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Filed June 6, 1962

2 Sheets-Sheet 1

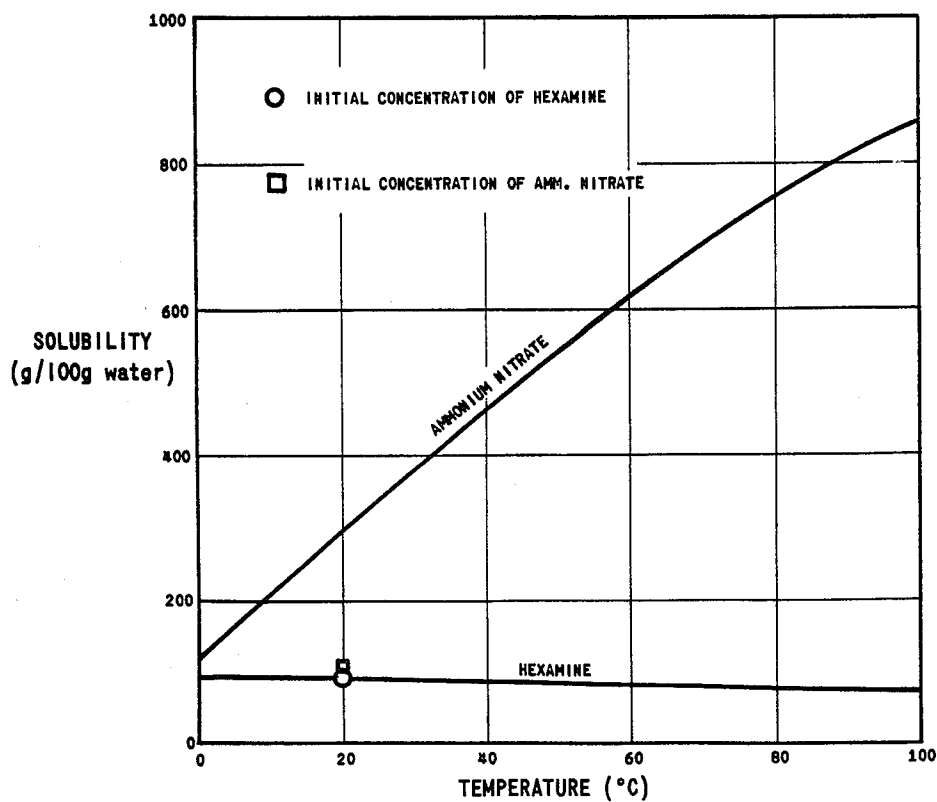


FIGURE 1

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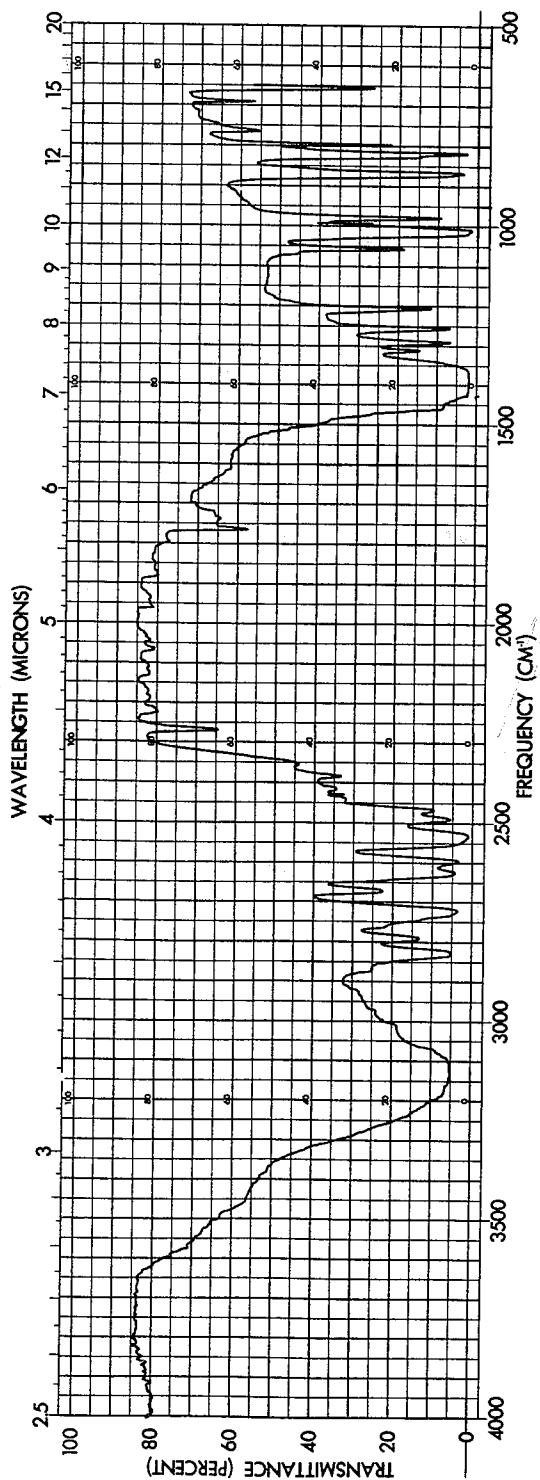


FIG. 2

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AMMONIUM NITRATE-HEXAMETHYLENE-TETRAMINE ADDUCT

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This invention relates to explosive compositions, and methods of making them, and, more particularly, to explosive compositions comprising hexamethylenetetramine and ammonium nitrate.

Explosive formulations comprising ammonium nitrate and hexamethylenetetramine are known. The ammonium nitrate serves as the oxidizer, and the hexamethylenetetramine as the fuel, or at least as a portion thereof, in such formulations. Such formulations, however, have been useful only as blasting agents, as distinguished from stick dynamites, i.e., cartridge explosives, unless ingredients of the molecular explosive type such as nitroglycerin are included in the formulations. Blasting agents require a large diameter charge and must be initiated with a high explosive primer. A cartridge explosive, on the other hand, is a stick-type charge that has a small diameter and is detonable by means of a No. 6 or a No. 8 blasting cap. In the trade, cartridge explosives are simply called dynamite. Throughout this specification the term "cap sensitive cartridge explosive" is intended to designate an explosive that may be detonated by a No. 6 or a No. 8 blasting cap in an eight-inch paper cartridge having a diameter of about 1.25 inches.

The primary object of this invention is to provide improved explosive formulations comprising ammonium nitrate and hexamethylenetetramine which not only may be used as blasting agents but also are eminently suitable as cap sensitive cartridge explosives.

Another object of this invention is to provide methods of making the afore-mentioned improved explosive formulations.

In accordance with my invention, I have discovered an adduct of hexamethylenetetramine and ammonium nitrate which significantly increases the cap sensitivity of explosive formulations. This adduct has the empirical formula $(CH_2)_6N_4 \cdot 2NH_4NO_3$.

Other objects and advantages of my invention will become apparent from the following description of this invention, and from the accompanying drawing in which:

FIGURE 1 is a plot of the solubilities of ammonium nitrate and hexamethylenetetramine in water at various temperatures.

FIGURE 2 is the infrared spectrogram of the adduct of ammonium nitrate and hexamethylenetetramine of this invention.

I. ADDUCT: METHODS OF PREPARATION

A. Crystallization from water solution

I prefer to prepare the adduct of this invention by crystallization from an aqueous solution of hexamethylenetetramine and ammonium nitrate. However, it is essential to the successful production of the adduct by this method to conduct the crystallization under the following two conditions.

