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PELLETED AMMONIUM NITRATE BLASTING EXPLOSIVES

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This invention has to do with blasting explosives and more particularly with ammonium nitrate explosives produced in novel pellet forms. This application is a continuation-in-part application of my copending application Serial No. 316,181, filed October 14, 1963, now abandoned.

Ammonium nitrate has been used as a component of commercial blasting explosives for many years, primarily because of its economy. In recent years, an ammonium nitrate-fuel oil mixture has been widely used in the blasting industry as a less expensive substitute for dynamite, particularly in large dry bore holes.

The nitrate-fuel oil mixtures are recognized to have several prominent shortcomings, including uncertainty of detonation, low rate of propagation, and erratic performance. The erratic performance is evidenced in the frequent partial detonation of the ammonium nitrate and in the formation of toxic explosive or decomposition gases. Various attempts have been made to overcome these serious shortcomings of ammonium nitrate explosives including the boosting of the charges by distribution of dynamite at spaced intervals within the explosive column. In spite of various attempts to improve nitrate explosives, ammonium nitrate-fuel oil mixtures are still rated by the blasting industry as a substitute explosive of low velocity and shattering power. Conventional ammonium nitrate-fuel oil explosives are also characterized by a low density of loading. I have found that explosives which permit increases in normal loading density produce improved blast results.

Ammonium nitrate explosives have not been adapted to underwater use; that is, for use in bore holes containing water, because of the high water solubility of the ammonium nitrate material. It will be appreciated that ammonium nitrate in its customary prilled form mixed with fuel oil and carbon introduced to a water-filled bore hole dissolves almost immediately in the upper portion of the water with the result that the water adjacent the bottom of the hole has a low concentration of the nitrate. Several methods have been proposed to permit the underwater use of ammonium nitrate explosives. One proposed method involves the use of a water slurry containing at least 5% water, ammonium nitrate, and a high explosive, with the explosive present in amounts up to 40 weight percent of the mixture. In practice, such mixtures have proven unsatisfactory, separating in the water-filled bore hole with the insoluble components settling to the bottom thereof and the ammonium nitrate dissolving principally in the upper portions of the bore hole, thus rendering the charge very difficult or impossible to detonate.

It is a primary object of this invention to provide an economical, underwater, nitrate explosive in dry form.

It is a further object of the invention to provide an improved technique for the preparation of an ammonium nitrate explosive column of relatively high loading density in a dry bore hole.

It is a still further object of the invention to provide an improved technique for the preparation of an ammonium nitrate explosive column in a water-containing bore hole with both the ammonium nitrate component and a water-insoluble high explosive component being distributed substantially uniformly throughout the bore hole.

It is another object of the invention to provide a high density, ammonium nitrate-containing pellet having a specific gravity generally in excess of about 1.4.

It is a still further object of the invention to provide a high density pellet comprising a compacted mixture of ammonium nitrate, a solid, water-insoluble, detonatable sensitizer or high explosive, and a hydrocarbon binder.

Another object of the invention is to provide a dry high density, ammonium nitrate-containing pellet having relatively slow water solubility.

Another object of my invention is to provide a pelletized explosive which will sink effectively in a water-filled bore hole, and without bridging in the hole.

It is a still further object to provide a mixture of pellets made up of pellets A comprising water soluble nitrate and pellets B made up of ammonium nitrate, a solid, water-insoluble detonatable sensitizer or high explosive, and a hydrocarbon binder.

It is another object of the invention to provide a nitrate explosive having higher sensitivities to initiation and propagation and significantly higher detonation velocity without increasing the sensitivity to mechanical impact and otherwise impairing safe handling characteristics.

These and other objects and advantages of the invention will become more apparent in light of the following description.

Underwater explosives desirably have the following properties which are found in the pellets of the present invention: (a) water compatibility under high fluid heads and long immersion periods; (b) high energy content; (c) high loading density; (d) high detonation velocity; (e) nontoxic detonation fumes; (f) near neutral oxygen balance; (g) high initiation response in small diameter bore holes; (h) ease of loading; and (i) economy.

