

April 19, 1966

W. E. GORDON

3,247,033

HEXAMETHYLENETETRAMINE-AMMONIUM NITRATE EXPLOSIVE
COMPOSITIONS AND METHODS OF MAKING THE SAME

Original Filed Oct. 23, 1961

2 Sheets-Sheet 1

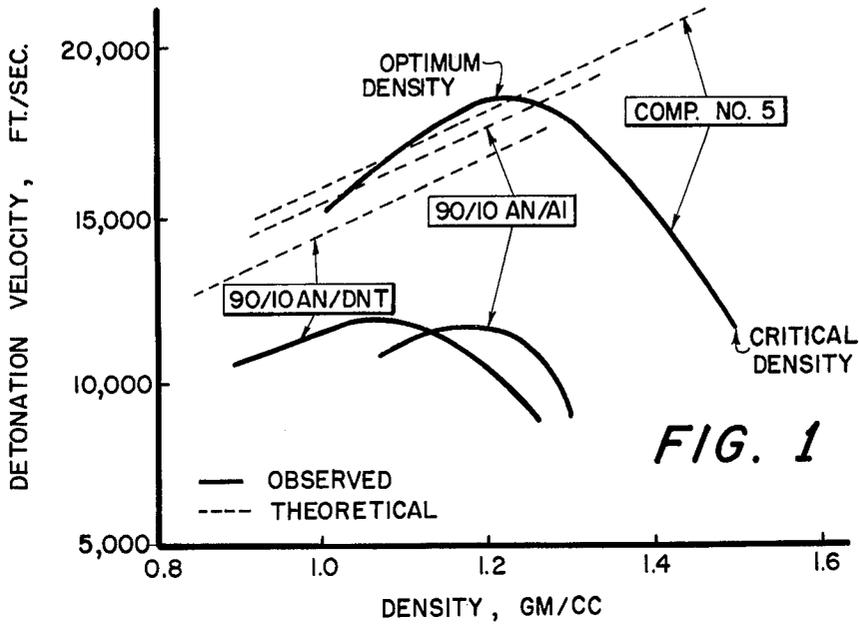


FIG. 1

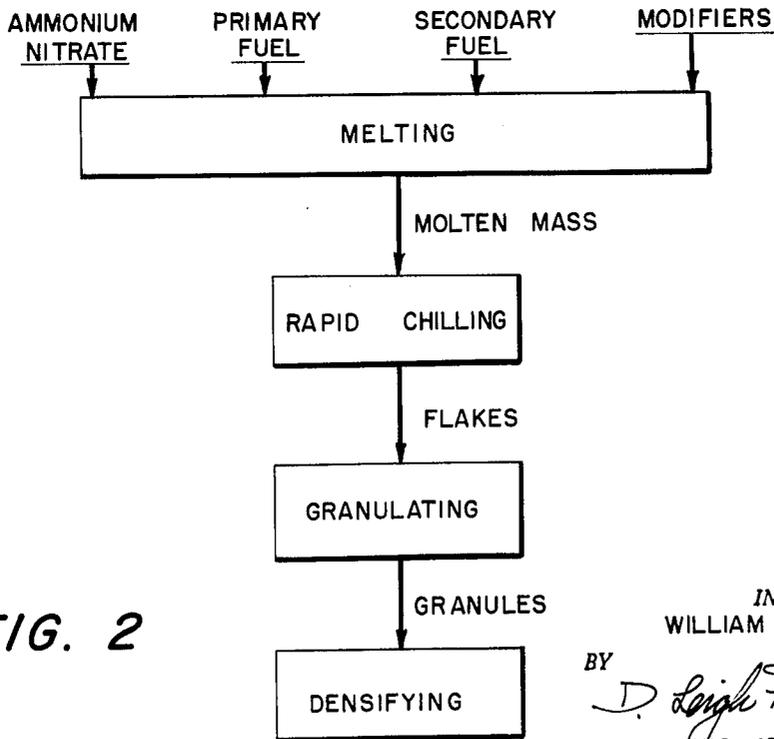


FIG. 2

INVENTOR.
WILLIAM E. GORDON

BY *D. Leigh Fowler, Jr.*
HIS ATTORNEY

April 19, 1966

W. E. GORDON

3,247,033

HEXAMETHYLENETETRAMINE-AMMONIUM NITRATE EXPLOSIVE

COMPOSITIONS AND METHODS OF MAKING THE SAME

Original Filed Oct. 23, 1961

2 Sheets-Sheet 2

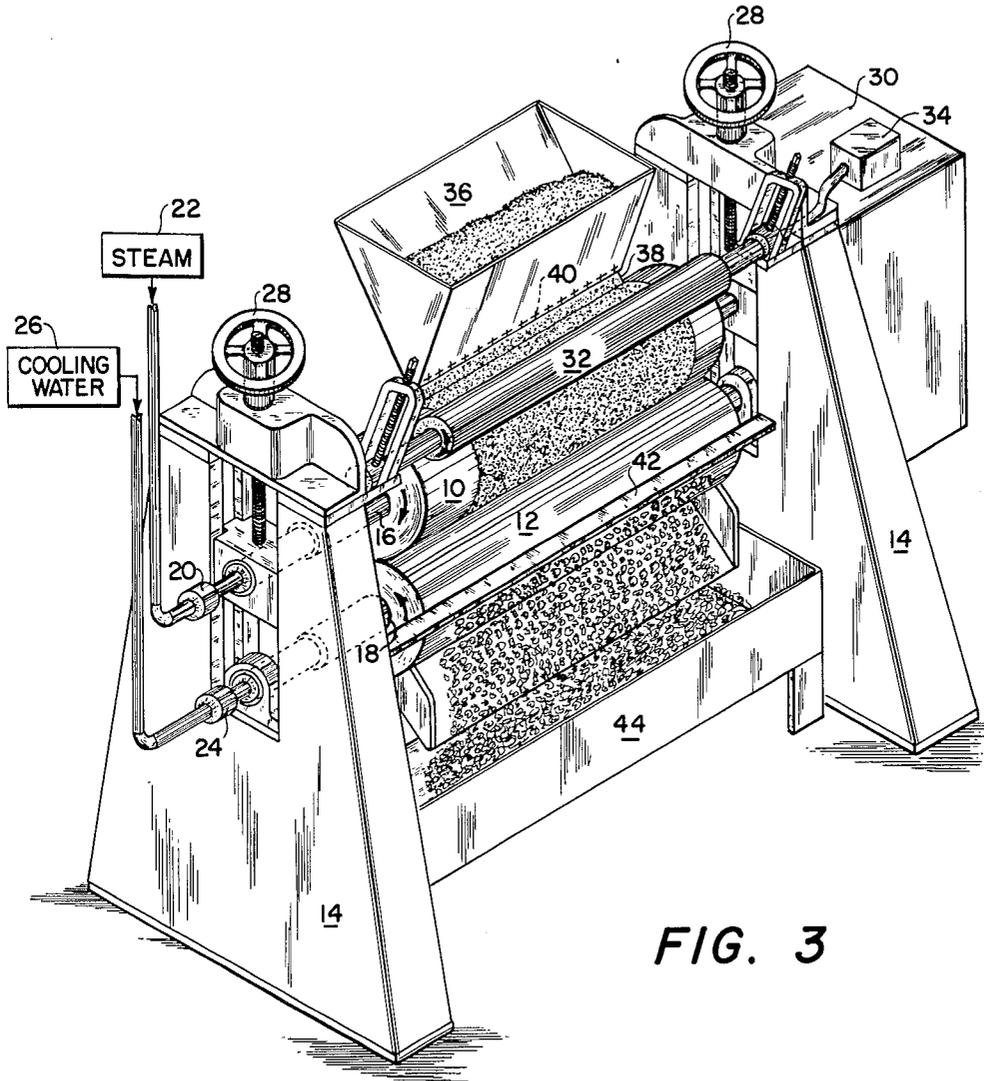


FIG. 3

INVENTOR.
WILLIAM E. GORDON

BY *D. Leigh Fowler, Jr.*
HIS ATTORNEY

1

2

3,247,033

HEXAMETHYLENETETRAMINE-AMMONIUM NITRATE EXPLOSIVE COMPOSITIONS AND METHODS OF MAKING THE SAME

William E. Gordon, Pittsburgh, Pa., assignor to Arthur D. Little Inc., Cambridge, Mass., a corporation of Massachusetts

Original application Oct. 23, 1961, Ser. No. 146,944. Divided and this application June 12, 1963, Ser. No. 287,291

8 Claims. (Cl. 149—18)

This application is a division of application Serial Number 146,944 entitled "Explosive Compositions and Methods of Making the Same," filed October 23, 1961, which is a continuation-in-part of application Serial Number 824,838 entitled "Explosive Compositions and Methods of Making the Same," filed July 3, 1959, now abandoned.

This invention relates to a novel family of high explosives and more particularly to high explosives suitable for use in small diameter cartridges and to the method by which these explosives are made.

Explosive compositions may be broadly classified as molecular or "fixed" explosives, heterogeneous explosives, and hybrid explosives. A molecular explosive contains both fuel and oxidizer within the same molecule and usually consists of CH-type groups linked with NO-type groups. Examples of molecular explosives are nitroglycerin and trinitrotoluene. A heterogeneous explosive is a mixture of separate macroscopic particles (or sometimes films) of oxidizer and fuel. A mixture of ammonium nitrate and fuel oil is a good example of a heterogeneous explosive. A hybrid explosive is a mixture of a molecular explosive and a heterogeneous explosive. The hybrid explosives constitute the most common class of commercial explosives—that is the nitroglycerin dynamites. The molecular explosive portion in the hybrid explosive is nitroglycerin, and the heterogeneous portion consists of ammonium nitrate and/or sodium nitrate together with wood pulp and other carbonaceous substances.