Firstly, the hexamethylenetetramine and the ammonium nitrate are dissolved in the water in a molar ratio corresponding substantially to one mole of the hexamethylenetetramine to two moles of the ammonium nitrate. Such a molar ratio corresponds to 46.66 percent by weight of hexamethylenetetramine and 53.34 percent by weight of ammonium nitrate.

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Secondly, crystallization of the adduct is effected by removal of the water at a temperature below about 40° C., and preferably below 30° C. Such removal is preferably accomplished by air drying, that is, by evaporating the water in a stream of air passing over or through the aqueous solution. However, the water may be removed by other conventional means such as under vacuum, by spray drying, by azeotropic distillation with a solvent, etc., provided, always, that the temperature be maintained below 40° C.

By way of example of the preferred method of preparation, 700 grams of hexamethylenetetramine and 800 grams of ammonium nitrate were dissolved in 700 grams of water at 20° C. The solution was placed in evaporating dishes and a stream of air was passed over the surface of the solution. After about 25 hours, virtually all the water was evaporated, leaving a heavy slush. The latter was filtered through a Büchner funnel and the crystals pressed with a rubber dam; rinsed twice with water-free acetone; and then again pressed to remove the acetone. The crystals were removed from the Büchner, transferred to large filter papers and allowed to dry. The crystals were established to be pure adduct, as will be later set forth.

Attempts to prepare the adduct in the manner set forth in the foregoing example failed when the molar ratio of the hexamethylenetetramine and ammonium nitrate was substantially different from one to two. For example, when the molar ratio was one to ten (the ratio corresponding to an oxygen-balanced system of oxidizer and fuel), no adduct was precipitated. The ammonium nitrate crystallized separately leaving the hexamethylenetetramine in the mother liquor. However, if this oxygen-balanced system of hexamethylenetetramine and ammonium nitrate is prepared by taking the solution to complete dryness by evaporation at room temperature, then the adduct can be detected in small quantities by X-ray diffraction techniques. Similarly, if an intimate mixture of hexamethylenetetramine and ammonium nitrate is allowed to stand for several hours in the presence of a small amount of adsorbed moisture, adduct can be detected.

Attempts to prepare the adduct by crystallization at a temperature above 40° C. failed, even though the molar ratio was one to two. For example, a solution of the two components in the proper ratio was prepared which was saturated with respect to the hexamethylenetetramine at 70° C. Upon removal of the water by vacuum drying at 70° C., crystals of the hexamethylenetetramine precipitated, but no adduct was detected by X-ray diffraction of the crystalline precipitate, and the melting point was that of the hexamethylenetetramine.

Reference to FIGURE 1 of the drawing suggests a possible explanation of the above-described behavior. It will be noted that the solubility of ammonium nitrate in water accelerates rapidly with rising temperature, while that of the hexamethylenetetramine actually declines. The circle and the square represent the initial concentrations of the hexamethylenetetramine and the ammonium nitrate, respectively, used in adduct preparation. At these concentrations, the two components precipitate together, thus giving the adduct an opportunity to form. However, at higher temperatures, or with widely disparate concentrations, one component crystallizes preferentially to the exclusion of the other.

B. Crystallization from melts

The adduct may also be made without water by melting the two ingredients hexamethylenetetramine and ammonium nitrate in the proper molar ratio, i.e., one to two, and

then quickly cooling the molten mixture. The adduct is successfully made provided that as soon as the mixture is molten, it is quickly cooled. Otherwise, the adduct decomposes as a result of exposure to the elevated temperatures. In my copending application Serial No. 146,944, I showed how the adduct is formed even when an oxygen-balanced mixture of hexamethylenetetramine and ammonium nitrate is melted and then rapidly cooled. It was in such a product that I first discovered the existence of the adduct. However, the separation of the adduct in pure form from that product is difficult. Accordingly, I prefer when making the adduct by the melting process to employ the proper molar ratio, but still to use the hot melting roll and the cooled crystallizing roll as described in the aforementioned application.