In making the pellets or granules of the present invention, conventional pelleting machine may be employed. Such machine and its design are no part of my invention, although it is to be understood that such machine must be capable of exerting sufficient compacting pressure to provide a pellet or granule of the materials, size, and characteristics discussed hereinafter. Such a machine will compact the feed material by forcing the same through suitable dies to continuously extrude a multiplicity of hard columns of the compacted material, which may, for example, be about one-quarter inch in diameter, and which are cut off by suitable knives to provide pellets about one-quarter to three-eights of an inch in length. Also, as will be understood such pellets could be circular, octagonal, square or otherwise shaped in cross-section, depending upon the dies used, although it usually may be impractical to extrude the pellets having a square cross-section.

A preferred form of one type of the pellet of the invention is made by mixing powdered ammonium nitrate, a non-explosive combustible lubricating material, and an explosive. Such materials are thoroughly mixed together by any suitable means to form a mixture which is fed to a pelletizing machine, as discussed above, which forms the mixture into the desired pellets of the invention. Such pellets are extruded from the pelletizing machine under a high pressure of from 3,000 to 40,000 pounds per square inch, to produce a pellet having a relatively high specific gravity of about 1.4 or higher. The pellets should be quite dry, containing less than about 0.4% by weight of moisture. Also, to pack best in a bore hole, each of the pellets should have a length not more than 1.5 times of its diameter.

The said lubricating material of the invention may be any one of a plurality of materials usually a hydrocarbon material, such as, for example, paraffin oil, paraffin wax, or a lubricating oil. Such material should have a

lubricating quality, to facilitate the compaction and extrusion of the feed mixture in the pelletizing machine, as such mixture is quite dry and without such a lubricating material the extrusion through the dies of the machine would require excessive pressures to attain the relatively high specific gravity desired and the high coefficient of friction would increase the die temperature above a safe level. Also, such lubricating material is insoluble in water and renders the mixture and resulting pellets water resistant, to delay solution of the ammonium nitrate thereof into water, which is highly desirable for reasons discussed hereinafter. Also, such lubricating material is combustible, but nonexplosive, which is oxidizable and is sometimes desirable to provide a means for reacting excess oxygen, as pointed out hereinafter.

The explosive of my mixture, sometimes referred to as a detonatable sensitizer, may be selected from a variety of suitable materials including the various nitroaromatics, cyclotrimethylenetrinitramine, cyclotetramethylenetranitramine, nitrocellulose, and nitrostarch. The nitroaromatics include the nitrobenzenes, particularly 1,3-dinitrobenzene and 1,3,5-trinitrobenzene, trinitrotoluene, and, particularly, 2,4,6-trinitrotoluene, and trinitroxylene. In addition, other explosives may be used such as mono or dinitrotoluene, nitrated benzene, or napthalene, having a smaller number of nitro groups or a small degree of nitration. Such materials may be used singly or in combination, although I have found that trinitrotoluene is generally satisfactory for use in the invention. Generally speaking, the explosive, or mixture thereof, employed in making my pellets should have a relatively low sensitivity to impact and friction, to provide safety in handling the mixture before and during pelleting and cutting and handling the finished pellets. Furthermore, the explosive used should preferably have a reasonably low degree of sensitivity to initiation by open flame, to further reduce the hazard of accidental exposure thereto. Also, such explosives have a low water solubility, which is desirable for the reasons pointed out hereinafter. The explosive must be sufficiently powerful to detonate or initiate the explosion of the ammonium nitrate, the latter alone being normally non-explosive.

