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LOW DENSITY, NITRATE-BASED EXPLOSIVE COMPOSITIONS

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This application is a continuation-in-part of our copending application Serial No. 281,752, filed May 20, 1963, now abandoned.

This invention relates to nitrate-based explosive compositions having unusually high explosive power and controlled low densities.

The explosives art has recently become more and more interested in explosive compositions comprised of an inorganic nitrate mixed with a carbonaceous fuel. These compositions, known in the art by the coined term "nitrocarbonitrates," are relatively insensitive, thus safe to handle, have moderate detonation rates and are considered by the trade as being well suited as economical blasting explosives in mining, quarrying and like operations. Consistent with a logical viewpoint, the art has considered it highly desirable to formulate such nitrocarbonitrates in high densities and with complete oxygen balance, the idea being that the higher the density of an oxygen-balanced composition, the greater will be the weight of the composition that can be loaded in the same borehole to achieve greater explosive power on complete detonation, as is theoretically ensured by oxygen balance. Thus, the usual range of densities in which nitrocarbonitrates are available commercially is from about 0.9 to about 1.15 g./cc.

It has now been discovered, completely contrary to all expectations, that the explosive power of nitrocarbonitrate compositions can be increased very substantially if the density of the compositions is reduced considerably even though the compositions may thereby become deficient in the amount of oxygen required for complete oxygen balance. Thus, while the explosive compositions of the invention have a maximum packing density of about 0.6 g./cc. and a maximum pouring density of about 0.5 g./cc., and are usually oxygen deficient, the explosive power of such compositions approaches and at times even surpasses twice that of the conventional high density, oxygen-balanced counterparts. This remarkable phenomenon goes directly contrary to the above-mentioned theoretical considerations and no cause-and-effect relationship, aside from low density, has yet been identified which might explain the reasons for it. However, the above-noted increased explosive power has been repeatedly and consistently achieved, in both the laboratory and under field conditions, with explosive compositions of properly controlled low density, notwithstanding a negative oxygen balance.

Generally speaking, the explosive compositions of the invention contain as essential ingredients an inorganic nitrate in major amount and a solid carbonaceous fuel, the actual ingredients and proportions thereof being selected to give a composition having a packing density of not more than about 0.6 g./cc. and a pouring density of not more than about 0.5 g./cc.

As the inorganic nitrate, ammonium nitrate alone or in admixture with an alkali metal nitrate can be used. Use of ammonium nitrate alone will result in a final composition having a relatively smaller oxygen content, all other

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things being equal, since the alkali metal nitrates are relatively richer in oxygen and will supply a greater proportion thereof if included in the composition. However, since oxygen balance is not required, the presence of ammonium nitrate and no other nitrate in the explosive composition is not objectionable and in fact is actually preferred in many cases since the explosive composition will have better sensitivity to detonation as the proportion of ammonium nitrate increases. At the same time, the ammonium nitrate may be admixed in any desired proportion with one or more alkali metal nitrates for use in the explosive compositions of the invention.

As previously mentioned, the inorganic nitrate constitutes the major ingredient of the explosive compositions of the invention. Thus, at least 50% of the weight of the total composition will consist of ammonium nitrate alone or a mixture of ammonium and alkali metal nitrates. The particle sizes of the ammonium and alkali metal nitrates should be such that substantially 100% thereof passes a U.S. Standard No. 18 screen and at least 50% thereof passes a U.S. Standard No. 60 screen. It has been found that, with such particle sizes, the initial low pouring density of compositions made according to the invention remains substantially the same, or at least does not increase substantially, over storage of the compositions even at temperatures which include the ammonium nitrate IV-III solid state transition point. This stability of the pouring density is important since as previously noted control of the pouring density at selected low values not exceeding 0.50 g./cc. is critical and necessary for achieving the benefits of the invention, and the fact that such benefits are retained on a long-term basis with the above-noted particle sizes enhances the practical and commercial value of the invention. Specific examples of ammonium nitrate samples which are within the above particle size limits and which have given excellent results in compositions made according to the invention are given in the following screen analyses:

Screen Size	No. 1	No. 2	No. 3
+18	0.5	Trace	Trace
-18+35	14.0	1.0	Trace
-35+60	34.5	13.0	12.0
-60+80	12.0	34.0	4.0
-80+120	11.5	35.0	37.0
-120+230	12.5	11.0	48.0
-230	15.0	6.0	10.0

On the other hand, ammonium nitrates with the screen analyses noted immediately below are susceptible to breakdown and densification when subjected to temperatures which include the ammonium nitrate IV-III transition point and have given rather poor results with respect to sensitivity to detonation and propagation in the finished explosive composition.

Screen Size	No. 5	No. 6
+18	31.5	16.0
-18+35	45.0	35.0
-35+60	15.0	37.0
-60+120	6.5	9.0
-120	2.0	3.0

It will be understood from the foregoing that coarser grades of nitrate are distinctly undesirable in the practice of this invention. However, larger sized nitrate particles

can be crushed in conventional manner to form useful smaller particles sizes within the limits given above.

A solid carbonaceous fuel is admixed as an essential ingredient with the inorganic nitrate particles to form the explosive compositions of the invention. Selection of a specific carbonaceous fuel is governed by the low density requirement of the final composition which also requires taking into account the density of the inorganic nitrate particles that are to be used. Generally speaking, low density materials such as bagasse, or shredded corn stalks, or shredded synthetic plastics may be employed as the solid carbonaceous fuel. Of these, bagasse, which is a commercially available form of shredded sugar cane stalks, has given excellent results and is preferred. One suitable commercial form of bagasse is sold under the trade name Low Density Pith in a packing density of 0.125 g./cc. Other more dense solid carbonaceous fuels such as various types of nut meals may also be used where the inorganic nitrate particles are themselves in a special physical form of low density, as will be more fully described hereinbelow. A commercially available form of pecan nut meal having a packing density of 0.66 g./cc., and of such particle size that 90% of the particles pass through No. 32 mesh screen and 100% of the particles are retained by No. 80 mesh screen (U.S. Standard Series), is suitable for use as a more dense solid carbonaceous fuel. However, the low density nitrate salts used to achieve a low density explosive composition when the carbonaceous fuel, such as the pecan nut meal noted above, is of higher density are quite fragile and break up easily during handling so that unless such compositions are handled with a degree of care not usually associated with commercial manufacturing, packaging and transportation practices, the said salts break up and allow for compaction of the product to a density greater than that desired.

The amount of solid carbonaceous fuel in the final composition may be from about 8% to about 25% of the total weight of the composition. Even at the low 8% level, the composition may lack sufficient oxygen for complete oxygen balance but, as long as the low density requirement for the composition can be met, these small amounts of carbonaceous fuel are satisfactory. Preferred amounts of the carbonaceous fuel are from about 10% to about 20% of the total weight of the composition. This range of proportions is satisfactory for virtually all commercial applications of explosive compositions of this type.

As previously mentioned, it is essential that the packing density of the explosive composition not exceed about 0.6 g./cc. and the pouring density about 0.5 g./cc. The packing density is the density of the composition when filled and bumped in cartridges or other suitable packages and containers for shipment or storage, at which time the density may increase slightly over the pouring density due to settling or compaction of the particles caused by the bumping. The pouring density is the density of the explosive composition when freshly mixed and unpackaged. Actually these two densities are related and not independent of each other. Thus, if the pouring density is about 0.5 g./cc., it would be very difficult to exceed a packing density of 0.6 g./cc. no matter how much the filled package or container is bumped. Accordingly, of the two values, the pouring density is the more critical and cannot be exceeded. The packing density, on the other hand, may increase to above 0.6 g./cc., even to 0.7 or 0.75 g./cc. when screw loaded. While this is not recommended or preferred, such packages of explosive composition are still of use in achieving increased explosive power in accordance with the invention.