By way of example of the melting process, the required proportions of hexamethylenetetramine and ammonium nitrate (1:2) were thoroughly mixed, and then hammer-milled. The resulting finely ground mixture was passed onto a hot metal roll which was maintained at a temperature of about 160° C. and which revolved at about one r.p.m. The molten material was then passed onto a counter-rotating cold metal roll which was maintained at about 10° C. where the molten material was congealed in the form of flakes. The latter consisted essentially of pure crystals of adduct.

II. ADDUCT: STRUCTURE

A. X-ray diffraction pattern

The fact that the crystals obtained as described above have a distinct crystalline structure different from either hexamethylenetetramine or ammonium nitrate was established by the use of X-ray diffraction techniques. The following table gives in approximate terms the relative intensities I/I_1 of the adduct for different values of the interplanar spacings expressed in angstrom units, $d(\text{Å})$.

TABLE I

$d(\text{Å})$	4.07	4.45	5.27	2.95	5.55	2.79
I/I_1	100	46	33	20	20	12

From this table it will be noted that the major peaks are at 4.07 Å., 4.45 Å., and 5.27 Å.

B. Infrared analysis

Infrared spectral analysis of adduct shows a unique fine pattern of absorption bands having frequencies in the 2460–2830 cm^{-1} range. This structure is not present for hexamethylenetetramine or ammonium nitrate, nor are the recorded peaks the result of a summation spectrum of these two compounds. FIGURE 2 of the drawing is the infrared spectrogram of the adduct. The characteristic absorption peaks occur at the following wave numbers: 2490, 2535, 2596, 2625, 2672, 2722, 2790, and 2826 cm^{-1} , as well as at 868, 1256 and 1291 cm^{-1} .

III. ADDUCT: PROPERTIES

- A. Empirical formula: $(\text{CH}_2)_6\text{N}_4 \cdot 2\text{NH}_4\text{NO}_3$.
- B. Solubility in water: Very soluble in hot or cold water. At 10° C. about 220 grams will dissolve in 100 grams of water.
- C. Solubility in organic solvents: Sparingly soluble in acetone, ethyl alcohol and ether.
- D. Melting point: About 122° C. (completely liquid by 132° C.). Prolonged heating above this temperature turns the melt yellowish. After eighteen hours at 125° C., the melt becomes a viscous tar-like liquid with a strong amine odor. Before reaching this state, fumes of ammonia are given off.
- E. Color: Colorless and transparent as individual crystal.
- F. Explosive properties: The adduct per se is a weak molecular explosive. It is heavily fuel-rich relative to oxygen balance. It has little sensitivity but is detonable with adequate boosting in proper confinement and diameter. In 2.0 inch diameter, 0.5 inch thick steel

walled tubes and boosted with a 25-gram tetryl pellet, adduct in a hammermilled form has a detonation velocity of 10,400 f./s. at a density of 0.84 g./cc.

IV. ADDUCT: EXPLOSIVE FORMULATIONS

As pointed out above, the adduct itself is weak as an explosive, presumably because it is deficient in oxidizer. When mixed with sufficient oxidizer to attain oxygen balance, explosive formulations are formed which are equal to or better than the presently available commercial cartridge explosives, and which, furthermore, are considerably less expensive because of the relatively cheap ingredients, particularly when the added oxidizer is ammonium nitrate. The following is an example of an explosive formulation made from the adduct of this invention.

Example 1

Adduct was blended with ammonium nitrate prills in the proportion of 1 to 4.02 parts by weight respectively. This proportion produces an oxygen-balanced formulation. The resulting mixture was tumbled to assure complete mixing and then passed through a hammermill. Sieve analysis gave 74 percent of the material through 200 mesh. Samples of the product were exploded in cartridges of different sizes. The detonation velocity for each explosion was determined in conventional fashion. The data obtained are presented in the following Table II.