A major objective in the explosive art has been to increase the proportion of the oxidizer, generally ammonium nitrate, and reduce the proportion of high cost, impact and friction sensitive molecular explosive ingredients in hybrid explosives. A further objective has been to develop a heterogeneous explosive composition that is free of molecular explosive ingredients and less hazardous than either a molecular explosive or a hybrid explosive while retaining the desirable properties of the latter. Some degree of success has been achieved in this last objective in that mixtures of petroleum oil and particulate ammonium nitrate in the form of prills are now in use as a blasting agent in strip mining applications. This heterogeneous explosive, while very inexpensive, is often variable in composition and physical state. Factors such as oil distribution and particle size are difficult to control: the oil tends to drain off or segregate or it is unevenly absorbed, giving a product of non-uniform composition; also the ammonium nitrate particles tend to sometimes disintegrate because of temperature induced phase changes and sometimes the ammonium nitrate has a tendency to fuse or set up because of moisture, or because of certain crystalline transformations brought on by temperature cycling. Since the strength of the mixture and its ability to support detonation in the bore hole are critically dependent on oil concentration and particle size, the simple "oil-prill" heterogeneous explosive blasting agents for reasons like those just mentioned often give variable and unsatisfactory results.

The simple oil-prill type of heterogeneous explosive is unsuitable as a cartridge explosive. Cartridge explosives should be distinguished from blasting agents. 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 number 6 or a number 8 blasting cap. At the present time, the only cartridge explosives commonly available are hybrid explosives called the nitroglycerin dynamites. In the trade cartridge explosives are simply called dynamite. There may be a further classification of blasting agents and cartridge explosives between high and low density in each classification. Generally speaking, high density connotes high detonation velocity, high detonation pressure and high bulk strength. There are, therefore, four classes of explosives: (1) high density cartridge explosives—gelatin dynamites; (2) low density cartridge explosives—ammonia dynamites; (3) low density blasting agents—heterogeneous explosives such as oil-prills or the like; and (4) high density blasting agents—hybrid explosives comprising trinitrotoluene and ammonium nitrate in the form of slurries and other hybrid combinations. It should be noted in the above classification only one of the four classes is a heterogeneous explosive, this being the low density blasting agent. The known cartridge explosives and the high density blasting agents all include as an ingredient a molecular explosive. Throughout the specification the term "cap sensitive cartridge explosive" is intended to designate an explosive that may be detonated by a number 6 or a number 8 blasting cap in an eight inch paper cartridge having a diameter of about 1.25 inches.

In accordance with this invention, I have now discovered that when certain fuels are combined with ammonium nitrate by a novel process, the product, a heterogeneous explosive, has properties surprisingly different from known conventional heterogeneous explosives such as ammonium nitrate-fuel mixtures. While the products of this invention retain the low impact, low heat and low friction sensitivity associated with conventional ammonium nitrate-fuel materials, they possess at the same time high sensitivity to initiation by shock waves from blasting caps as well as from other priming agents, and, unlike conventional mixtures of this type, the products of this invention have the properties of cartridge type explosives in that they support high velocity detonation in small paper cartridges such as those used for dynamite. These materials may also be loaded at bulk densities as high as about 1.5 grams per cubic centimeter and still retain their ability to propagate an explosion. The chemical and physical state of the products of this invention can be closely controlled, and they remain stable in storage if the material is suitably protected from ambient moisture.

By the practice of this invention, it is therefore possible to overcome many of the difficulties in using and handling that are normally associated with simple ammonium nitrate-fuel mixtures, and to eliminate in many applications the need for the addition of sensitive molecular explosive materials such as nitroglycerin, trinitrotoluene, tetryl and the like.

The process of this invention employs simple, commonly available equipment and eliminates many of the hazards heretofore present in explosive manufacture.

It is, therefore, an object of this invention to produce a heterogeneous explosive suitable for use as a cartridge explosive.

Another object of this invention is to produce simple ammonium nitrate-fuel compositions suitable for a wider range of blasting and other high explosive applications than similar materials heretofore available.

It is another object of this invention to provide simple ammonium nitrate-fuel compositions that can be used in

almost all cartridge sizes where now only molecular explosives find application.

It will be evident to those familiar with the subject that many ancillary advantages follow from the substitution of a simple heterogeneous explosive for a hybrid explosive that contains molecular explosive ingredients in any proportion. Thus, another object of this invention is to reduce hazards to health and safety resulting from the presence of molecular explosives such as nitroglycerin, trinitrotoluene, tetryl and the like in explosive compositions, by the substitution for such compositions materials that are very insensitive to stimuli of impact, heat and friction, and which are not injurious to health in either manufacture or use. It is still a further object of this invention to eliminate the added cost of molecular explosives by providing heterogeneous explosives that use only inexpensive, readily available fuel components in conjunction with a major portion of a low cost oxidizer.

It is a further object of this invention to provide a heterogeneous explosive that may be mixed with additional oxidizer to provide a heterogeneous explosive of improved properties that may be used either as a cartridge explosive or as a blasting agent.

It is another object of this invention to provide an improved method of mixing the oxidizer and fuel of a heterogeneous explosive.

It is another object of this invention to provide a heterogeneous explosive that may be combined with other nonmolecular explosive materials to obtain high density blasting agents having the desirable properties of high density hybrid explosive blasting agents.

It is a further object of this invention to provide a novel process for the manufacturing of ammonium nitrate explosives which eliminates the hazards previously present in the manufacture of explosives having the same desirable properties as the heterogeneous explosive herein described.

These and other objects will become apparent in the following discussion and description of this invention.

The process and products of this invention will now be described in detail with reference to the accompanying drawings, in which:

FIGURE 1 is a plot of the relationship between density and detonation velocity for two ammonium nitrate fuel mixtures of the prior art and for a typical explosive of this invention;

FIGURE 2 is a flow diagram of the process of this invention.

FIGURE 3 is an isometric view of the apparatus employed in practicing the process of this invention.

Briefly, the explosive of this invention may be defined as a melt explosive, the major portion by weight of which is an oxidizer and the minor portion by weight of which is a fuel material, the explosive being further characterized as having the oxidizer in the form of crystals enveloped by or imbedded in a matrix of the fuel and any reaction products of the oxidizer and fuel, whereby upon initiation the oxidizer decomposition products are released at a sufficiently rapid rate for reaction with the fuel to sustain detonation.

In order to provide the explosive of this invention it is necessary to surround the crystals of ammonium nitrate with a matrix of fuel and any reaction products of the fuel and ammonium nitrate. The process of this invention may then be generally defined as one comprising the steps of rapidly heating a mixture of an oxidizer and a fuel to form a molten mass, and subsequently rapidly chilling the molten mass to form crystals of the oxidizer that are surrounded by a matrix of the fuel material and any reaction products thereof. It is preferred that the chilling be sufficiently rapid to form oxidizer crystals that have a maximum dimension not exceeding 100 microns. In practice, most of the oxidizer crystals will be much smaller than the maximum specified.

The process may include additional steps such as incorporating certain specified additives in the melt, granulating the solid explosive product formed by chilling, and densifying the granulated material.

Although I do not wish to be bound by the theory offered below, I believe that the key to the unexpected behavior of the explosives of this invention, as compared with that of conventional explosives of this type, lies in the improved scale of mixing between the oxidizer and the fuel component. Before describing this invention in detail, therefore, it will be helpful to review briefly the effects of the scale of mixing on the behavior of heterogeneous explosives and in particular the behavior of conventional explosives containing major portions of ammonium nitrate.

As is well known, the detonation velocity of an explosive composition can be calculated according to the so-called Chapman-Jouguet theory. This is the ideal detonation velocity; the actually observed velocity is usually less. Hereafter the term "velocity decrement" is intended to designate the fractional difference between the actual velocity and the ideal velocity.

It is also well known that detonation passes through the explosive as a front with a given velocity. The front is a shock wave that suddenly raises the pressure and temperature within the explosive. This instant rise in temperature starts the chemical reaction, which then goes on at a rate that depends on a number of different factors. It is the energy released by the chemical reaction that maintains the continued propagation of the shock front. If the rate of the chemical reaction is too slow, only part of the total chemical energy is released in time to contribute its support to the shock wave. In this instance the detonation velocity will be less than the maximum or ideal velocity. Since the reaction requires a finite time for completion, there is always a zone of a given length undergoing reaction. The smaller the reaction zone length, the more likely the shock wave will continue to propagate throughout the length of the explosive charge. It is the ratio of the reaction zone length to the diameter of the cartridge that determines the velocity decrement or the fractional difference between the actual velocity and the ideal velocity. Thus, if one knows the reaction zone length of a particular explosive, it can then be determined whether the explosive can be used in small diameter cartridges or whether it is a blasting agent type of material that can be used only in large diameter cartridges. I have found that to be of practical use for small cartridges of about 1 inch in diameter the reaction zone length must not be greater than about 0.4 inch.

The chemical reaction rate on which the reaction zone length is dependent is also a function of the burning rate of the ingredients of an explosive. This is best described by referring to a typical granular molecular explosive such as trinitrotoluene. The particles of a molecular explosive are considered to burn like powder grains. When the shock wave passes over a grain, it heats up the surface and starts the grain burning. The flame, thus started, consumes the grain in a steady erosion from outside in. In a molecular explosive, therefore, the velocity decrement is proportional to the grain radius. The larger the grain size, the greater the velocity decrement under given conditions of cartridge diameter, confinement and bulk density.