The foregoing density requirements are readily obtained by judicious selection of the inorganic nitrate and the solid carbonaceous fuel. Where the ammonium nitrate and alkali metal nitrates are to be used in their usual commercial forms of relatively high density, a solid carbonaceous fuel of lower density, such as the bagasse, will have to be used. On the other hand, ammonium nitrate

and alkali metal nitrates can be obtained in dendritic physical form of extremely low density, such as 0.4 g./cc. or even lower. These dendritic salts are composed of very fine needle-like, brittle crystals or particles which are obtained through special processing control employed during manufacture. With these low density inorganic nitrates, relatively more dense solid carbonaceous fuels, such as the nut meals, may be employed to prepare explosive compositions not exceeding the density limitations stated hereinabove, but such compositions are subject to compaction as has been noted already.

If desired, a small amount of a liquid carbonaceous fuel, up to about 5.0% and preferably from about 1.0 to 3.0% by weight of the total composition, may be included in the explosive compositions of the invention. Such liquid carbonaceous fuel may be an aromatic or paraffinic hydrocarbon oil, for example, mineral oil and the like. Use of the liquid carbonaceous fuel is of aid in maintaining the explosive compositions in stable admixture due to the slight adhesion between particles given by the liquid coating on the solid particles.

If desired, a small amount of a siliceous earth such as diatomaceous earth, fuller's earth or kieselguhr may be included as an anticaking agent in the explosive composition. One commercially available form of siliceous earth is sold under the trade name Celite No. 379 in a packing density of 0.255 g./cc. and has been used with excellent results. Such anticaking agents may be used in conventional amounts, about 1.0% thereof, based on the weight of the entire composition, having been found to give the desired results in the particular applications noted in this invention.

The explosive compositions of the invention are prepared by simply admixing the various ingredients together. Water is excluded from the compositions to avoid caking, agglomeration or other physical compaction that would tend to increase the pouring density of the simple admixture and thereby impair or destroy the efficacy of the compositions to provide the benefits of the invention. Thus, except for water which is normally present in the component ingredients, such as water of hydration, or water of adsorption, etc., the compositions are admixtures of dry particles without any separately added amounts of water.

Where a liquid carbonaceous fuel is employed, it is preferred that this fuel first be mixed with the inorganic nitrate and the resulting mixture then be mixed with the particles of solid carbonaceous fuel. The explosive compositions may be packaged in cartridges, flexible plastic packages or any other suitable form of container. The composition may be loaded in packaged form in boreholes or the compositions may be poured unpackaged into a borehole for detonation.

The following examples will serve to illustrate further details of the invention. The data given in each example were obtained by means of standard tests as follows.

The "D" sensitivity was measured by detonation of the explosive composition in a two inch by eight inch unconfined stick with pentaerythritol tetranitrate (PETN) boosters. The ballistic pendulum value was obtained by detonation initiated with a number 16 standard blasting cap. The rates of detonation were first determined in 3 inch diameter unconfined columns in a paper tube and then confined in 1½ inch diameter standard iron pipe.

The crater values were obtained by placing a 6 inch by 12 inch cartridge of the explosive composition, in a vertical position, in a hole 42 inches deep and 1 foot in diameter, dug into the ground. On top of the cartridge was placed a 1 pound PETN booster and the earth then replaced and packed into the hole to ground level. After detonation, the size of the crater formed and the corresponding volume of earth moved was determined by fast measuring two diameters at 90° to each other and measuring the depth, and calculating the resultant volume using the average of the two diameters. The volume of earth moved

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per pound of explosive composition was then calculated, applying a correction factor for the PETN booster.