TABLE II.—EXPLOSIVE DATA

Cartridge Size (in.)	Density, g./cc.	Primer	Velocity (f./s.)
1.25 x 8.....	0.95	No. 6 EBC ¹	13,300
1.0 x 8.....	0.95	No. 6 EBC.....	11,900
0.75 x 10.....	0.95	No. 6 EBC.....	10,400
0.63 x 10.....	0.95	No. 6 EBC.....	9,500

¹ No. 6 Electric Blasting Cap.

From the above, it will be seen that the blend of adduct and ammonium nitrate is a cap sensitive stick explosive. In general, it has a reaction zone length, a_0 , of about 0.27 inch and a critical diameter, $d_c=0.50$ inch (approx.). Its velocity in 1.25 inch diameter is about 13,300 f.p.s. at 0.95 density. Its gap sensitivity is about 3 inches.

Oxygen-balanced explosives containing the adduct of my invention may be prepared by the method described in the aforesaid application Serial No. 146,944, that is, by melting a mixture of ammonium nitrate and hexamethylenetetramine in oxygen balanced proportions, and thereafter rapidly chilling the molten mass. By rapidly chilling the melt, crystals of ammonium nitrate are obtained that have a maximum dimension not exceeding 100 microns. At least a portion of these crystals is enveloped in a continuous crystalline matrix of the adduct and any hexamethylenetetramine which may not have formed adduct. X-ray diffraction tests performed on the resulting products showed a prominent X-ray diffraction pattern peak at about 4.45 Å. This peak is not associated either with hexamethylenetetramine or ammonium nitrate. The density of explosives prepared in such fashion is about 0.95 in an unpacked state. They are capable of being detonated in a cartridge having a diameter of about 1.25 inch by a No. 6 Electric Blasting Cap with a detonation velocity of about 14,500 ft./sec. The gap sensitivity is about 4 inches. The following is an example of such an explosive formulation.

Example 2

Into an electrically heated stainless steel kettle were placed 900 grams ammonium nitrate (uncoated prills which were about 99.8 percent pure ammonium nitrate), 90 grams hexamethylenetetramine and 10 grams abietic acid ($\text{C}_{19}\text{H}_{39}\text{COOH}$), the latter two components having been first briefly ground together in a mortar in order to disperse the abietic acid throughout the hexamethylene-tetramine. Without this preliminary mixing the abietic

acid would tend to coagulate on the surface in the melt.

The mixture therefore consisted of 90 percent by weight ammonium nitrate, 9 percent by weight hexamethylenetetramine as the primary fuel and 1 percent by weight abietic acid as a crystallization modifier.

The mixture in the kettle was continuously stirred with moderate speed until a clear melt was formed at a temperature of about 145° C.

The resulting molten mass was then poured into a heated vessel having a multiplicity of small perforations in the bottom. The melt was then allowed to drip onto a clean, smooth stone table top from a height of about two feet while the vessel was moved about in such a way as to distribute the resulting solidified splattered droplets uniformly over the surface. This material was then scraped together in a pile by means of a steel blade and briefly kneaded with gloved hands in order to break up or granulate the flakes. It was then sifted and rubbed through a 16 mesh screen and finally stored in a polyethylene bag. As an alternative to the kneading and sifting operation, the scraped-up flakes were placed directly in the polyethylene bag and the granulation accomplished by suitable kneading on the bag.

Due to the hygroscopic nature of ammonium nitrate, it is important to avoid high ambient humidity (greater than 50 to 60 percent relative humidity) and to keep the stored material in a moisture resistant container.

The resulting granulated material when packed into a 1.5 inch steel pipe, 12 inches long, at increasing densities gave the following measured detonation velocities.

