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DETONATING EXPLOSIVE

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This invention relates to a detonating explosive in granular form, and more particularly to an explosive of this nature having a relatively high ammonium nitrate content and capable of effective use in the presence of water.

Free-flowing explosives offer a number of advantages in use, particularly with respect to loading, since they can be poured into the borehole and made to fill it completely, without the necessity of cartridging or tamping. Black powder and various explosives containing high ammonium nitrate contents are examples of free-flowing explosives of the prior art. Such compositions have been satisfactory from the viewpoint of loading properties under dry conditions, but have been out of the question when the boreholes contained, or were filled with, water. Because of the high content of water-soluble salts in such explosives, notably sodium nitrate or ammonium nitrate, or both, such compositions not only lost much of their content by leaching but ceased to be capable of functioning as explosives under the wet conditions.

The object of the present invention is a high explosive of free-flowing nature capable of functioning effectively after immersion in water. A further object is an ammonium nitrate explosive in granular form, which is water compatible. A still further object is such an explosive possessing high strength. Additional objects will be disclosed as the invention is described more fully hereinafter.

I have found that the foregoing advantages are accomplished, and the disadvantages of the prior art overcome, when I prepare compressed aggregates or granules of flowable size by balanced blends of oxidizable materials, particularly carbonaceous combustibles, and at least one inorganic oxidizing agent. Such grains are given the desired degree of absorbency by suitable choice of carbonaceous ingredients and are then mixed with not less than 15% of an explosive liquid nitric ester, calculated on the total weight of grain and liquid explosive. Under the conditions of my invention, the liquid explosive becomes substantially completely absorbed within the grains so that these latter retain their free-flowing characteristics, yet are capable of propagating the explosion, when this has once been initiated.

While I preferably employ ammonium nitrate as the inorganic oxidizing agent because of the additional strength imparted by its use, this salt may be replaced in part or completely by other oxygen-supplying salts such as sodium nitrate, potassium nitrate, various perchlorates, and the like.

The presence of not less than 15% of a liquid explosive nitric ester has been found to be preferable in order to assure detonating properties in the explosive after immersion in water. Preferably, I employ no more than 30% of said liquid sensitizer. Nitroglycerin is the preferred sensitizer, though explosive equivalents such as ethylene glycol dinitrate, tetranitrodiglycerin, and other freezing point depressants may be dissolved in the nitroglycerin. In fact, nitroglycerin may be substiuted entirely or in part by other explosive materials (although a sensitizing agent in liquid form and having a nitric ester base is preferred). Thus, other suitable sensitizers include both explosives per se, such as nitrocellulose, smokeless powder, nitrostarch, PETN, TNT, and the like, and certain non-explosive sensitizers including hydrocarbons, e. g., paraffin, certain nitrated hydrocarbons, e. g., dinitrotoluene, and certain forms of carbon, such as coal and the like. Various compositions of these types are disclosed and claimed in copending application Serial No. 387,919, filed April 10, 1941.

If free-flowing properties are to be retained, it is essential that the nitroglycerin or other liquid explosive be absorbed within the grain and not be present on the surface. Surface wetting of the final explosive by nitroglycerin would be undesirable also because of the unduly high degree of sensitiveness to shock that would then be present. In order to assure the desired degree of absorptive power for the granules for nitroglycerin, control of the density of the grain as prepared is necessary, as well as proper selection of carbonaceous combustible ingredients. I have found that the apparent density of the grains or aggregates initially prepared preferably should lie between 1.05 and 1.35. If a grain of density lower than 1.05 is used, the aggregate is not sufficiently compact to hold together satisfactorily under the leaching effect of the water on the considerable percentage of soluble salts. If, on the other hand, the density is above 1.35, the grain is not sufficiently absorbent. When grains of the foregoing intial densities are used and mixed with nitroglycerin, the latter is absorbed without substantial change in the volume of the grain. Hence, a final detonable grain is obtained of a preferred density range between 1.25 and 1.6.

An additional ingredient for the assurance of sufficient absorptive power in the granular aggregates is the presence of a minimum amount of a fibrous carbonaceous material, which pre-

sumably functions by binding the aggregate together, yet maintaining sufficient air spaces within the grains to provide opportunity for absorption of the desired amount of nitroglycerin. I have found that if a liquid sensitizer is used, the grain, as initially prepared, preferably should have a content of woodpulp or other fibrous carbonaceous material of not less than 2%, which would mean a preferred minimum content in the final explosive of around 1.5%. A content of woodpulp or the like of between 5 and 6% is suitable under many conditions, and 10% or more may be used.