EXAMPLE 1

An explosive composition was prepared in accordance with the invention as follows:

Ingredients:	Amounts (weight)
Crushed prilled ammonium nitrate	81.5
Mineral oil, 200 SSU	1.5
Bagasse	16.0
Diatomaceous earth	1.0
	100.0

Testing of the foregoing composition gave the following data:

Oxygen balance, percent	60
Packing density	0.505
Pouring density	0.42
"D" sensitivity, g. PETN	2
Ballistic pendulum	10.7
Rate of detonation (3 inch unconfined), m./sec.	1923
Rate of detonation (1½ inch confined), m./sec.	2457
Crater value, ft. ³ /lb.	30.5

EXAMPLE 2

Ingredients:	Amounts (weight)
Crushed prilled ammonium nitrate	56.5
Sodium nitrate	25.0
Mineral oil, 200 SSU	1.5
Bagasse	16.0
Diatomaceous earth	1.0
	100.0

Testing of the foregoing composition gave the following data:

Oxygen balance, percent	85
Packing density	0.515
Pouring density	0.425
"D" sensitivity, g. PETN	6
Ballistic pendulum	8.4
Rate of detonation (3 inch unconfined), m./sec.	1811
Rate of detonation (1½ inch confined), m./sec.	1988
Crater value, ft. ³ /lb.	22.7

EXAMPLE 3

Ingredients:	Amounts (weight)
Mill grained ammonium nitrate	81.5
Mineral oil, 200 SSU	1.5
Bagasse	16.0
Diatomaceous earth	1.0
	100.0

Testing of the foregoing composition gave the following data:

Oxygen balance, percent	60
Packing density	0.505
Pouring density	0.40
"D" sensitivity, g. PETN plus ¹	10
Ballistic pendulum	10.4
Rate of detonation (3 inch unconfined), m./sec.	1857
Rate of detonation (1½ inch confined), m./sec.	2372
Crater value, ft. ³ /lb.	23.6

¹The "plus" indicates failure to detonate completely with the booster designated.

EXAMPLE 4

Ingredients:	Amounts (weight)
Mill grained ammonium nitrate	56.5
Mill sodium nitrate	25.0
Mineral oil, 200 SSU	1.5
Bagasse	16.0
Diatomaceous earth	1.0
	100.0

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Testing of the foregoing composition gave the following data:

Oxygen balance, percent	85
Packing density	0.510
Pouring density	0.42
"D" Sensitivity, g. PETN plus	10
Ballistic pendulum	8.5
Rate of detonation (3 inch unconfined), m./sec.	1550
Rate of detonation (1½ inch confined), m./sec.	1955
Crater value	24.8

As will be noted, the explosive compositions of Examples 1-4 were all effective to the extent of moving at least 23 cubic feet of earth per pound of explosive when detonated in the boreholes used in the crater test. A series of conventional nitrocarbonitrates explosive compositions were subjected to the same tests to compare with the explosive compositions of Examples 1-4.

EXAMPLE 5

In this example a commercially available standard 40% ammonium nitrate dynamite was used for test purposes. The composition was substantially oxygen balanced and gave the following data:

Packing density	1.185
Pouring density	0.905
"D" Sensitivity, cap	1½-2
Ballistic pendulum	8.8
Rate of detonation (3 inch unconfined), m./sec.	3668
Rate of detonation (1½ inch confined), m./sec.	3372
Crater value, ft. ³ /lb.	12

EXAMPLE 6

In this example a standard commercial nitrocarbonitrates explosive composition comprising a mixture of ammonium nitrate and mineral oil was used for test purposes. The composition was substantially oxygen balanced and gave the following data:

Packing density	1.022
Pouring density	0.775
"D" Sensitivity, g. PETN plus	10
Ballistic pendulum	12.3
Rate of detonation (3 inch unconfined), m./sec.	2681
Rate of detonation (1½ inch confined), m./sec.	3267
Crater value	14.4

EXAMPLE 7

In this example a standard nitrocarbonitrates explosive composition consisting of a mixture of prilled ammonium nitrate, carbon black and mineral oil was used for test purposes. The composition was substantially oxygen balanced and gave the following data:

Packing density	0.845
Pouring density	0.815
"D" Sensitivity, g. PETN plus	10
Ballistic pendulum	11.8
Rate of detonation (3 inch unconfined)	Failed
Rate of detonation (1½ inch confined)	Failed
Crater value	8.8