Density, gm./cc.:	Detonation Velocity, ft./sec.
1.01	15,300
1.24	18,700
1.36	15,200
1.38	15,900
1.41	14,600
1.44	13,400

Explosive formulations may also be made using the adduct of this invention in which the fuel is not exclusively hexamethylenetetramine. However, in order to assure a formulation which is sensitive to a No. 6 Electric Blasting Cap, the adduct should be present in an amount corresponding to at least ten percent by weight of the total amount of fuel and oxidizer in the formulation. The maximum amount of adduct is, of course, set by that required for oxygen balance with the ammonium nitrate when no other fuel than the hexamethylenetetramine is used. In the latter case, the amount of adduct is about twenty percent by weight of the total amount of fuel and oxidizer in the formulation. Accordingly, the range of effective amount of adduct in a cap sensitive explosive formulation is 10 to 20 percent by weight of the total amount of fuel and oxidizer in the formulation.

Examples of explosive formulations in which other fuels were used in addition to hexamethylenetetramine are as follows. A formulation was made which consisted of a mixture of 83 percent by weight of ammonium nitrate, 12.5 percent by weight of the adduct, and 4.5 percent by weight of wood flour. This formulation was introduced into a 1.25-inch x 8-inch cartridge. Its density was 0.95. It was detonable by a No. 6 Electric Blasting Cap and had a detonation velocity of 12,300 f./s. Similarly, a formulation was made which consisted of 85.7 percent by weight of ammonium nitrate, 11.7 percent weight of adduct, and 2.7 percent by weight of finely divided anthracite coal. This second formulation was also introduced into a 1.25-inch x 8-inch cartridge. Its density

was 0.95. It, too, was detonable by a No. 6 Electric Blasting Cap and had a detonation velocity of 11,900 f./s.

Not only may the fuel of the explosive formulations of this invention be in part other than hexamethylenetetramine, but also the oxidizer may in part be other than ammonium nitrate. Many oxidizers are known in the art. However, even as described above with respect to the partial use of other fuels, the adduct should be present in an amount between 10 and 20 percent by weight of the combined weight of fuel and oxidizer if the maximum cap sensitivity is to be reliably attained.

A natural question is why not simply mix ammonium nitrate and hexamethylenetetramine, instead of resorting to such methods of making adduct, as presented above. A good blasting explosive formulation can be obtained by using the simple mixture with an adequate primer. However, when packed in cartridge form, 1.25 inches in diameter, the mixture is not detonated by a No. 6 Electric Blasting Cap and furthermore its gap sensitivity, even when initiated with a tetryl pellet primer, is only one inch. For these reasons the simple mixture is not suitable for use as stick dynamite, although quite useful, as mentioned, in normal blasting operations.

In view of the improved performance resulting from the presence of the above-described adduct in explosive formulations, I have concluded that the improvement results from the pseudo-molecular mixture formed by the fuel and the oxidizer. In other words, the adduct of fuel and oxidizer acts as a molecular explosive, and thereby improves the performance of any explosive formulation in which it is present.

According to the provisions of the patent statutes, I have explained the principle, preferred construction and mode of operation of my invention and have illustrated and described what I now consider to represent its best embodiment. However, I desire to have it understood that, within the scope of the appended claims, the invention may be practiced otherwise than as specifically illustrated and described. In particular, it should be understood that other ingredients conventionally used in explosive formulations for special purposes may be included in my explosive formulations.

I claim:

1. The adduct of ammonium nitrate and hexamethylenetetramine in the molar ratio of 2 to 1.

2. The crystalline adduct of ammonium nitrate and hexamethylenetetramine which has a melting point of about 122° C. and which has an infrared spectrogram showing characteristic absorption peaks at the following wave numbers: 868, 1256, 1291, 2490, 2535, 2596, 2625, 2672, 2722, 2790 and 2826 cm.⁻¹; and an X-ray diffraction pattern with major peaks at 4.07 Å., 4.45 Å., and 5.27 Å.

3. The method of making an adduct of ammonium nitrate and hexamethylenetetramine which comprises dissolving said ammonium nitrate and hexamethylenetetramine in water in the molar ratio of about 2 to 1, and removing the water at a temperature below about 40° C. until the adduct is formed.

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