The behavior of heterogeneous fuel oxidizer explosives is different and in some respects opposite to that of molecular explosives. It is believed that the burning reaction of a heterogeneous fuel oxidizer explosive is of a diffusion type. In molecular explosives the reaction is really the rearrangement of the atoms within the individual molecules, but in a fuel-oxidizer system the two types of molecules must get mixed by diffusion before reaction can take place. Thus, in a heterogeneous explosive that contains separate fuel and oxidizer particles, the heat of the shock wave vaporizes or decomposes the particles and the en-

suings reaction occurs when the separate pockets of fuel and oxidizer interdiffuse. The rate for diffusion, and hence the reaction time, is dependent on the average distance that a fuel or oxidizer molecule must diffuse in order to react. The smaller the distance the fuel or oxidizer molecule must diffuse, the shorter the reaction time and the smaller the velocity decrement. The principle to be obtained from the above discussion is that in a heterogeneous fuel oxidizer explosive the shorter the distance that a fuel or oxidizer particle must diffuse in order to react, the shorter the reaction time and the more closely the actual detonation velocity approaches the ideal detonation velocity. If it were possible, therefore, to mix the oxidizer and the fuel on a molecular scale so that the molecules of oxidizer and fuel were in intimate contact the actual detonation velocity would approach the ideal detonation velocity.

In heterogeneous explosives, the initial rate of heat release by the chemical reaction has an influence on primer sensitivity. The initial rate of heat release is a resultant of the negative rate of heat release by vaporization or endothermic decomposition and the positive rate of heat release by the fuel-oxidizer reaction. The oxidizer, that is the ammonium nitrate, contributes little to the negative rate of heat release by vaporization because it decomposes mainly by exothermic processes. The main heat absorbing process is the vaporization of the fuel. Where the fuel particles are all exposed to the shock wave from the beginning, all the fuel will vaporize and, therefore, contribute to the negative rate of heat release by vaporization. The sensitivity of an explosive can, therefore, be improved by exposing not all but only a portion of the fuel to the shock wave initially. In my explosive the fuel is distributed through the grains and intimately mixed with the ammonium nitrate. Therefore only a small fraction of the fuel on the surface of the grains is initially exposed to the shock wave and therefore contributes less to the negative rate of heat release by vaporization. The principle to be obtained from the above discussion is that the primer sensitivity of a heterogeneous explosive can be improved if only a small fraction of the fuel on the surface of the grains is initially exposed to the shock wave.

Before discussing how I am able to obtain a cartridge type heterogeneous explosive that is detonable by a number 6 blasting cap in small diameter cartridges, a distinction should be made between the terms grain or particle, and crystal. A grain or particle is an entity of solid material generally bounded by an air interface that remains intact in ordinary handling and appears as a distinct entity under the microscope. The matter within the grain may be heterogeneous or homogeneous; it may be a single crystal, a fragment of a single crystal, a coherent mass of microcrystals of a single substance, or a coherent mass of crystals of two or more chemical components as formed, for example, by freezing of a eutectic system. A crystal, on the other hand, is an entire unit of homogeneous crystalline matter as it is formed originally from the liquid state.

I have found by combining an oxidizer and a fuel by rapid melt and rapid chill process, that I am able to obtain a scale of mixing far smaller than by other known methods of mixing the oxidizer and fuel of heterogeneous explosives. The fuel and oxidizer are heated to form a solution wherein they are mixed on a molecular scale. In solution the two substances are in as intimate a mixture as it is possible to get without chemical reaction. The solution is then rapidly chilled to keep the crystals that form on freezing to a minimum size. In my system during the rapid chilling the oxidizer crystals form numerous spontaneous nuclei when the solution is supercooled.

Upon continued chilling to the point where fuel begins to crystallize, the primary crystals, which in this instance are the crystals of the oxidizer, are enveloped in a continuous matrix of the fuel, any reaction product of the

fuel and oxidizer and smaller crystals of the oxidizer. The first crystals to form, that is, the oxidizer crystals, can be called the primary crystals and the smaller crystals which form the matrix can be called the secondary crystals. It is believed the secondary crystals are crystals of the fuel, oxidizer and any reaction products of the fuel and oxidizer. Thus not only are the primary crystals of the oxidizer surrounded by a matrix which includes the fuel, but within the matrix itself smaller crystals of the oxidizer are also in intimate relation with the small crystals of fuel. For brevity throughout the remainder of the specification the matrix will be called a matrix of the fuel and any reaction products of the oxidizer and fuel. It should be understood, however, that there may also be included in the matrix smaller crystals of the oxidizer. The secondary crystals which form the matrix are smaller than the primary crystals by a factor of 10 or more. I have found by rapidly chilling the melt that I am able to obtain primary crystals of oxidizer that have a maximum dimension not exceeding 100 microns. These crystals are enveloped in a continuous matrix of fuel and any reaction products of the oxidizer and fuel. The solidified and subsequently comminuted melt then consists of particles or grains which include numerous crystals of oxidizer imbedded in a matrix of the fuel and any reaction products of fuel and oxidizer. It is believed that the intimate relationship of the oxidizer crystals and the fuel in the matrix contributes to the unexpectedly high chemical reaction rate of my heterogeneous explosive. The oxidizer and fuel being in intimate contact within the particle or grain minimizes the distance that the molecule of fuel and molecule of oxidizer must diffuse upon vaporization or decomposition in order to react. The reaction zone length is, therefore, substantially reduced when compared with other known heterogeneous explosives and my explosive, therefore, propagates in small diameter cartridges. Also, because a major portion of the fuel is entrapped within the grain or particle, all of the fuel is not exposed to the shock wave from the beginning and is not vaporized at that time. Therefore, it is believed that by means of including a portion of the fuel within the grain or particle the negative rate of heat release by vaporization or endothermic decomposition is reduced and the sensitivity of my heterogeneous explosive is superior to that of other known heterogeneous explosives.

Several examples will illustrate the improved properties of my explosive when compared with other known heterogeneous explosives and certain hybrid explosives. Cook ("The Science of High Explosives," by Melvin A. Cook, published by Reinhold Publishing Corporation, 1958) reports (page 57) that a mixture of ammonium nitrate and fuel oil in a five inch diameter cardboard tube had a measured detonation velocity of only 8,300 feet per second. If one assumes that this reported material had a typical density of 0.8 grams per cubic centimeter, the ideal detonation velocity for this composition is calculated to be about 13,000 feet per second, over 50 percent higher than the observed figure. In comparison, I have found that one of my melt explosives in a similar cartridge (5 inch diameter cardboard tube) has a measured detonation velocity of 15,400 feet per second. The density of my explosive in this case was 0.95 grams per cubic centimeter and the ideal detonation velocity was 16,200 feet per second, only 5 percent higher than the observed figure.

Even compositions containing nitroglycerin, that is, hybrid explosives with a predominantly ammonium nitrate content, show large deviations from ideal velocity when they are fired in standard 1.25 inch diameter paper cartridges. For example, Taylor ("Detonation and Condensed Explosives," by J. Taylor, published by Oxford University Press, 1952) reports (page 12) the velocity for a dynamite containing 10 percent nitroglycerin, 80 percent ammonium nitrate, and 10 percent carbonaceous fuel at 8,600 feet per second, whereas the calculated

velocity at the stated density of 0.98 grams per cubic centimeter was 14,000 feet per second. For comparison with the above figure I have found that an explosive of this invention detonates with a velocity of 13,900 feet per second in a standard 1.25 inch diameter cartridge and a loading density of 0.95 grams per cubic centimeter, the ideal velocity at this density being 16,200 feet per second. These conditions are equivalent to essentially no confinement, under which most simple ammonium nitrate-fuel mixtures will not detonate at all in charges of this diameter. The composition of this explosive was 90 percent ammonium nitrate, 8.5 percent hexamethylenetetramine and 0.3 percent soap. From this example it is seen that the explosive of this invention which contains no sensitive molecular explosive like nitroglycerin detonated with a velocity of 80 percent of its ideal value in a standard cartridge; the conventional blasting composition with 10 percent of nitroglycerin as reported by Taylor had a velocity of only 61 percent of the ideal value under similar conditions.

Further examples showing the superiority of the explosive of my invention to a simple fuel oil-ammonium nitrate mixture are seen in the following table. In this table the results for such a fuel oil mixture were obtained under conditions identical with those used in evaluating the explosives of this invention. For these experiments the various explosives were loaded in a 12 inch length of standard steel pipe, 1.5 inch nominal diameter. The detonation velocity was measured over a six inch interval at the end opposite from the detonator by the well known Dautriche method. The first composition of Table I is a specially prepared "oil prills" explosive that has considerably higher sensitivity to explosive primers and greater ability to sustain detonation in narrow charges and light confinement than typical oil-prill mixtures in common use. It should, therefore, be considered for this comparison as a highly favorable example of this class of explosives. Those materials designated compositions number 1-5 represent typical explosive compositions of this invention.

rates higher than ammonium nitrate-fuel compositions of the prior art. The higher reaction rate is manifested in these examples by the ability of the explosives of this invention to sustain detonation in narrow charges with velocities that closely approach ideal values. The practical significance of this fact is that these explosives can be loaded in small cartridges for the many applications where explosives are used in this form and where conventional compositions of the simple ammonium nitrate-fuel type are inapplicable.

The explosives of this invention have been successfully detonated in paper tubes of diameter as low as 0.34 inch. This compares with the limiting diameter under similar conditions for some nitroglycerin dynamites. Explosives with these properties qualify for use in shaped charges and in other small-charge applications such as the so-called "explosive forming" of metals.

A further manifestation of the unusually high reaction rate of the new explosives of this invention is their ability to sustain detonation even when considerably densified. Although molecular explosives such as nitroglycerin, trinitrotoluene, tetryl and the like will readily detonate in dense charges, it is characteristic of simple ammonium nitrate-fuel compositions that they cannot be used in high density form.

