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3,356,544

INORGANIC OXIDIZER SALT AQUEOUS BLASTING COMPOSITIONS CONTAINING A NITROPARAFFIN

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No Drawing. Filed May 5, 1966, Ser. No. 547,777
16 Claims. (Cl. 149—38)

ABSTRACT OF THE DISCLOSURE

An inorganic oxidizer salt explosive of the aqueous slurry type containing a nitroparaffin having from 1 to 3 carbon atoms in the molecule, as a sensitizer, together with a supplemental sensitizer when the nitroparaffin content is below about 9 percent; and method for manufacture of said explosive.

This invention relates to aqueous inorganic oxidizer salt slurry-type blasting compositions containing a nitroparaffin, or a nitroparaffin mixture, as a sensitizer component.

Inorganic oxidizer salt blasting compositions of the aqueous slurry type have had wide use in the explosives industry in recent years. These compositions comprise an inorganic oxidizer salt, water, a sensitizer, and generally a thickening agent in at least an amount to impart sufficient consistency to the slurry to prevent settling of ingredients.

Various sensitizer materials have been utilized in these compositions, including smokeless powder as disclosed and claimed in U.S. 3,235,425, and particulate metals and high explosives, such as TNT and/or aluminum as disclosed and claimed in U.S. 2,930,685.

This invention is concerned with aqueous slurry blasting compositions of the type above described, generally of the class of nitrocarbonitrates (NCN_s), containing a nitroparaffin or a nitroparaffin mixture as a sensitizer component, alone or in conjunction with a supplemental sensitizer.

In accordance with the invention, aqueous inorganic oxidizer salt slurry-type explosives are provided which contain a sensitizing amount, generally from about 3 to 40 weight percent, or any suitable amount outside that range, of a nitroparaffin having from 1 to 3 carbon atoms in the molecule, or a mixture of such nitroparaffins, as a sensitizer component, and when the total nitroparaffin content is below about 9 weight percent, the said slurries contain a supplemental sensitizer ingredient. The slurry compositions of the invention generally contain from 8 to 25 percent water, from about 40 to 75 percent of an inorganic oxidizer salt, the above-described sensitizer component, and from about 0.2 to 5 percent of a thickener.

By the term "inorganic oxidizer salt," as is well known in the explosives art, is meant one which under the conditions of the detonation, liberates oxygen for the combustion of the fuel component.

Now preferred compositions of the invention contain (weight basis) from 12 to 20 percent water, from 40 to 60 percent ammonium nitrate and from 5 to 20 percent sodium nitrate as the total oxidizer salt, from 5 to 35 percent nitroparaffin and from 0.2 to 2 percent guar gum, the latter generally in cross-linked form; and, when the proportion of nitroparaffin sensitizer is below about 9 percent, the said composition containing from 3 to 17 percent particulate aluminum as a supplemental sensitizer, the latter preferably in flake form.

Although, as above described, a supplemental sensitizer

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is generally required when the total nitroparaffin content is below about 9 percent, it is within the scope of the invention to supplement the nitroparaffin sensitizer whenever desired, the proportion of supplemental sensitizer generally being from about 2 to about 20 percent. Exemplary supplemental sensitizers are powdered aluminum, preferably in flake form, powdered coal, DNT (solid or oil), hydrocarbon oil, and the like.

Although ammonium nitrate alone, or with sodium nitrate, is in most instances the inorganic oxidizer salt component, other inorganic oxidizer salts can be used alone or with ammonium nitrate as a supplemental oxidizer salt, the alkali metal nitrates being now preferred. Often when ammonium nitrate is utilized with a supplementary oxidizer salt, it comprises a major proportion of the total oxidizer salt, i.e. at least 50 percent of the total. Exemplary inorganic oxidizer salts that can be used alone, or together with ammonium nitrate, are alkali metal (including ammonium) and alkaline earth metal nitrates and perchlorates as, for example, sodium nitrate, magnesium nitrate, calcium nitrate, potassium nitrate, barium nitrate, sodium perchlorate, ammonium perchlorate, calcium perchlorate and magnesium perchlorate.