A typical pellet of the invention has a specific gravity of about 1.4 or greater, is circular in cross-section, is about one-quarter to three-eight inch long and one-quarter inch in diameter, and has a composition which includes a mixture of ingredients in the following range:

	Percent by weight
Ammonium nitrate	38 to 73
Detonatable sensitizer	25 to 60
Hydrocarbon binder, e.g., paraffin wax	1 to 3.5

The foregoing pellet of my invention hereinafter sometimes referred to as pellet A is primarily designed for use in a wet bore hole, such as an oil well containing water or a mixture of water, mud, and other materials, as is commonly found in the oil industry. As will appear hereinafter, my pellets may also be used advantageously in dry bore holes. Also, of course, my pellets may be employed as an explosive charge in other unrelated applications. When used in a bore hole, at least one high explosive booster-primer may be first disposed in the hole, as is well known in the art. My pellets are then poured or dropped into the bore hole around the booster and the bore hole is filled therewith to the desired depth.

The hydrocarbon binder content is desirably less than 3.5%. It has been found unexpectedly that an increase of hydrocarbon binder much above 3.5% will objectionally desensitize the pellet. It is highly desirable that the amount of explosive employed in the pellet be within the range of 25 to 60% for the reason lower content may cause detonation failure. Higher content may produce secondary explosion of excess carbon on the surface such as observed with oxygen coefficient explosives.

It has now been determined by numerous tests that the explosive properties of pellet A can be substantially improved if these pellets are used in combination with pellets or granules of substantially pure ammonium nitrate or a high percent of ammonium nitrate. Hereinafter the ammonium nitrate pellets will sometimes be referred to as "pellets B." Pellets B desirably contain at least 2% of sodium nitrate or potassium nitrate to stabilize the ammonium nitrate and prevent phase changes which sometimes occur in pure ammonium nitrate pellets. There is a tendency in the absence of potassium or sodium nitrate for pellet B to disintegrate in a dry state. Ammonium nitrate and potassium nitrate may be used in amounts up to 30% of the weight of the pellet where it is economically desirable to do so.

In a series of tests, steel pipes of various diameters and 10 feet long with bottom plugs were placed vertically in the ground and filled with water. Explosives, in some instances made up solely of pellets A and in other instances of mixtures of pellets A and B, were poured into the pipes until full. An initiating primer charge was then placed on top of the explosive column and detonated with a blasting cap after a period of time adequate to permit substantial dissolution of the ammonium nitrate into the water in the hole. Velocities of detonation of the several explosives were recorded.

Example I

Explosive A of the tables below was made up of pellets A composed of 30% trinitrotoluene, 2% paraffin wax, and 68% ammonium nitrate. Pellets were formed under high pressure into cylinders of ¼ inch diameter and ¼ inch length having a density of 1.4.

Explosive B of Tables I and II was made up of a blend or mixture of pellets A having the composition of the explosive A and an equal amount by weight of ammonium nitrate pellets B. The ammonium nitrate pellets B were of dimensions of approximately ¼ inch diameter and ¼ inch length and possessed a density of 1.4.

Explosive C was made up of 70% by weight of pellets A and 30% by weight of ammonium nitrate pellets B used in the mixture of explosive B.

TABLE I

Explosive	TNT Content, Percent	Pipe Dia., Inch	Detonation Velocity Meters/Sec.
A	30	3	0
B	15	3	3,800
C	21	3	4,000

TABLE II

Explosive	TNT Content, Percent	Pipe Dia., Inch	Detonation Velocity Meters/Sec.
A	30	4	3,500
B	15	4	4,100
C	21	4	4,200

An examination of Table I will disclose that the sensitivity and the velocity of detonation in the instance of 3-inch pipe were unexpectedly improved when the trinitrotoluene content was reduced from 30 to 15%. It will be recalled that explosive A which has the TNT content of 30% was made up wholly of pellets A. Explosive B comprised a mixture of pellets A and ammonium nitrate pellets B.

Example II

In this example an explosive D made up of pellets A having a composition of 50% trinitrotoluene, 2% paraffin wax, and 48% ammonium nitrate were prepared under high pressure to have configurations not exceeding ¼ inch diameter, about ¼ inch length, and a density of 1.4.