As conventional ammonium nitrate-fuel mixtures are densified, the detonation velocity may at first increase, but usually not as much as would be expected from theory, and on further densification the velocity begins to fall after a shallow maximum is reached. Finally, beyond a certain point detonation fails to propagate at all. This behavior is illustrated by the experimental (solid line) curves in FIGURE 1 for an ammonium nitrate-dinitrotoluene mixture and an ammonium nitrate-aluminum mixture. These curves, reproduced from Cook (loc. cit., page 49), show the behavior of these explosives in 4 inch diameter charges, presumably under light confinement. The velocity in these mixtures is very much below ideal, as may be seen from a comparison of the experimental

TABLE I.—MEASURED DETONATION VELOCITIES

Composition (percent by weight)	Density (g./cc.)	Initiator	Velocity (ft./sec.)		Ratio, Obs./Ideal
			Observed	Ideal ¹	
5.1 No. 2 fuel oil.....	0.86	No. 8 cap.....	8,300	13,100	0.63
94.9 ammonium nitrate.....	0.87	25 g. tetryl.....	9,400	13,200	0.71
Composition No. 1:					
20.0 urea.....	0.87	No. 8 cap.....	13,400	12,700	1.05
80.0 ammonium nitrate.....	0.87	25 g. tetryl.....	12,500	12,760	0.98
Composition No. 2:					
10.0 urea, 7.5 diacyandiamide.....	1.08	No. 8 cap.....	13,600	14,800	0.92
82.5 ammonium nitrate.....	1.01	25 g. tetryl.....	13,600	14,100	0.96
Composition No. 3:					
6.6 urea, 10.0 diacyandiamide.....	0.92	No. 8 cap.....	13,900	13,200	1.05
83.4 ammonium nitrate.....	0.90	25 g. tetryl.....	15,100	12,900	1.17
Composition No. 4:					
6.6 urea, 5.0 diacyandiamide.....	1.02	No. 8 cap.....	13,500	14,400	0.94
2.5 carbon, 85.9 ammonium nitrate.....	1.05	25 g. tetryl.....	14,700	14,700	1.00
Composition No. 5:					
9.0 hexamethylenetetramine.....	1.01	No. 6 cap.....	15,000	15,800	0.95
1.0 abietic acid, 90.0 ammonium nitrate.....	1.01	25 g. tetryl.....	15,300	15,800	0.97

¹ Ideal detonation velocity D was calculated from the semi-empirical formula:

$$D(\text{m./sec.}) = 1410 \sqrt{T/M} + 3,500 (d-1)$$

Where T is calculated adiabatic explosion temperature (° K.), M is the average molecular weight of product gases, and d is loading density (gm./cc.).

The results in Table I show, in consideration of the accuracy limitations both of the measurements and the calculations, that the explosives of this invention detonate with nearly ideal velocity under these experimental conditions. On the other hand, the conventional ammonium nitrate-fuel mixture (ammonium nitrate and fuel oil) achieves a velocity of only some 70 percent of its ideal value.

The foregoing measurements illustrate the fact that the explosives of this invention can be made with reaction

(solid line) curves with the theoretical (broken line) curves in FIGURE 1.

The experimental curve labeled "Comp. No. 5" near the top of the diagram in FIGURE 1 shows the behavior of Composition No. 5 (Table I) of this invention. The data for this curve were obtained with the explosive loaded in 1.5 inch diameter steel pipes as previously described. These conditions are thought to be fairly equivalent to those under which the reported data were taken for the other two compositions in FIGURE 1, since the

additional confinement of the steel walls can be shown to approximately offset the effect of the diameter reduction. It will be noted that the explosive composition of this invention behaves under these conditions as an almost ideal explosive up to a density of 1.25 gm./cc., beyond which the velocity falls off with further densification. Thus, under these conditions the composition of this invention is much more brisant than the conventional materials, as is evidenced by the much higher detonation velocity. It is also capable of detonating at considerably higher loading density and therefore has a substantially higher possible bulk strength than the two conventional mixtures. Therefore, performance differences between the explosives of this invention and conventional ammonium nitrate-fuel materials when they are densified are clearly marked and unexpected, and as the data in FIGURE 1 illustrate, the differences are of such a magnitude that for many practical purposes where high bulk strength and high brisance are needed, the explosives of this invention can now qualify whereas conventional ammonium nitrate-fuel mixtures cannot be used.

Further experimental results also illustrate the unusual properties of these new explosives in comparison with conventional ammonium nitrate-fuel explosives. For example, in experiments in which the material was loaded in 0.5 inch diameter copper tubes, it was found that Composition No. 5 (see Table I) would support detonation up to a loading density of 1.49 g./cc. Under the same conditions, a mixture of finely crushed ammonium nitrate and No. 2 fuel oil, in conventionally used proportions, which detonated well at a density of 0.83 g./cc. did not sustain detonation when compressed to 1.12 g./cc. The limit for propagation of this commonly used material under these conditions, therefore, lies much lower than that for the explosive of this invention, and is somewhere between 0.83 and 1.12 g./cc.

It is clear from the foregoing examples that the explosives of this invention achieve the objects of this invention. Unlike conventional ammonium nitrate-fuel compositions, they behave like nearly ideal molecular explosives under most conditions. Therefore, they can be applied to practical use in narrow cartridges and in densified charges where before only compositions containing major quantities of molecular explosives could be employed.

It might be expected that since the compositions of this invention are more readily detonated and are generally more brisant than conventional ammonium nitrate-fuel compositions they should therefore be more sensitive toward ignition by impact, friction and fire. On the contrary, however, experiments show that the explosives of this invention are characteristically very insensitive to these agents. For example, under impact from a 38 pound hammer dropped from a height of 17 feet on a 3 inch diameter steel anvil, only weak explosions were obtained with these new compositions and these in only about 20 percent of the trials. Under the same conditions, finely ground ammonium nitrate and fuel oil mixtures exploded about 50 percent of the time and with more violence than the compositions of this invention. Likewise these new explosives have proved even less sensitive to ignition by friction and fire than certain conventional ammonium nitrate-fuel mixtures. For example, a bag containing 60 pounds of one of my explosives was dumped on a vigorous petroleum and wood bonfire and the material was consumed without explosion or any marked degree of violence.

In their reaction to rifle bullet fire, the explosives of my invention are similar to mixtures of fuel oil and ammonium nitrate, but much less sensitive than dynamites containing nitroglycerin. We have found that the explosives of this invention can be set off only by bullets with extremely high muzzle velocity from the so-called "220-swift" rifle fired at close range. Cartridges of fuel oil and ammonium nitrate mixtures can also be detonated by this means. With a bullet from a .30 caliber rifle my

explosives could not be detonated even when the explosive cartridges were backed up by a heavy steel plate. In contrast, commercial ammonia dynamites were set off by a .30 caliber rifle bullet even when the cartridge was freely suspended in air without a steel backing plate.

According to this invention there is disclosed a range of explosive compositions and a process for formulating them which permit control and optimization of such factors as explosive strength, primer sensitivity, detonation velocity and density.

The novel explosives of this invention comprise intimate mixtures which have as the major component ammonium nitrate serving primarily as an oxidizer and as the minor component a compound or a mixture of compounds from a class of melt soluble fuel materials hereinafter referred to as primary fuels. The terms "major" and "minor" components will be more precisely defined with relation to the various primary fuel components. The preferred composition ranges depend upon the theoretical reaction assumed. Alternatively, the minor component may include a fuel-adduct or mixture of adducts formed by reaction of the primary fuel with the ammonium nitrate in the melt.

The melt soluble primary fuels may be characterized as compounds capable of undergoing exothermic reaction with ammonium nitrate during the explosion process and also capable of forming stable miscible melts with ammonium nitrate at temperatures below the melting point of the latter (170° C.). The preferred group of such melt soluble fuels comprises organic compounds containing at least one nitrogen atom and selected from the group consisting of amines, amides, imides and substituted amines, amides and imides.

Besides the melt soluble primary fuels, there may be present in explosive compositions of this invention secondary fuel materials. These may be substances such as sugar which are soluble in the melt formed by ammonium nitrate and the primary fuel, particulate materials like carbon that can be dispersed in such a melt, or particulate or liquid substances such as the so-called "atomized" aluminum or fuel oil, respectively, that may be mechanically admixed with the dry product formed from ammonium nitrate and the primary fuel.

The fourth category of materials that may be present in the explosives of this invention beside ammonium nitrate and the primary and secondary fuels, consists of substances that may be classed as modifiers. These may be added for the purpose of modifying crystal habit, inhibiting crystal growth, increasing melt viscosity, altering the physical nature of the product or reducing its moisture susceptibility.

The various components of the explosive of this invention may now be further described and defined. The ranges in which these components may be present in the final explosive are given and illustrated by examples.

The ammonium nitrate suitable for compounding the explosive of this invention may be any commercial grade ammonium nitrate. It may be completely dry or it may contain up to about 3 percent water, which means that the highly concentrated ammonium nitrate solutions can be taken from the high pans in the ammonium nitrate manufacture and used directly in the compounding of the explosive of this invention. Fertilizer grade "prills" which are coated with a material to prevent caking may be used, but it is preferable to use some uncoated material with it or to crush the material before use in order to aid the melting process.

It is essential to the process of this invention to form a melt with ammonium nitrate; therefore, at least part of the fuel must be capable of forming such a melt. This melt soluble portion is designated the primary fuel. The requirement to form a miscible and stable solution with ammonium nitrate at a temperature, preferably below about 150° C., and to have a high fuel value (heat of

combustion) somewhat restricts the choice of suitable materials.

Primary fuels suitable for the practice of this invention may thus be defined as organic compounds which form a homogeneous melt with ammonium nitrate at temperatures below about 170° C. and preferably below about 150° C. and which are capable of being oxidized by ammonium nitrate to form substantially all gaseous products and to release energy, preferably at least 0.6 kg. calories per gram of mixture when present in amounts sufficient to give an oxygen balanced mixture with the ammonium nitrate. In addition, the primary fuel is preferably one that is capable of lowering the melting point of the fuel-ammonium nitrate mixture. The primary fuel may, of course, be a single compound, or a mixture of two or more fuel materials as defined.