Particle size and type of the oxidizer salt ingredients are generally not critical. For example, ammonium nitrate can consist of prills such as used in fertilizers and which are substantially all on 20 mesh, or it can be granular and in that form vary from coarse to fine. Other oxidizer salt ingredients are generally of comparable particle size. However, when desired, any or all of the oxidizer salt component can be added to the formulation, in aqueous solution.

The thickener content may be as high as 5 weight percent, dependent upon the particular thickener and the desired consistency of the finished composition. Generally a thickener content up to about 2 percent is sufficient. When the thickener content is within the range of from about 0.2 to 0.5 percent, there is generally sufficient thickening to prevent settling of the composition ingredients although additional thickener is often required in order to impart a satisfactory degree of cohesiveness so that the composition retains its form as a unit mass, preferably plastic but deformable. Exemplary thickeners are sodium carboxymethyl cellulose, karaya gum, water-soluble starches, mannogalactans, locust bean gum, cereal products and the like. When the thickener is guar gum in cross-linked form, in accordance with preferred practice, the guar gum content is most advantageously within the range of from 0.5 to 2.0 percent, under which conditions the finished composition is a plastic, rubbery, but deformable mass.

The nitroparaffin ingredient, generally a liquid, is advantageously present in the explosive slurry composition in partially gelled form for optimum uniformity of its distribution. Although nitrocellulose is a generally preferred agent for the gelation, any suitable gelling agent can be utilized, the requisite amount not generally exceeding about 6 weight percent of the nitroparaffin, from 3 to 5 percent of the nitrocellulose agent being more often utilized.

The compositions of the invention are in most instances insensitive to detonating action of a No. 8 commercial blasting cap but are, in all events, detonatable by conventional "booster" charges, such as PETN (pentaerythritol tetranitrate), RDX (cyclotrimethylenetrinitramine), Pentolite (PETN-TNT, 50/50), tetry, Composition B (RDX-TNT, 60/40) and the like. One booster advantageously employed is a dispersion of a crystalline high explosive, e.g. PETN or RDX in a plastic carrier such as disclosed and claimed in U.S. 2,965,466 and which is detonatable by either a commercial blasting cap or a detonating fuse. A now preferred booster comprises a cast

cylindrical body of cap- and fuse-insensitive explosive, and a tube assembly within the cast body, containing cap-sensitive crystalline high explosive together with structure for support of initiator means therefor, as disclosed and claimed in U.S. 3,212,438.

In preferred practice, the explosive compositions of the invention are nitrocarbonitrates, by which term it is meant there are no ingredients which in themselves are high explosives and the mixture will not detonate in response to a No. 8 commercial blasting cap when packed for shipment.

The invention is illustrated with reference to the following formulations:

TABLE

Run No. ¹⁰	1	2	3	4	5	6	7	8	9	10
Water	24.0	8.0	9.0	8.5	14.0	18.0	22.0	10.0	22.0	24.0
Ammonium Nitrate ¹	51.5	44.9	51.9	54.5	54.6	54.2	51.2	53.8	50.3	59.3
Sodium Nitrate ²		11.0	11.0	16.0	14.0	14.0	14.0	13.0	13.0	
Guar Gum ³	2.0	0.5	0.5	0.5	1.0	1.5	1.5	0.7	1.5	1.5
Nitromethane ⁴	22.5	35.0						1.0		5.0
Nitroethane ⁵			27.0							
2-nitropropane				20.0	16.0	12.0	11.0		6.0	
2,2-dinitropropane								9.5		
Nitrocellulose ⁶	1.5	1.8	0.6	0.5	0.4	0.3	0.3	0.4	0.2	0.4
Aluminum ⁷								11.0	7.0	10.0
Density, grams/cc.	1.24	1.37	1.35	1.42	1.34	1.33	1.30	1.53	1.27	
Detonation Rate ⁸	2,800	5,700	2,450	2,650	2,000	4,350	2,450	4,340	3,500	4,650
Funnel Test										
Flow Time, Sec.	2 3/4	2			3 1/2		3		3 1/2	

¹ Substantially all through 40 mesh and 70 percent through 100 mesh screen, Runs 2, 3, 4, 8; prills, in all other runs.