While the grains described will give a suitable free-flowing explosive, I find the desired degree of compatibility with water to be best attained when an ingredient is included in the grain composition comprising a plant product capable of forming a cohesive paste on contact with unheated water. Various ingredients of this type may be used, for example, a pregelatinized cereal product such as a flaked corn product in finely divided condition where the cereal product has been preheated to an elevated temperature or otherwise treated so that it is capable of forming a cohesive paste with cold water. Other suitable paste-forming vegetable products are rye flour, barley flour, oat flour, spelt meal, linseed meal, and the like. Preferably, I employ linseed meal or barley flour, since these tend to cause a contractive effect on wetting with water and formation of the cohesive protective paste. The formation of this paste at the initial penetration of water into the explosive tends to keep the interior of the explosive from being leached out. Pulverulent explosives containing such ingredients are claimed in the copending application of Winning, Serial No. 288,131, filed August 3, 1939. I find it preferable to use the linseed meal or barley flour, or other paste-forming material, in an amount between 2.5 and 10% of the entire composition.

The following will serve as examples of methods of carrying out my invention and obtaining the desired free-flowing, water-compatible explosive:

Example 1

The ingredients for the initial grain were weighed and introduced under heavy, revolving wheels, the following relative amounts being used:

	Per cent
Ammonium nitrate	74.5
Sodium nitrate	10.0
Sulfur	2.0
Woodpulp	6.0
Flaked corn product	7.0
Chalk	0.5
	100.0

All the above ingredients, with the exception of the flaked corn product, were first wheeled after the addition of about 4% of water. The corn product was added toward the end of the mixing and stirred in. The intimate wheel cake mixture was then pressed and dried at around 140° F. The dried cake was broken up and granulated, grains being retained that were of such size that they passed a 6-mesh screen and were held on 16-mesh. The grains were then placed in a dynamite mixer and nitroglycerin was slowly added, the grain-nitroglycerin ratio being such as to give a 20% nitroglycerin content in the final product. The grains and liquid explosive were mixed for 5 to 7 minutes. The grains, prior to mixing with nitroglycerin, had a density of 1.18 and, after incorporation of the liquid explosive, about 1.47. The grains were free flowing, as shown by their ability to flow through a 5/8" or 7/8" funnel. The ability of the above explosive to function after prolonged immersion in water was shown by filling a 2 x 8" tin tube with water, then pouring in the granular explosive until it reached the top of the tube, at which time the water present amounted to about 33⅓% of the total content by weight. After exposure to water for 3 hours, four successive detonations of the explosive were obtained with four different tin tubes, similarly loaded. The detonability of the explosive was tested by placing the tube on a lead block and priming it with a half-cartridge of 40% straight dynamite. The bulk density of the explosive, as poured into the receptacle, was 0.78 and the volume occupied by it in water indicated it there to have an apparent density of about 0.66.

Example 2

A mixing (75 lbs.) was made in a dynamite mixing bowl of the following materials:

	Per cent
Ammonium nitrate	76.5
Sodium nitrate	8.5
Sulfur	3.0
Woodpulp	5.0
Vegetable meal	2.0
Rye flour	4.5
Chalk	0.5
	100.0

The above ingredients, with the exception of the rye flour, were mixed for about 20 minutes, with the bowl heated to 140° F. and with enough water added to give a 4% content. The rye flour was then added and mixed for a short time, giving cohesiveness to the whole. The freshly mixed material was pressed into cakes having a density of 1.35. The cake was then broken into pieces about 1½" square and dried at 140° F. for 12 hours, or to a high degree of hardness. The material was then granulated and screened, and that portion was retained which passed a 6-mesh and was held on a 16-mesh screen. The grains were then mixed with nitroglycerin, the relative proportions of grains and nitroglycerin being 80–20. The bulk density of the dry powder was 0.715 and 0.85 after immersion in water. Using a half-stick of 40% straight dynamite as primer, detonations resulted on successive tests after immersions of 15 minutes, 3 hours, and 7 days.