Because of the ready availability, low cost and highly suitable properties in other respects, the preferred group of primary fuels are urea, dicyandiamide, hexamethylenetetramine, and combinations of these. The preferred primary fuel of the group is hexamethylenetetramine. Although the above-named compounds are generally preferred in the practice of this invention, it will be understood that the choice is not limited to these but may be made from the category of suitable primary fuels as defined above.

The secondary fuel, although not necessary in the explosives of this invention, may be used and chosen from a wide range of possible substances. The only requirement is that it be capable of oxidation under the conditions of the explosion with the yield of a large quantity of heat and also preferably of a large amount of gas. Most carbonaceous materials and some finely divided metals such as aluminum can fill this function. However, it is preferred to select secondary fuels that have certain other desirable properties as well. For example, finely divided carbon serves a number of functions. It is a highly energetic fuel, absorbs radiation and thus assists the propagation of the detonation; and it thickens the melt, thus tending to reduce migration of molecules and prevent the growth of large crystals. A sugar, such as dextrose, is also excellent as a secondary fuel. It has a high heat of combustion, increases the viscosity of the melt, and as a result tends to inhibit crystal growth. Moreover, sugar remains in an amorphous, highly dispersed and reactive state in the product; and it tends to stabilize the product against harmful effects from absorption of ambient moisture.

Still other materials may be preferred as secondary fuels in certain applications because of their low cost, high energy yield, or the improvement they impart to the physical state of the product. For example, a highly effective explosive with improved water resistance can be made by mixing 3 percent fuel oil with a composition of 10 percent urea and 90 percent ammonium nitrate prepared in accordance with this invention.

The examples given of secondary fuel materials serve to illustrate the factors to be considered in choosing this component for an explosive of this invention, and a number of such secondary fuels and mixtures thereof will occur to those skilled in the art and are within the contemplation of the scope of this invention.

The total amount of primary fuel and secondary fuel which should be present in the explosive, but not necessarily in the melt portion of the explosive, may be expressed in terms of the quantity and quality of reaction products theoretically resulting from the over-all detonation reaction. In the reaction it is assumed that the oxygen available (usually substantially all being provided by the ammonium nitrate) will react first with the carbon to form CO, then with the hydrogen to form H₂O and finally with the CO to form CO₂. No appreciable quantities of the oxides of nitrogen are assumed or taken into account in calculating the ammonium nitrate-fuel ratio.

Inasmuch as an excess amount of ammonium nitrate, which would in effect introduce unreacted oxygen into the final gaseous products, would be neither practical nor capable of enhancing the final properties of the explosive, a lower limit of fuels may be set at that quantity required to obtain an oxygen balanced mixture. This may, of course, be varied to some extent within practical limits. An upper limit on the amount of primary and secondary fuels may be defined as that quantity which will react with the available oxygen to burn substantially all of the carbon to CO and substantially all of the hydrogen present to H₂O. It may be seen that the actual weight percentages of the fuel will vary depending upon the fuel or fuels chosen, but that these can be readily calculated for each system.

Conversely, the amount of ammonium nitrate (which will always be present in a major portion by weight) may be said to range from that quantity sufficient to supply oxygen to burn substantially all of the carbon and hydrogen to CO and H₂O to that quantity sufficient to supply oxygen to burn substantially all the carbon and hydrogen to CO₂ and H₂O.

In the mixture of primary and secondary fuels the weight percentages of primary fuel may vary from 100 percent, i.e. no secondary fuel, to that quantity required to furnish at least 15 percent of the total fuel required to give an oxygen balanced ammonium nitrate-fuel mixture. The remaining of the total amount of fuel present in the total fuel range defined above is then a secondary fuel. It should be understood, however, that it is within the scope of this invention to provide an explosive wherein a portion of the ammonium nitrate is melted with either a portion or all of the primary fuel to obtain the heretofore discussed scale of mixing. To this melt product, additional ammonium nitrate or secondary fuels may be added to obtain the desired oxygen balance previously discussed.

In the practice of this invention, it is preferred to use the quantity of fuel in the explosive composition which closely approximates an oxygen balanced explosive composition. For example, if only a primary fuel is used, the mixture would include, by weight, about 20 percent urea, or 15 percent dicyandiamide or 9 percent hexamethylenetetramine. As will be discussed later, it is possible to form a melt of all the fuel with a portion of the ammonium nitrate. The remaining ammonium nitrate can be mechanically mixed with the resultant melt product to obtain an oxygen balanced explosive composition.

Inasmuch as the ultimate crystal size of the ammonium nitrate in the explosive products of this invention contributes substantially to the scale of mixing, it may be desirable to add what may be conveniently termed "crystallization modifiers." Although it is not possible to state definitely what the exact role of each of these modifiers is, it is possible to offer plausible explanations of how they behave. Some serve to increase the viscosity of the melt, others affect the crystal habit of the solidified ammonium nitrate, while others appear to offer barriers to molecular migration in the solidifying or quick chilling process. Illustrations will be given of these various crystallization modifiers.

One of the most effective crystallization modifiers is abietic acid which has a profound effect on the crystal habit of ammonium nitrate. Ammonium nitrate in the presence of abietic acid forms small scales or plates not more than two or three microns thick. Moreover, even these little platelets are permeated with fissures and holes which further increase the relatively enormous specific surface area presented by the ammonium nitrate in the product. The abietic acid need not be present in amounts exceeding about 1 percent by weight, while amounts as low as 0.2 percent by weight have been found quite effective.

Another crystallization modifier that may be incor-

porated in the melt and which causes rather profound changes in the product is a colloiddally dispersed thickening agent such as a hydrophilic gum. It is believed that such a gum is a particularly good example of this type of crystallization modifier. For example, when 1 percent of methyl cellulose is added to a melt containing 20 percent urea and 80 percent ammonium nitrate, the resultant explosive is much more sensitive toward primers than the same product without the methyl cellulose. Other thickeners of this type include, but are not limited to, vegetable gums and starches. Although the effect of these is less pronounced than that of methyl cellulose, they do contribute to the desired inhibition of crystal growth.

Materials which are added to the melt specifically as crystallization modifiers may generally be used in amounts up to about 3 percent by weight of the explosive composition mixture. However, they have been found to be effective in amounts as low as 0.2 percent by weight. The preferred amount for each type of individual crystallization modifier may easily be determined experimentally by making up sample compositions and observing the size of the ammonium nitrate crystals under a microscope.

Other types of modifiers may be added to the finished product. These will be discussed in detail in reference to high density blasting agents and slurries prepared of the heterogeneous explosives of this invention.

The process of this invention has been generally defined as one which comprises heating a mixture of the ammonium nitrate and the primary fuel, along with any other components, to form a molten mass and then solidifying the molten mass in a manner to effect intimate contact among the mixture components comprising the ammonium nitrate, the primary fuel and any reaction products therebetween and to form crystals of ammonium nitrate imbedded in a matrix of the primary fuel and any reaction product of the fuel and ammonium nitrate. It is preferred that substantially all of the ammonium nitrate crystals have maximum dimensions not exceeding 100 microns. The steps of the process are illustrated diagrammatically in FIGURE 2.

The step of forming the molten mass should be performed in equipment that can rapidly melt the ammonium nitrate and the primary fuel in a manner that there is a minimum decomposition of the components. The melting temperature should be less than the decomposition temperature of ammonium nitrate and preferably not higher than about 150° C. Once melting of the ammonium nitrate and the primary fuel has been accomplished, it is preferable to perform the next step of quick chilling as rapidly as possible rather than to maintain the molten mass at the melting temperature for an extended period of time.

The secondary fuels, the crystallization modifiers and other additives may be added either before melting, during the process, or after melting but before chilling. The point in the melting process at which these are added will be at least in part dictated by the nature of the material added. Thus, for example, if the melting stage is appreciably long it is desirable to add a sugar such as dextrose after the melting has been accomplished in order to prevent any appreciable charring of the sugar.

In order to achieve the required intimacy and uniformity of mixing (scale of mixing) and the required crystal size of the ammonium nitrate, it is necessary to chill or freeze the molten mass under conditions which effect extremely rapid heat transfer from the molten mass to a medium capable of absorbing the heat. This is required in order to form rapidly a large number of crystal nuclei or growth centers and to inhibit the growth of large crystals of ammonium nitrate. Rapid freezing also virtually prevents any degree of fractional crystallization which characterizes slow freezing and which leads to segregation and non-homogeneity in the solid product. Rapid freezing also leads to extremely fine division of the fuel and the high degree of intimacy of contact be-

tween the ammonium nitrate crystals and the fuel matrix that is required in order for sufficiently rapid reaction to occur during explosion. It is believed the numerous crystals of ammonium nitrate imbedded in a matrix of the fuel contained within each particle or grain of the explosive is responsible for the rapid reaction rate achieved and, hence, for the approach to ideal detonation conditions.

The step of rapid chilling or freezing may be accomplished in one of several different ways, and the choice will depend upon the type of equipment used. The step of rapid chilling may be accomplished by spreading the melt in a thin film on a chilled surface such as, for example, a water cooled metal surface which may be either stationary or, if convenient, a moving one.

In practice it has been found that when the molten mass has been transferred to form a thin film on a chilled surface in order to perform a solidifying step, it is preferable that the complete solidification take place within a matter of seconds. However, if a crystallization modifier is added to the melt, it may be possible to extend the chilling time.

The manner in which chilling is accomplished and the time required is one which may be determined by simple experiments to find the one which best and most economically gives ammonium nitrate crystals in the size range desired and imbeds these crystals in a matrix of the fuel.