As will be seen, the ballistic pendulum values for the explosive compositions of Examples 1-4 and those for Examples 5-7 were in the same order of magnitude and the rates of detonation of the compositions of Examples 5-7 were slightly higher than those of Examples 1-4. Ordinarily, this would be considered an indication that the explosive compositions of Examples 5-7 would have at least about the same or slightly more explosive power than the compositions of Examples 1-4. However, the crater values obtained for these compositions show that these conclusions are not correct. The volume of earth moved per pound of explosive by the compositions of Examples 1-4 was on the order of twice the volume moved by the compositions of Examples 5-7. The crater value test more realistically simulates the actual field use of

nitrocarbonate explosive compositions and shows that the explosive compositions of Examples 1-4 had surprisingly and unexpectedly greater explosive power than those of Examples 5-7, notwithstanding the lower densities and oxygen deficiencies of the compositions of Examples 1-4. The surprising and unexpected results found here were supported further by field tests as noted below.

EXAMPLE 8

In the removal of overburden in a coal stripping operation, 175-200 pounds of nitrocarbonate explosive composition consisting of a mixture of ammonium nitrate and mineral oil was being loaded in 6½ inch diameter holes, 25 feet deep. The breakage yield on detonation was 4 tons of broken material per pound of explosive composition in the mine. When this amount of standard nitrocarbonate explosive was replaced with 100 pounds of the explosive composition of Example 1, the breakage factor increased to 7.9 tons per pound of explosive. In addition to the increase in breakage, the breakage pattern with the explosive composition of Example 1 was improved considerably wherein the incidence of large chunks of material was reduced so that correspondingly less work with the shovel was required.

EXAMPLE 9

In a gypsum quarry, 4,200 pounds of a standard nitrocarbonate explosive consisting of a mixture of ammonium nitrate and fuel oil was loaded into 50 boreholes each 3 inches in diameter and 40 feet deep and spaced in a 9 x 9 foot pattern. The explosive charge gave two tons of breakage per pound of explosive.

1,650 pounds of the explosive composition of Example 1, in 40 boreholes, were substituted for the standard nitrocarbonate explosive compositions and the breakage increased to 3.25 tons per pound of explosive composition, wherein the incidence of large chunks of material was reduced so that correspondingly less work with the crusher was required.

EXAMPLE 10

In a limestone quarry, boreholes 7¾ inches in diameter and 67 feet deep were each being loaded with 100 pounds of standard dynamite at the bottom and 400 pounds of a standard nitrocarbonate explosive composition consisting of a mixture of ammonium nitrate and fuel oil on top of the dynamite.

When the 400 pounds of standard nitrocarbonate were replaced in each hole with 240 pounds of the composition of Example 1, the breakage results were as good or better than given by the standard nitrocarbonate and the savings realized was \$1.37 per borehole.

EXAMPLE 11

In a limestone quarry, 550 pounds of a standard nitrocarbonate were being used in a borehole 6½ inches in diameter and 75 feet deep, each hole being deck-loaded with alternating layers of explosive and tamped dirt. Upon detonation, a rather poor fragmentation was obtained wherein the areas of the borehole surrounding the alternate layers of explosive developed a large proportion of wasteful fines and the areas surrounding the alternating layers of tamped dirt were broken only into very large chunks requiring excessive work for crushing. Also, several failures were experienced using this form of explosive and loading.

When 550 pounds of the composition of Example 1 was fully loaded into each borehole without decking, no failures occurred and the amount of breakage was at least equal to that given by the standard nitrocarbonate. However, the fragmentation achieved with the composition of Example 1 was superior, there being less waste in the form of fines and fewer large chunks requiring excessive work for crushing.

It will be understood that it is intended to cover all changes and modifications of the preferred embodiments

of the invention, herein chosen for the purpose of illustration, which do not constitute departures from the spirit and scope of the invention.