Example 3

A grain was formed in similar manner from the following materials:

	Per cent
Ammonium nitrate	81.5
Sodium nitrate	10.0
Sulfur	2.0
Woodpulp	6.0
Chalk	0.5
	100.0

The above mix in the form of blended aggregates of the desired size was blended with nitroglycerin in an 80–20 proportion. Excellent absorption of nitroglycerin by the grains was obtained. The finished grains showed satisfactory free-flowing properties after 1 day. When immersed in an amount of water comprising 33⅓% of its weight, detonations in all trials were obtained after 3 hours and 7 days. The apparent density of the grain, previous to addition of the nitroglycerin,

was 1.27. The bulk density of the dry final explosive was 0.78, and between 0.73 and 0.76 after immersion in water.

Example 4

A grain was prepared, free from ammonium nitrate, having the following composition:

	Per cent
Sodium nitrate	76.5
Sulfur	10.0
Woodpulp	6.0
Flaked corn product	7.0
Chalk	0.5
	100.0

The above material, after compacting into aggregates, was mixed with nitroglycerin in an 80–20 proportion. The material had a bulk density, dry, of 0.79, and 0.71 after immersion in water. Detonations were obtained after immersion in water, though the sensitiveness was not uniform and was less than with ammonium nitrate compositions.

From the foregoing description of the explosive of my invention, it will be appreciated that said explosive possesses remarkable properties. In its ability to give satisfactory blasting execution after immersion in water for several hours, it is equalled only by the gelatin dynamites or ammonium nitrate explosives completely enclosed in metal or other waterproof containers. No other free-flowing explosive can approach it in this respect. Preferably, I employ compositions containing more than 50% ammonium nitrate, and lower-strength explosives are obtained when the above salt is replaced partly or entirely by sodium nitrate. Increased velocity may be obtained, if desired, by increasing the nitroglycerin content, for example to 30%.

In carrying out the manufacturing operations, various methods and forms of apparatus may be employed. In preparing the grain, for example, I find it satisfactory to incorporate the materials under wheels, as is the practice with black powder, the successive operations of wheeling, pressing, and corning being performed, if desired. Mixing may be carried out also in any type of dynamite mixing apparatus, or otherwise. Pressing may take place under revolving wheels or between rolls, or in any desired manner.

When the explosive of my invention is poured into water, the grains quickly become wet and sink rapidly to the bottom. While a portion of the grains is dissolved and lost in the water, the grains retain their structure and appearance and no nitroglycerin is lost or segregated.

In describing my explosive, it has been stated that nitroglycerin is commonly used as the liquid explosive nitric ester, which sensitizes the explosive. By the term "nitroglycerin," I intend to designate not only that compound itself but nitroglycerin containing dissolved materials which function as freezing point depressants. Likewise, many other departures may be made from the details of operations and compositions cited without departure from the scope of the invention. I intend therefore to be limited only by the following patent claims:

I claim:

1. A free-flowing granular detonating explosive comprising blended aggregates of a carbonaceous combustible material and an inorganic oxidizing agent, and at least 15% of a liquid explosive nitric ester, said aggregates having an initial apparent density between 1.05 and 1.35 and the combustible content being sufficiently absorbent that the liquid explosive is absorbed within said aggregates, the completed grain having a dry surface.

2. A free-flowing granular detonating explosive comprising blended aggregates of a carbonaceous combustible material and ammonium nitrate, and at least 15% of a liquid explosive nitric ester, said aggregates having an initial apparent density between 1.05 and 1.35 and the combustible content being sufficiently absorbent that the liquid explosive is absorbed within said aggregates, the completed grain having a dry surface.

3. A free-flowing detonating explosive in granular form and capable of functioning effectively after immersion in water, said grains having densities between 1.25 and 1.6 which is sufficient to cause them to sink in water and comprising blended aggregates of combustible material and ammonium nitrate, and a liquid explosive nitric ester substantially absorbed within said blended aggregates, said combustible material comprising a fibrous carbonaceous ingredient and a plant product capable of forming a cohesive paste on contact with unheated water.

4. The explosive of claim 3, in which the paste-forming material is present in an amount between 2.5 and 10% of the total composition.