The importance of quick chilling or solidifying may be illustrated by the fact that the well-known mold casting and slow granulation techniques generally used in the explosive industry are not applicable to the formation of the explosive of this invention. These conventional process steps result in crystals of substantial size and in some degree of segregation of the components because of fractional crystallization of the melt.

After the explosive of this invention has been formed, that is the ammonium nitrate crystallized in the size required, it may be further granulated and densified. The granulation may be accomplished by grinding or rubbing or brushing the material through a sieve. The resulting material varies from a fine granular to a flour-like product depending on the composition and the freezing and granulating conditions, and it remains in this condition if precautions are taken to prevent any appreciable moisture absorption. Densification of the product may be accomplished in several ways. The product may also be combined with other materials to form a high density blasting agent.

The apparatus illustrated in FIGURE 3 will be described in conjunction with the use of my preferred primary fuel, hexamethylenetetramine. It should be noted that the apparatus illustrated in FIGURE 3 provides a means to quickly melt a small quantity of the ammonium nitrate and primary fuel and to subsequently rapidly freeze the melted material. The type of apparatus illustrated in FIGURE 3 provides the following advantages.

There is little or no hold up time of large quantities of molten explosive. This is a desirable feature from the safety aspect.

The decomposition of the product or components is largely eliminated by the short period in which the materials are subjected to the heating process on the hot roll.

The fire or fume-off hazards are virtually eliminated. Superheating of the small masses of components at any stage of the melting process is not possible because the material is in intimate contact with a large heat sink.

The danger of explosion by activation from an external source is improbable because of the thin film of molten explosive.

The physical form of the product can be regulated by adjusting the roll clearance and varying the speed of the rolls.

The melting time and the melting temperature can be varied by regulating the roll speed, the feed rate, and the roll temperature.

The apparatus illustrated in FIGURE 3 includes a pair of rolls 10 and 12 supported in a frame mechanism 14. The rolls have shafts 16 and 18 rotatably secured in the frame 14. The shaft 16 includes coupling means 20 which is connected to a source of steam 22 and the shaft 18 includes coupling means 24 connected to a source of cooling medium 26 such as water or the like. Means 28 are provided on the frame 14 to vary the gap between the rolls 10 and 12. The rolls 10 and 12 are connected to a driving mechanism generally designated by the numeral 30 to rotate the rolls in opposite directions to each other. A third roll 32 is positioned adjacent to the first roll 10 and may be called an idler roll. Suitable heating means 34 is provided for roll 32. The roll 32 rotates in a direction opposite to or the same as that of roll 10. A feed hopper 36 is positioned above the roll 10 and has a lower distributing slot 38 adjacent its lower portion. A distributing means 40, such as a vaned distributing paddle, is positioned in the lower portion of hopper 36 so that the material is discharged evenly through the slot 38. A doctor blade 42 is positioned adjacent the lower roll 12 and is arranged to remove the flaked material therefrom and discharge the same into a receiver 44. The top roll 10, which will hereinafter be called the melting roll, is steam heated to a pressure of between 80 and 85 pounds per square inch and has a surface temperature of between 156 and 163° C. (313 to 325° F.). The diameter of the upper roll 10 is about 16 inches and the roll rotates normally at about 4 r.p.m. The surface speed of the melt roll is, therefore, about 16.5 feet per minute. The temperature of lower roll 12, which will hereinafter be called the flaker roll, can range between 4 and 45° C. The flaker roll 12 rotates preferably at a speed about five times that of the melt roll 10 and has a surface speed of about 90 feet per minute. Increasing the speed of the flaker roll 12 results in a thinner flake type product and consequently in a more rapid chilling rate. The idler roll 32 serves as a means to smooth and spread out the material fed to the hot roll from the hopper 36 through the slotted feed aperture 38 and also serves in certain instances as a hold-up means to provide preheat for the feed material to hasten the melting process.

It should be understood that the previously described apparatus illustrated in FIGURE 3 is suitable for preparing my explosive in a continuous manner and may be modified appreciably without departing from the scope of this invention.

The process for preparing my explosive will be described in conjunction with the use of my preferred primary fuel, hexamethylenetetramine. Ammonium nitrate in commercial prill form and hexamethylenetetramine are mixed in the following proportions:

	Parts by Weight
Ammonium nitrate	91.2
Hexamethylenetetramine	8.5
Soap	0.3

The material is charged into a blender (not shown) and blended until an intimate mixture is obtained. The blended material is then transferred to a pulverizer (not shown) where the material is subjected to a comminution process to facilitate the melting of the various components on the melt roll. The material is then transferred from the pulverizer to the hopper 36 and discharged from the hopper 36 in an elongated stream through slotted aperture 38. The hot roll 10 is at a temperature preferably between 156 and 163° C. and the flaker roll 12 is at a temperature between 4 and 45° C., the rolls rotating in the opposite directions at the previously described speeds. The rolls 10 and 12 are set at a clearance of between 4 and 25 mils to obtain a thin flake product. The blended components are discharged through slot 38 from hopper 36 onto the hot melting roll 10 at a predetermined rate. The material is distributed across the roll in an even film by idler roll 32 and as the hot roll 10 rotates the solid components change state and from a homogenous melt. As the

melted material on the hot roll contacts the flaker roll 12, the melt material is transferred to the flaker roll where it solidifies or freezes in a short period of time. The congealed material is carried on the flaker roll 12 around to the doctor blade 42 where it is removed therefrom and discharged into the product receiver 44.

Depending upon the ultimate use of the melt material, the product may be either packaged directly from the receiver 44 or may be introduced into a comminuting means where the flakes are reduced in size. A hammer mill has been successfully employed to reduce the particle size of the flaked product.

It has been found that the addition of the 0.3 part by weight of soap to the formulation minimizes the adherence of the product to the flaker roll and has no adverse effects on the explosive properties.

Another formulation that has been prepared on the apparatus illustrated in FIGURE 3 had the following component proportions:

	Parts by Weight
Ammonium nitrate	90.4
Hexamethylenetetramine	8.3
Soap	0.3
Dextrose	1.0

A melt explosive was prepared with the above material in substantially the same manner as above described on the apparatus illustrated in FIGURE 3.

I have also discovered it is possible to obtain a heterogeneous explosive with the highly desirable properties previously discussed by melting only a portion of the components on the apparatus previously described and subsequently intimately mixing the product with additional ammonium nitrate to provide an oxygen balanced explosive. For example, a typical formulation prepared on the apparatus illustrated in FIGURE 3 is as follows:

	Parts by weight
Ammonium nitrate	80.0
Hexamethylenetetramine	20.0
Soap	0.3
Dextrose (optional)	1.0

This material was blended and fed to the melt roll 10 in a similar manner as previously described and melted on the melt roll 10 at substantially the same melt temperature for substantially the same time and solidified on the flaker roll 12. The product solidifies well and is easily prepared. The product is then blended with ammonium nitrate (135 parts by weight) to 100 parts by weight of the formulation to obtain an oxygen balanced explosive. The mixture is blended in blending apparatus and subjected to comminution in a pulverizer such as a hammer mill or the like. The advantage of this latter method of preparing my explosive is that the amount of material subjected to the melt process is reduced substantially without adversely affecting the desirable explosive properties of the resultant mixture. It is, therefore, now possible, as long as a fine scale of mixing is obtained by at least part of the oxidizer (ammonium nitrate) and the fuel (hexamethylenetetramine), to obtain a heterogeneous cartridge type explosive by mechanically admixing a portion of the oxidizer with the melt product of fuel and oxidizer.

It is believed that the preparation of my explosive by means of the process heretofore described is instrumental in preparing a heterogeneous explosive having the previously described highly desirable explosive properties. If the components, that is the hexamethylenetetramine and ammonium nitrate, are mechanically blended and comminuted without melting the components, an inferior explosive is obtained that is not detonatable by a No. 6 blasting cap in a 1.25 inch diameter cartridge. If the components are heated to an elevated temperature and retained in a molten state for a substantial period of time, a chemical reaction occurs resulting in a resinous substance that does not readily crystallize. It is believed that the rapid heat-

ing and rapid cooling of the components as is experienced on the apparatus illustrated in FIGURE 3 minimizes this chemical reaction and yet provides the fine scale of mixing which is believed to be highly desirable in heterogeneous explosives.

X-ray diffraction tests were performed on the product made by my process on the apparatus illustrated in FIGURE 3 and similar X-ray diffraction tests were made on material which was maintained in a melted state for a substantial period of time. It was discovered that a prominent X-ray diffraction pattern peak was obtained at about 4.45 A. with the explosive material prepared on the apparatus previously described. This peak is not associated either with hexamethylenetetramine or ammonium nitrate. In the material that was permitted to remain in a molten state for a substantial period of time, the peak is not present and a new prominent peak is present at 3.14 A. The presence of the 4.45 A. peak in the material made according to my process indicates that an adduct of ammonium nitrate and hexamethylenetetramine is present in the product. The absence of the 4.45 A. peak and the presence of the 3.14 A. peak in the material that remained in a molten state for a substantial period of time clearly indicates that a different type of chemical reaction is occurring while the ammonium nitrate and hexamethylene tetramine are in a molten state. By the use of my process wherein the material is rapidly heated and rapidly chilled, the chemical reaction is arrested at the desirable adduct stage; whereas if the material was permitted to remain in a molten state for a substantial period of time, the reaction continues to a point where other new compounds are formed and the desirable physical properties are lost.