Explosive E was made up of a mixture of pellets A of

the composition described in explosive D above and ammonium nitrate pellets B having a small percentage of potassium nitrate. Pellets A were present in explosive E in the amount of 62% by weight with the balance being ammonium nitrate pellets B. Pellets B had approximately the same configuration and density as pellets A and contained a smal amount of potassium nitrate.

Explosive F was a mixture of pellets A and B having the composition of the pellets of explosive E but differing in that pellets A were present in the amount of 40% by weight of the total mixture with the ammonium nitrate pellets B making up 60% by weight. Explosives D, E, and F were placed in a water filled hole of the description above and detonated in the fashion previously described. The velocities of detonation of the several explosives were recorded and are reported below in Table III and Table IV. Again, it will be seen that reduction of trinitrotoluene content in the instance of the small diameter pipe test improved the initiation response.

TABLE III

Explosive	TNT Content, Percent	Pipe Dia., Inch	Detonation Velocity Meters/Sec.
D	50	1½	0
E	31	1½	4,500
F	20	1½	3,800

TABLE IV

Explosive	TNT Content, Percent	Pipe Dia., Inch	Detonation Velocity Meters/Sec.
D	50	4	3,800
E	31	4	5,700
F	20	4	4,500

Desirably the size of the pellets A and pellets B is within the range of ⅛ to ¼ inch diameter and the pellets have a maximum length of 1.5 times the diameter. Smaller sized pellets are slow in settling while larger pellets will not pack to a high enough density; i.e., the void space is excessive. In the instance where a blend of pellets A and B is employed, it has been found that the trinitrotoluene or other detonatable sensitizer content, based on the total weight of the pellets A and B, should be in an amount of at least 15% and not above about 35%.

As shown on Tables I, II, III, and IV, the single pellet explosive will not detonate and propagate in small diameter holes even with a high trinitrotoluene content. Even if this charge is overboosted with a very large primer of several pounds, the detonation wave decays after a two diameter distance from the priming charge. Also, as shown in the foregoing tables, the single pellet explosive does not exhibit the same order of detonation velocities as the blended pellets, in the larger diameter holes where detonation is maintained. The blend of pellets, when poured in a water-filled hole will settle at a uniform rate, particularly if both types of pellets are approximately the same size and weight. As the pellets come to rest at the bottom, the ammonium nitrate pellets begin to dissolve, the saturated nitrate solution filling all the spaces between the remaining pellets containing the explosive sensitizer. It must be assumed that the vast improvement in the detonation properties of the blended pellets under water is attributable to the fact that the ammonium nitrate solution between remaining pellets takes part in the reaction thus releasing considerable energy and improving detonation wave propagation.

If the bore hole contains water, the pellets, due to their relatively high specific gravity, readily sink through the liquid. Due to the water resistance of the wax or other lubricating material and the explosive in the pellets A, the ammonium nitrate in the pellets dissolves in the water of the bore hole but slowly and fairly uniformly throughout the water in the hole. Neither the lubricating material nor the explosive of the pellets dissolves, and the pellets retain a skeletonlike structure throughout the liquid in the bore hole. Since part or all of the ammonium nitrate of the pellets dissolves substantially uniformly throughout the column of liquid in the bore hole and since the other materials form a column therein, there is a substantially uniform loading of the materials throughout the length of the liquid column in the hole, resulting in an explosive column of high and relatively uniform loading density, which is highly desirable to provide an increase in bore hole pressure and shattering power upon detonation. Even after the dissolution of the ammonium nitrate, the remaining skeleton structure of the pellets retains sufficient compressive strength to resist collapse under the weight of the overlying column thereof. The high explosive component of the pellets, therefore, remains susbtantialy evenly distributed in the column and is in effective condition to be initiated by the fuse and boosters and to propagate detonation waves throughout the entire column, which is very desirable. Under the influence of such high pressure detonation waves, the ammonium nitrate, both that dissolved in the bore hole water and any remaining solid ammonium nitrate, enters into the chemical reaction through explosive decomposition to enhance detonation propagation throughout the bore hole.