5. The explosive of claim 3, in which the paste-forming material comprises a pregelatinized cereal product.

6. The explosive of claim 3, in which the paste-forming material comprises barley flour.

7. The explosive of claim 3, in which the paste-forming material comprises rye flour.

8. A free-flowing detonating explosive in granular form and capable of functioning effectively after immersion in water, said grains having an apparent density between 1.25 and 1.6 and comprising blended aggregates of oxidizable material and ammonium nitrate, and not less than 15% of nitroglycerin substantially absorbed within said blended aggregates and dispersed therethrough, said oxidizable material comprising a fibrous carbonaceous ingredient and a plant product capable of forming a cohesive paste on contact with unheated water.

9. The explosive of claim 8, in which the blended aggregates are of such size that they will pass substantially a 4-mesh screen but are held on a 16-mesh screen.

10. A free-flowing detonating explosive in granular form and capable of functioning effectively after immersion in water, said grains having an apparent density between 1.25 and 1.6 and comprising blended aggregates of oxidizable material and ammonium nitrate, said grains comprising over 50% ammonium nitrate, more than 1.5% of a fibrous carbonaceous ingredient, between 2.5 and 10% of a plant product capable of forming a cohesive paste on contact with water, and between 15 and 30% nitroglycerin substantially absorbed within said blended aggregates and dispersed therethrough.

11. The method of preparing a granular explosive which comprises preparing aggregates of intimate mixtures of carbonaceous combustible material and at least one inorganic oxidizing agent said carbonaceous material comprising a fibrous ingredient, compressing said aggregates to apparent densities for the individual aggregates of between 1.05 and 1.35, admixing said granular aggregates with an amount of a liquid

explosive nitric ester of not less than 15% of the total weight of grains and liquid explosive, causing said liquid nitric ester to become substantially absorbed in and dispersed through said aggregates, thereby producing a free-flowing, granular, detonable explosive.

12. The method of preparing a granular explosive which comprises preparing aggregates of intimate mixtures of carbonaceous combustible material and ammonium nitrate said carbonaceous material comprising a fibrous ingredient, compressing said aggregates to apparent densities for the individual aggregates of between 1.05 and 1.35, admixing said granular aggregates with an amount of a liquid explosive nitric ester of not less than 15% of the total weight of grains and liquid explosive, causing said liquid nitric ester to become substantially absorbed in and dispersed through said aggregates, thereby producing a free-flowing, granular, detonable explosive.

13. The method of preparing a granular explosive capable of functioning effectively after immersion in water, which comprises preparing aggregates of intimate mixtures of carbonaceous combustible material and at least one inorganic oxidizing agent, including as said combustible material a fibrous carbonaceous ingredient and a plant product capable of forming a cohesive paste on contact with unheated water, compressing said aggregates to apparent densities for the individual aggregates of between 1.05 and 1.35, admixing said granular aggregates with an amount of liquid explosive nitric ester of not less than 15% of the total weight of grains and liquid explosive, causing said liquid explosive to become substantially absorbed in and dispersed through said aggregates, thereby producing a free-flowing, granular, detonable explosive.

14. The method of claim 13, in which the paste-forming material is used in an amount between 2.5 and 10% of the total composition.

15. The method of claim 13, in which the paste-forming material comprises a pregelatinized cereal product.

16. The method of claim 13, in which the paste-forming material comprises barley flour.

17. The method of claim 13, in which the paste-forming material comprises rye flour.

18. The method of preparing a granular explosive which comprises mixing intimately carbonaceous combustible materials and ammonium nitrate said carbonaceous combustible material comprising a fibrous ingredient, compressing the blended mixture into aggregates having apparent densities for the individual aggregates of between 1.05 and 1.35, admixing said granular aggregates with an amount of nitroglycerin sufficient to bring about densities for said aggregates of between 1.25 and 1.6, causing said liquid explosive to become substantially absorbed in and dispersed through said aggregates, thereby producing a free-flowing, granular, detonable explosive.

19. The method of preparing a granular explosive capable of functioning effectively after immersion in water, which comprises mixing intimately carbonaceous combustible materials and ammonium nitrate, including as said combustible material a fibrous carbonaceous ingredient and a plant product capable of forming a cohesive paste on contact with unheated water and in an amount between 2.5 and 10% of the finished explosive, compressing the blended mixture into aggregates having apparent densities for the individual aggregates of between 1.05 and 1.30, admixing said granular aggregates with an amount of nitroglycerin of between 15 and 30% of the final explosive, causing said nitroglycerin to become substantially absorbed within said aggregates and dispersed therethrough, thereby producing a free-flowing granular, detonable explosive.

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