The following table clearly illustrates the superior explosive properties of the heterogeneous explosive prepared according to the process previously described as compared with material that is mixed mechanically. All of the material appearing in the following table is comminuted so that it has substantially the same size and the following screen analysis:

On 100 mesh 8% by weight
On 200 mesh 36% by weight
Through 200 mesh 56% by weight

The components of the explosive included 8.9 percent by weight hexamethylenetetramine and 91.1 percent by weight ammonium nitrate. The density of the explosive was about 0.95. The explosive which was mixed mechanically in a blender and comminuted in a pulverizer will be termed "mechanical mixture"; the explosive prepared on the apparatus illustrated in FIGURE 3 will be termed "machine product"; the explosive wherein 80 parts by weight ammonium nitrate and 20 parts by weight hexamethylenetetramine were subjected to the melting process on the apparatus illustrated in FIGURE 3 and subsequently mechanically mixed with additional ammonium nitrate to provide an oxygen balanced explosive will be termed "fuel rich melt product."

	Charge diameter, inch	Primer Type	Detonation velocity, ft./sec.
Mechanical mixture	1.25	No. 6 blasting cap...	Failed
	1.25	0.5" x 0.5" tetryl pellet.	12,200
Machine Product	.34	No. 6 blasting cap...	7,000
	.50do.....	9,500
	.75do.....	11,000
	1.0do.....	12,500
	1.25do.....	12,700
	1.50do.....	12,800
Fuel rich melt	0.75do.....	8,500
	1.0do.....	10,300
	1.25do.....	13,700
	1.25	No. 8 blasting cap...	12,700

The above table clearly illustrates the high degree of sensitivity of the heterogeneous explosive prepared according to the process of this invention and its superiority

over the mechanical mixture of the components. Under similar conditions, 60 percent dynamite having a density of 1.20 and a charge diameter of 1.25 inch had a detonation velocity of 11,100 ft./sec.

An additional test devised for measuring sensitivity is the gap test. This test indicates the distance the explosion will propagate through an open air gap. To perform this test, the cartridge was cut radially into two halves and the halves were separated from each other a predetermined distance (the gap) with the cut ends facing each other. One half of the cartridge was initiated with a blasting cap and an observation was made to determine whether the detonation propagated across the gap and set off the other half of the cartridge. In this manner a critical gap separation is determined. It was found that the mechanical mixture had a critical gap of about 1.5 inches, the fuel rich melt product of the table above had a gap of about 4 inches, and the machine product of the above table had a gap of 5 inches. In the above example the mechanical mixture had to be detonated by a 0.5 inch x 0.5 inch tetryl pellet. It is believed that a minimum gap of between 3 and 4 inches is required for a cartridge type explosive.

It should be understood that the preceding examples and the following examples are meant to be illustrative and not limiting. The following examples show the use of several different primary fuels, the addition of secondary fuels and the effect of different additives. Unless otherwise noted, the process for the preparation of the explosive products was the same as that given in detail in Example I.

Example I

Into an electrically heated stainless steel kettle were placed 900 g. ammonium nitrate (uncoated fertilizer prills about 99.8 percent pure ammonium nitrate), 90 g. hexamethylenetetramine and 10 g. abietic acid

(C₁₉H₂₉COOH)

the latter two components having been first briefly ground together in a mortar in order to disperse the abietic acid throughout the hexamethylenetetramine. 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 R.H.) 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

These data are plotted in FIGURE 1.

Example II

In the same manner as in Example I, explosive products were made up containing 90 percent ammonium nitrate and 10 percent urea; 80 percent ammonium nitrate and 20 percent urea; and 79 percent ammonium nitrate, 20 percent urea and 1 percent methylcellulose as a crystallization modifier. Samples of each of these three mixtures were loaded separately into 3/8-inch copper tubes three inches long, and detonated by a No. 6 electric blasting cap to determine the level of damage to the tube to be achieved. The tube containing the explosive consisting of 20 percent urea and 80 percent ammonium nitrate did not detonate and only the upper portion of the tube was damaged by the detonator cap. But when the 10 percent urea mixture was used the damaged portion of the tube extended almost to the bottom; the very bottom section which was filled by a cork, however, remained intact. When 1 percent methylcellulose was added to the 20 percent urea mixture, the tube was completely disintegrated and scattered in small fragments including the section filled by the cork at the bottom. These experiments illustrate on the one hand the importance of a crystallization modifier, in this case methylcellulose, and, on the other hand, the improvement to be gained in explosive strength by the use of an oxygen-balanced mixture (20 percent urea) compared to that from a fuel-deficient mixture (10 percent urea).

Example III

This example is designed to show the use of a secondary fuel which in itself is also capable of acting as a crystallization modifier.

A first explosive product was made up by the process of Example I containing 91 parts by weight ammonium nitrate and 9 parts by weight hexamethylenetetramine to give an oxygen balanced composition. The granules of this explosive contained ammonium nitrate crystals in both rhombic and needle forms and the average diameter of these crystals was 40 microns. The range of sizes was relatively large.

A second explosive product, also oxygen-balanced, was made by first melting 89.5 parts by weight of ammonium nitrate and 6.5 parts by weight of hexamethylenetetramine. After melting was complete, 4 parts by weight of dextrose was added and allowed to dissolve in the melt which was then chilled rapidly by sprinkling on a cold surface as described above. In the resulting granules of this second composition the ammonium nitrate crystals were all in rhombic form, very uniform in size and ranged from 20 to 30 microns.

The primer sensitivity of both of these products and the extent of densification possible was essentially of the same degree, showing that the finer crystal size of the second product compensated for the somewhat lower energy yield from the fuels present.

Example IV

Other additives may be added to improve moisture resistance or serve as a secondary fuel. The explosive composition of Example I was modified, first, to incorporate 2 percent by weight of a diatomaceous earth to improve moisture resistance; and, second, to incorporate 0.7 percent carbon black as a secondary fuel.

The samples thus prepared were packed into standard

dynamite cartridges of waxed kraft paper, 1.25 inches in diameter, and 9 to 12 inches long. They were fired lying on the ground with a No. 8 electric blasting cap and their detonation velocities were measured by the Dautriche method. The results were as follows:

Composition	Density	Detonation velocity, ft./sec.
Example I -----	1.01	11,750
Example I plus 2% diatomaceous earth -----	0.99	11,100
Example I plus 0.7% carbon black -----	0.99	11,250

Although these detonation velocities are somewhat below the theoretical value of about 15,500 ft./second, these data illustrate clearly that the explosives of this invention detonated at high velocity in relatively small diameters with virtually no confinement. These data also illustrate the fact that a small amount of unreactive additive (diatomaceous earth) may be added without detracting from the performance of the explosive.

In addition to these examples, the data in Table I may be cited to illustrate other variables. Thus Compositions No. 2 and No. 3 illustrate the use of a mixture of two primary fuels, namely, urea and dicyandiamide; while Composition No. 4 shows a combination of these two primary fuels with carbon as a second fuel.

HIGH DENSITY BLASTING AGENTS

I have discovered it is possible to utilize the heterogeneous explosive previously described as the principal component of high density blasting agents. For certain applications high density blasting agents are preferred to other classes of explosives. A high density blasting agent is advantageous in that it is possible to place more explosive per unit volume in the bore hole. The higher density blasting agents provide high detonation velocity and high detonation pressure and brisance and, because of the higher density the high density blasting agents offer better water resistance.

In all heterogeneous explosives there is a limitation on the upper density limit due to the diffusion limited reaction. The density must, therefore, be below what may be termed the critical failure density and should preferably be controlled to be in the neighborhood of the optimum density (see FIGURE 1). The density of the explosive prepared on the apparatus illustrated in FIGURE 3 is approximately 0.95 which is below the optimum density. It is, therefore, necessary to increase this density to this optimum density in order to obtain a high density blasting agent of about 1.2.

There are two general means to limit the density in melt explosives so that they are below the critical density and approach the optimum density. These methods have led to two general types of products—rigid blasting agents, and wet blasting agents.

RIGID BLASTING AGENTS

The methods employed include sintering and the use of bulking agents. The sintered, or rigid blasting agent, may be prepared by the following method. The apparatus illustrated in FIGURE 3 is employed and the melt explosive, that is, the explosive previously prepared on the apparatus illustrated in FIGURE 3, is again inserted in the feed hopper 36 and fed to the hot roll 10. The steam pressure of the hot roll 10 is kept between 40 and 50 pounds per square inch. A scraper chute is used to take the partly melted material off the hot roll 10 and convey it to a heated kettle which is maintained at about 90° C. The material is removed from the kettle and placed in a cartridge and lightly tamped in place. By varying the rate of feed of the melt explosive to the hot melt roll 10, the speed of the melt roll 10 and the temperature of the receiving kettle, it is possible to control the density of the cartridge from between about 1.2 gm./

cc. to about 1.4 gm./cc. Material prepared in the above manner had the following detonation velocities at differing densities.

DETONATION VELOCITY OF RIGID BLASTING AGENT

Density (g./cm. ³)	Cartridge dimensions (inches)	Detonation velocity (ft./sec.)
	<i>Steel</i>	
1.23	4.0 diam x 36 long x 0.5 wall	20,000
1.23	4.0 diam x 36 long x 0.5 wall	20,300
1.25	4.0 diam x 36 long x 0.5 wall	20,800
1.22	4.4 diam x 27 long x 0.4 wall	19,080
1.38	4.4 diam x 32 long x 0.4 wall	13,200

WET BLASTING AGENTS

Another manner of controlling density of the high density blasting agents is to add a very small, carefully controlled amount of water. The water tends to partially melt or dissolve the particles and thus increase the density. However, a better method was discovered which makes it possible to add much greater quantities of water and even to reach the point of water saturation, which is highly desirable for some purposes. This is by the addition of selected bulking agents. Suitable bulking agents are fuels such as wood pulp, or urea formaldehyde micro balloons. The micro balloons have a density of about .05 grams per cubic centimeter and the addition of about 1 percent by weight of the micro balloons added to the wet blasting agent reduces the density by about 0.07 grams per cubic centimeter. The micro balloons are of the order of between 20 and 40 microns in diameter and provide a multitude of tiny air pockets intimately distributed throughout the wet blasting agent. It is believed the micro balloons, in addition to serving as a bulking agent, also serve as heat centers in the shock wave and improve the properties of the explosive. Although only wood flour and micro balloons have been indicated as suitable bulking agents, other materials would also serve this purpose.