When the pellets contain a relatively high percentage of ammonium nitrate and relatively low percentage of explosive, the reaction of the ammonium nitrate upon such detonation may release excess free oxygen which are not reacted with the explosive and which form toxic oxygen compounds. Such free oxygen compounds may be highly toxic to human beings, and their release into the air above a bore hole is very undesirable. However, by using a lubricating material which is non-explosive but combustible or oxidizable, it permits a substantial part, if not all, of any such excess oxygen to be reacted therewith, to reduce or eliminate the formation of such toxic oxygen compounds, and this is an object of the invention. Of course, the lubricating material alone may provide such secondary function, or a separate combustible or oxidizable, but nonexplosive, insoluble material may be used therefore in the pellet material mixture, such as, for example, carbon powder, or wheat flour.

The pellets of this invention may be detonated after water immersion for about one-half hour and for a period of at least several hours after immersion. As will be understood, the high specific gravity of the pellets is desirable both to provide rapid sinking of the pellets through water in a bore hole and also to increase the loading density of the explosive column in the bore hole.

The pellets of this invention may also be used advantageously in a dry bore hole, by feeding a mixture of pellets A and B or pellets A alone and powdered or prilled ammonium nitrate into a bore hole around a conventional detonating fuse having spaced boosters thereon, the powdered or prilled ammonium nitrate filling the voids between the pellets. Using powdered or prilled ammonium nitrate powder alone would provide a loading density of only about 0.7 gram per cc., whereas by using a mixture of my high density pellets and such powdered or prilled ammonium nitrate the loading density may be raised to about one gram per cc., which provides a substantial improvement in explosive effect. Under suitable initiation with an adequate booster, such as 100 grams of high explosive detonated by a suitable fuse, the powder constituent of the mixture is initiated and propagates throughout the explosive column, and, in so doing, generates sufficient heat and pressure to initiate the detonation of the high density pellets.

Although exemplary embodiments of the invention have been described herein, various changes and modifications will be apparent to those skilled in the art, and I do

not intened to be limited to the particular examples described but desire to be afforded the full scope of the following claims.

I claim:

1. A free-flowing explodable product immediately accessible and pregnable by water, comprising a plurality of loose, explodable pellets free of containment by a water-tight container, said pellets each having a dry specific gravity of at least 1.4 and each being a compacted mixture of a combustible hydrocarbon lubricating material, nitrated organic detonatable sensitizer, having low water solubility being selected from the group consisting of nitro-aromatics, cyclotrimethylenetrinitramine, cyclotetramethylenetrinitramine, and nitrocelluluose, and ammonium nitrate in the proportions by weight of the mixture of ammonium nitrate, about 38% to 73%; said detonatable sensitizer, about 25% to 60%; and combustible hydrocarbon lubricating material, about 1% to 3.5%.

2. An explodable pellet in accordance with claim 1 wherein each pellet has a length not exceeding about 1.5 times its shortest cross-sectional dimension.

3. An explosive comprising: pellets A and pellets B, said pellets A being a compacted mixture of a combustible hydrocarbon lubricating material, nitrated organic detonatable sensitizer having low water solubility, and ammonium nitrate, in the proportions by weight of the mixture of ammonium nitrate, about 38% to 73%; and said detonatable sensitizer, about 25% to 60%; and combustible hydrocarbon lubricating material, about 1% to 3.5%; and pellets B comprising a compacted mixture of water soluble nitrates comprising predominant ammonium nitrate; said pellets A and B each having a dry specific gravity of at least 1.4; and said pellets B being present in the explosive in a ratio of pellets B to pellets A sufficient to substantially fill any spaces between pellets A, not already filled with said water soluble nitrates, with said water soluble nitrates.

4. An explosive in accordance with claim 3 wherein the percentage by weight composition of the nitrated organic detonatable sensitizer having low water solubility based on the combined weights of pellets A and B is within the range of 15% to about 35%.

