially frozen each year. Such frozen egg matter is consumed chiefly by the baking industry. Frozen yolk magma is prepared in large quantities principally for mayonnaise manufacturers.

Eggs to be frozen are carefully selected before the candle. Those which appear satisfactory are broken into cups by expert egg breakers. Before the contents of a given egg is added to the bulk container, it is critically examined for appearance and odor. If unsatisfactory, the egg is discarded, the cup containing it sterilized, and the hands of the operator are thoroughly cleansed before breaking another egg.

The edible portions of the eggs are churned in order to break the yolks and to mix thoroughly the materials of the yolks and the whites to form a uniform egg magma. It is obviously necessary to exclude even one egg of doubtful quality under such a system. This churned whole-egg magma is then placed in 30-pound (13.6-kg.) containers which are immediately stored at  $-5^{\circ}$  to  $0^{\circ}$  F. ( $-21^{\circ}$  to  $-18^{\circ}$  C.).

When such frozen egg magma is stored for a few weeks and then thawed, it is generally very thick in consistency. The thickness, or state of gelation, has been found quite variable. Heretofore there has been no knowledge concerning the control of the state of gelation other than that the addition of common salt or sugar, etc., prevents this phenomenon.

Moran (9) found that, when eggs in the shell were frozen below  $-6^{\circ}$  C. and then thawed, the normal fluidity of the yolk was lost, and there resulted a stiff pasty mass. An irreversible change in volume also occurred, as indicated by dilatometric measurements which he made. Moran's publication is the first scientific study of the changes in the nature of the egg as a result of freezing.

The present investigation was undertaken with the hope of developing a method for the study of the gelation phenomenon and of discovering the controlling factors.

## MATERIALS USED

The eggs used in these experiments were fresh eggs of commerce shipped from various parts of the United States. They were taken from carload lots received at an egg breaking and freezing establishment in Jersey City; expert employees care-

fully selected the eggs and broke them out of the shells, placing the contents in pails. This was done under the supervision of the authors, one of whom then churned the eggs and stored the egg magma in a room at  $-21^{\circ}$  to  $-18^{\circ}$  C.

Since it was foreseen that as constant conditions as possible were essential to a study of the influence of mechanical treatment of the eggs, one commercial churn provided with a direct-drive motor was obtained and used throughout the investigation. When empty, the motor shaft was found to revolve 1750 revolutions per minute. The construction of the apparatus was such that measurements of the speed of the shaft while churning eggs were impracticable.

Through experience with egg churning in 1929, it was discovered that, if the churn was allowed to operate until all of the yolks or all but three or four resistant yolks were disrupted, a highest possible viscosity of uniform egg magma was obtained. Consequently, this end point was used as a guide when egg magma of high viscosity was desired. When lower viscosities were desired, the churning was continued beyond this end point. Throughout the investigation the amounts of egg matter churned consisted of 45 or of 90 kg. After churning, the whole-egg magma was passed through a screen (seven holes per cm.) and approximately 800 grams of it were placed in 2-pound (0.9-kg.) capacity tin cans which were immediately closed and put in a storage room at  $-5^{\circ}$  to  $0^{\circ}$  F. ( $-21^{\circ}$  to  $-18^{\circ}$  C.) until removed for experimental use. These cans were taken out at intervals, the contents were thawed under comparable conditions, and the degree of gelation was measured. Most of the other measurements were carried out on the unfrozen whole-egg magma on the day the samples were prepared.

In the course of the investigation, determinations of pH, total solids, and ether extract (fat) were made upon a series of 45 to 90 kg. mixtures of fresh eggs of commerce. Since no such data<sup>1</sup> are available in the literature, they are set down

<sup>1</sup> In commercial egg breaking (as also in household practice) a small amount of white is left adhering to the shells. The whole egg matter thus obtained contains a slightly higher ratio of yolk to white than would be the case if the edible matter were quantitatively removed from the shell. Unless stated otherwise, all analytical data reported in this paper were obtained from this sort of egg matter consisting of a homogeneous mixture of about 1000 or about 2000 eggs.