The melt explosive prepared from ammonium nitrate and hexamethylenetetramine was mixed directly with water until maximum density was obtained. To this wet blasting agent potassium dichromate was added as a catalyst. Okra gum was also added to make the paste thicker and more cohesive. This material had a density of 1.45 gm./cc. which is greater than optimum, and explosion would propagate only in a large diameter cartridge or

At this lower density the wet blasting agent propagated in a 2 inch cardboard tube. It will be appreciated that other density reducing materials can be added to the wet blasting agent to reduce its density below the critical density.

From the above it will be appreciated that water can be added to the melt explosives of this invention and the explosive will still propagate. The velocity of the wet blasting agent is improved by the addition of 0.5 percent potassium dichromate.

The following various formulations of wet blasting agents were prepared and tested. All percentages are intended to be understood as percent by weight. Wet blasting agent 1 had 67 percent by weight melt explosive (8.5 percent hexamethylenetetramine, 91.2 percent ammonium nitrate, 0.3 percent soap), 7.4 percent wood flour, 8.9 percent ammonium nitrate, 11.9 percent sodium nitrate, 0.3 percent okra gum, 0.2 percent potassium dichromate and 4.4 percent water. The melt explosive, wood flour, okra gum and part of the sodium nitrate were dry mixed, then mixed with a solution of ammonium nitrate, sodium nitrate, potassium dichromate, and water to obtain wet blasting agent 1 with the foregoing over-all composition.

Wet blasting agent 2 has the same composition as wet blasting agent 1 with the addition of 0.3 percent urea formaldehyde micro balloons, as mixed with the dry solids.

Wet blasting agent 3 has the same composition as wet blasting agent 1 except that 1.0 percent cellulose ether gum was substituted for 1.0 percent wood flour. The okra gum was not included.

Wet blasting agent 4 was composed of 64 percent melt explosive (8.5 percent hexamethylenetetramine, 91.2 percent ammonium nitrate, and 0.3 percent soap), 5 percent wood flour, 1 percent urea formaldehyde micro balloons, 0.3 percent okra gum, 14 percent ammonium nitrate, 7 percent sodium nitrate, and 9 percent water. The solids, melt explosive, wood flour, micro balloons, and okra gum, were dry blended. A solution containing 30 percent water, 46 percent ammonium nitrate, 23 percent sodium nitrate, and 1 percent potassium dichromate was added slowly to the blended solids and mixed therewith.

Wet blasting agent 5 was the same as wet blasting agent 4 except that 4 percent wood flour and 2 percent micro balloons were used.

The following table sets forth the velocity of the various wet blasting agent formulations.

TABLE II
UNSATURATED

Formula	Cartridge ¹ Mat.—D x L x W (in.)	Density (g./cm. ³)	Primer	Velocity (ft./sec.)
WBA-1	S—3 x 36 x 0.6	1.23	25 g. tetryl	18,400
	S—3 x 36 x 0.6	1.32	do	18,200
WBA-2	C—2 x 12	1.18	do	14,700
WBA-3	C—2 x 12	1.26	do	13,500

SATURATED

WBA-4	C—4 x 24	1.39	25 g. tetryl	13,500
	S—3 x 36 x 0.6	1.39	do	18,800
WBA-5	C—4 x 24	1.30	do	17,000
	S—3 x 36 x 0.6	1.32	do	19,800
WBA-5	C—2 x 12	1.15	do	15,600

¹ "Mat"=Material: "C" cardboard; "S" steel; "D" diameter; "L" length; "W" wall thickness.

under heavy confinement; and then the velocity was much less than the maximum value. Sodium bicarbonate was added to the wet blasting agent to generate gas and thereby create voids in the wet blasting agent and reduce its density. The density by employing sodium bicarbonate was lowered from the usual value of 1.45 to about 1.20.

In the previously recited formulations the heterogeneous explosive component of the high density blasting agent was prepared according to my process. It may be possible for these specific applications that a suitable heterogeneous explosive may be prepared by a process other than my process. For these specific high density

blasting agents I do not intend to be restricted to a specific method of preparing the heterogeneous explosive component of the high density blasting agent.

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.

I claim:

1. Process of forming a heterogeneous explosive which comprises heating a mixture of ammonium nitrate and hexamethylenetetramine to a temperature of between 150° C. and 165° C. to form a homogeneous molten mass, and thereafter rapidly cooling said molten mass to form primary crystals of ammonium nitrate and a crystalline matrix comprising an adduct of ammonium nitrate and hexamethylenetetramine, said primary ammonium nitrate crystals being dispersed in said crystalline matrix.

2. A process for making a heterogeneous explosive which comprises preparing a mixture of ammonium nitrate and hexamethylenetetramine, feeding said mixture onto a heated surface having a temperature between 150° C. and 165° C., maintaining said mixture on said heated surface for a sufficient time to form a homogeneous molten mass, thereafter transferring said mixture onto a second surface having a temperature below the temperature at which said molten mass solidifies, controlling the amount of said molten mass being transferred to said second surface so that said molten mass rapidly solidifies and forms primary crystals of ammonium nitrate having maximum dimensions not exceeding 100 microns and a crystalline matrix comprising an adduct of ammonium nitrate and hexamethylenetetramine, said primary crystals being enveloped by said crystalline matrix.

3. A process of forming a heterogeneous explosive consisting essentially of an oxidizer and a fuel which comprises preparing a mixture consisting essentially of about 91 parts by weight ammonium nitrate, about 8.7 parts by weight hexamethylenetetramine, and about 0.3 parts by weight soap, feeding said mixture onto a moving heated surface to provide rapid heat transfer from said heated surface to said mixture, said heated surface being at a temperature of between about 150° C. and 165° C., maintaining said mixture on said heated surface for a time sufficient to form a molten mass and to react said ammonium nitrate and hexamethylenetetramine to yield an adduct having a characteristic X-ray diffraction peak at 4.45 A., and thereafter rapidly solidifying said molten mass in a manner to stop the reaction of ammonium nitrate and hexamethylenetetramine at said adduct stage and to form primary crystals of ammonium nitrate having maximum dimensions not exceeding 100 microns, said primary crystals of ammonium nitrate being imbedded in a matrix comprising said ammonium nitrate-hexamethylenetetramine adduct.

4. A process of forming a heterogeneous explosive consisting essentially of an oxidizer and a fuel which comprises preparing a mixture consisting essentially of about 91 parts by weight ammonium nitrate, about 8.7 parts by weight hexamethylenetetramine, and about 0.3 parts by weight soap, feeding said mixture onto a moving heated surface at a rate sufficient to provide rapid heat transfer from said heated surface to said mixture, said heated surface being at a temperature of between about

150° C. and 165° C., maintaining said mixture on said heated surface for a time sufficient to react said ammonium nitrate and hexamethylenetetramine to form an adduct having a characteristic X-ray diffraction peak at 4.45 A. and for a time insufficient to react said ammonium nitrate and said hexamethylenetetramine to produce an X-ray diffraction peak at 3.14 A., transferring said molten mass from said moving heated surface to a second surface as a thin film, said second surface moving faster than said heated surface and having a temperature below 50° C., and rapidly solidifying said film on said second surface to form a thin sheet containing primary crystals of ammonium nitrate imbedded in a matrix comprising said adduct of ammonium nitrate and hexamethylenetetramine.

5. A process for making a rigid blasting agent which comprises preparing an intimate mixture of ammonium nitrate and hexamethylenetetramine having a density of about .95 gram per cubic centimeter, said mixture having a size which will pass through a 16 mesh Tyler Standard screen, heating the mixture in a manner to partially melt said mixture, and compressing said mixture while in said partially melted state to form a rigid blasting agent having a density of about 1.2 grams per cubic centimeter.

6. The process for making a rigid blasting agent which comprises heating a mixture of ammonium nitrate and hexamethylenetetramine to form a homogeneous molten mass, rapidly cooling said molten mass to form primary crystals of ammonium nitrate having a maximum dimension not exceeding 100 microns and a crystalline matrix comprising an adduct of ammonium nitrate and hexamethylenetetramine, said primary crystals of ammonium nitrate being dispersed in said crystalline matrix, granulating said resulting solidified explosive to the extent that substantially all of the resulting grains will pass through a 16 mesh Tyler Standard screen, said granulated solidified explosive having a density of about .95 gram per cubic centimeter, reheating said granulated solidified explosive to a temperature of about 90° C., to partially melt the same, and compressing said reheated granulated explosive while in said partially melted state to form a rigid blasting agent having a density of about 1.2 grams per cubic centimeter.

7. A high explosive capable of being detonated in relatively small diameter cartridges, comprising an intimate mixture of ammonium nitrate and hexamethylenetetramine, at least a portion of said ammonium nitrate in said mixture being present as crystals, the maximum dimensions of which do not exceed 100 microns, dispersed in a crystalline matrix comprising said hexamethylenetetramine.

8. A high explosive capable of being detonated in relatively small diameter cartridges, comprising an intimate mixture of ammonium nitrate and dicyandiamide, at least a portion of said ammonium nitrate in said mixture being present as crystals, the maximum dimensions of which do not exceed 100 microns, dispersed in a crystalline matrix comprising said dicyandiamide.

References Cited by the Examiner

UNITED STATES PATENTS

1,720,459	7/1929	Wyler	149—2
2,345,582	4/1944	Carey	149—46
2,548,693	4/1951	Whetstone	149—46
2,817,581	11/1957	Rinkenbach	149—46

REUBEN EPSTEIN, *Primary Examiner.*

CARL D. QUARFORTH, *Examiner.*