5. An explosive in accordance with claim 3 wherein pellets B contain a predominant amount of ammonium nitrate.

6. An explosive in accordance with claim 5 wherein pellets B contain a small amount of a nitrate selected from the group consisting of sodium nitrate and potassium nitrate.

7. An explosive column dispersed in a water-containing bore hole, said explosive column comprising:

a pile of explosive pellets submerged in the water of said bore hole comprising initially a compacted mixture of ammonium nitrate, a combustible hydrocarbon lubricating material, and a nitrated organic detonatable sensitizer having low water solubility, said pellets having a dry specific gravity of at least 1.4 and containing in proportions by weight about 38% to 73% of ammonium nitrate, about 25% to 60% of the detonatable sensitizer, and about 1% to 3.5% of the combustible lubricating material, said ammonium nitrate being at least partially dissolved in the water of the bore hole with skeleton structures of said pellets being maintained by the lubricating material and the detontable sensitizer.

8. An explosive column dispersed in a water-containing hole, said explosive column comprising:

a pile of explosive pellets submerged in the water of said hole and comprising initially a mixture of pellets A and pellets B, said pellets A and B each having a dry specific gravity of at least 1.4, said pellets A being a compacted mixture of a combustible hydrocarbon lubricating material, nitrated organic detonatable sensitizer having low water solubility, and ammonium nitrate, in proportions by weight of the mixture of ammonium nitrate about 38% to 73%, said detonatable sensitizer, about 25% to 60%, and combustible hydrocarbon lubricating material about 1% to 3.5%, and said pellets B comprising compacted water soluble nitrates comprising predominantly ammonium nitrate, said ammonium nitrate of pellets A and B being at least partially dissolved in the water of the bore hole with the skeleton structures of said pellets A being maintained by the lubricating material and the detonatable sensitizer, and said pellets B being present in the initial mixture of pellets A and pellets B in a ratio of pellets B to pellets A sufficient to release, when pellets B are at least partially dissolved in the water of the bore hole, a quantity of said water soluble nitrates sufficient to substantially fill any water spaces between pellets A not already filled with said water soluble nitrates.

9. An explosive column in accordance with claim 8 wherein the percentage composition of the detonatable sensitizer based on the total weight of the pellets A and B is in the range of 15% to about 35%.

10. An explosive column disposed in a dry bore hole, said column comprising: a pile of explosive pellets A and B, said pellets A being compacted mixtures of hydrocarbon lubricating material nitrated organic detonatable sensitizer having low water solubility, and ammonium nitrate in the proportions by weight of the mixture of ammonium nitrate about 38% to 73%, said detonatable sensitizer about 25% to 60%, and combustible hydrocarbon lubricating material about 1% to 3.5%; and pellets B comprising a compacted mixture of water soluble nitrates comprising predominantly ammonium nitrate, said pellets A and pellets B each having a density of at least about 1.4; said pellets B being present in the pile of explosive pellets A and B in a ratio of pellets B to pellets A sufficient to substantially fill any voids between pellets A.

11. An explosive column in accordance with claim 9 wherein the voids between the several pellets are filled with ammonium nitrate powder.

12. An explosive column in accordance with claim 9 wherein the percentage composition of the detonatable sensitizer based on the overall weight of the two types of pellets is within the range of about 15% to 35%.

13. An explosive comprising:

in the proportions by weight about 40% to 60% pellets A having a dry specific gravity of at least 1.4 and about 30% to 70% pellets B having a dry specific gravity of at least 1.4; said pellets A being a compacted mixture of a combustible hydrocarbon lubricating material, a nitrated organic detonatable sensitizer having low water solubility, and ammonium nitrate, in the proportions by weight of the mixture of ammonium nitrate, about 38% to 73%; said detonatable sensitizer, about 25% to 60%; and combustible hydrocarbon lubricating material, about 1% to 3.5%; and pellets B comprising a compacted mixture of water soluble nitrates predominantly comprising ammonium nitrate.

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BENJAMIN R. PADGETT, *Primary Examiner.*