We claim:

1. An explosive composition comprising an admixture of dry particles which is free of any added amounts of water except for water which may be normally present in said particles, at least about 50% of the weight of said composition being an inorganic nitrate selected from the group consisting of ammonium nitrate and ammonium nitrate in admixture with alkali metal nitrate, said inorganic nitrate having such particle sizes that substantially 100% thereof passes a U.S. Standard No. 18 screen and at least 50% thereof passes a U.S. Standard No. 60 screen, and a solid carbonaceous fuel in an amount within the range from about 8% to about 25% by weight of the composition, said composition having an initial pouring density up to about 0.5 g./cc. and said pouring density not substantially increasing over storage of said composition at temperatures which include the ammonium nitrate IV-III solid state transition point.

2. A composition as in claim 1 which includes up to about 5% by weight of a combustible liquid hydrocarbon fuel.

3. A composition as in claim 1 which includes up to about 1% by weight of a siliceous earth.

4. A composition as in claim 1 having a packing density not exceeding about 0.6 g./cc.

5. An explosive composition comprising an admixture of dry particles which is free of any added amounts of water except for water which may be normally present in said particles, at least about 50% of the weight of said composition being an inorganic nitrate selected from the group consisting of ammonium nitrate and ammonium nitrate in admixture with alkali metal nitrate, said inorganic nitrate having such particle sizes that substantially 100% thereof passes a U.S. Standard No. 18 screen and at least 50% thereof passes a U.S. Standard No. 60 screen, and a combustible solid carbonaceous fuel in an amount within the range from about 10% to about 20% by weight of the composition, said composition having an initial pouring density up to about 0.5 g./cc. and said pouring density not substantially increasing over storage of said composition at temperatures which include the ammonium nitrate IV-III solid state transition point.

6. A composition as in claim 5 which includes up to about 5% by weight of a combustible liquid hydrocarbon fuel.

7. A composition as in claim 5 which includes up to about 1% by weight of a siliceous earth.

8. A composition as in claim 5 having a packing density not exceeding about 0.6 g./cc.

9. A composition as in claim 5 in which said solid carbonaceous fuel is bagasse.

10. A composition as in claim 5 having an oxygen balance less than 100%.

11. An explosive composition comprising about 81.5% by weight of ammonium nitrate having particle sizes such that substantially 100% thereof passes a U.S. Standard No. 18 screen and at least 50% thereof passes a U.S. Standard No. 60 screen, about 16% by weight of bagasse, about 1.5% by weight of mineral oil and about 1.0% by weight of siliceous earth, said composition having an initial pouring density up to about 0.5 g./cc. and said pouring density not substantially increasing over storage of said composition at temperatures which include the ammonium nitrate IV-III solid state transition point.

12. An explosive composition comprising about 56.5% by weight of ammonium nitrate and about 25% by weight of sodium nitrate, said ammonium and sodium nitrates having particle sizes such that substantially 100% thereof passes a U.S. Standard No. 18 screen and at least 50% thereof passes a U.S. Standard No. 60 screen, about 16% by weight of bagasse, about 1.5% by weight of mineral oil and about 1% by weight of siliceous earth, said com-

position having an initial pouring density up to about 0.5 g./cc. and said pouring density not substantially increasing over storage of said composition at temperatures which include the ammonium nitrate IV-III solid state transition point.

13. An explosive composition comprising an admixture of dry particles which is free of any added amounts of water except for water which may be normally present in said particles, at least about 50% of the weight of said composition being an inorganic nitrate selected from the group consisting of ammonium nitrate and ammonium nitrate in admixture with alkali metal nitrate, said inorganic nitrate having such particle sizes that substantially 100% thereof passes a U.S. Standard No. 18 screen and at least 50% thereof passes a U.S. Standard No. 60 screen, and a combustible solid carbonaceous fuel in an amount within the range from about 8% to about 25% by weight of the composition, said composition having an initial packing density up to about 0.75 g./cc. and said packing

density not substantially increasing over storage of said composition at temperatures which include the ammonium nitrate IV-III solid state transition point.

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