² Fine, Runs 2, 3, 4, 8; Coarse, all others.

³ In cross-linked form.

⁴ Mononitromethane.

⁵ Mononitroethane.

⁶ Present as agent for gelation of the nitroparaffin. Dynamite grade.

⁷ Flaked, Runs 9, 10; granular (nonsensitizing), Run 8.

⁸ Measured as average detonation velocity over 20 cm. length, at the end of a 23" column of explosive. The explosive is confined in black iron pipe and the time for detonation to proceed across the 20 cm. length of

are well known. Exemplary agents functioning to inhibit hydration and subsequently promote cross-linking are those which liberate borate, cuprous, calcium and aluminum ions, the inhibiting and cross-linking action being promoted under a different pH condition. For example, sodium borate is commonly utilized as an ingredient of the guar gum at a pH of from about 5 to 6 to promote inhibition of hydration and at a pH increase to about 7 to promote cross-linking.

When referring herein to hydration, it is meant the reaction that takes place between the guar gum and water components to form a sol; and, when referring to cross-linking, it is means the cross-linking that takes place be-

explosive is measured electronically with a counter-chronograph. Runs 3 and 4, detonations measured in 4" x 28" pipe; Run 8, 3" x 28" pipe; all others, 5" x 28" pipe (all pipes black iron, Schedule 40). All detonations were initiated by 475 grams of Pentolite booster except 350 grams, Run 8.

⁹ Approximately 5,000 grams of slurry is poured into an aluminum funnel having a 1 1/8" diameter by 1" length orifice. When the orifice is opened to permit flow, the timing period is begun. When light is visible through the orifice (looking down into the funnel), timing is stopped. The time difference is designated as the flow time. Run 2 measured through a 5" diameter by 1" length orifice.

¹⁰ Runs 1, 2, and 10 on weight basis; all others, weight percent.

tween the guar gum and the particular cross-linking agent to form a gel.

As will be evident to those skilled in the art, various modifications can be made or followed in light of the foregoing disclosure and discussion, without departing from the spirit or scope of the disclosure or from the scope of the claims.

What we claim and desire to protect by Letters Patent is:

1. In an inorganic oxidizer salt explosive composition of the aqueous slurry type, the improvement comprising, from 3 to 40 weight percent of a nitroparaffin component, as a sensitizer, selected from the group consisting of nitroparaffins containing from 1 to 3 carbon atoms in the molecule, and mixtures thereof, and said slurry also containing a supplemental sensitizer selected from the group consisting of particulate aluminum, powdered coal, dinitrotoluene, and a hydrocarbon oil when the total amount of said nitroparaffin sensitizer component of said slurry is below about 9 percent.

2. A composition of claim 1 containing from 2 to 20 percent of said supplemental sensitizer.

3. A composition of claim 1 containing from 8 to 25 percent water, from 40 to 75 percent of said inorganic oxidizer salt, and from 0.2 to 5 percent of a thickener.

4. A composition of claim 1 wherein said supplemental sensitizer is flake aluminum.

5. A composition of claim 2 containing less than 9 percent of said nitroparaffin sensitizer component.

6. A composition of claim 5 wherein said supplemental sensitizer is flake aluminum.

7. A composition of claim 3 wherein said thickener is guar gum in cross-linked form and is present in an amount of from 0.5 to 2.0 percent.

8. A composition of claim 3 wherein said nitroparaffin is mononitromethane.

9. A composition of claim 3 wherein said nitroparaffin is a mononitropropane.

10. A composition of claim 3 wherein said nitroparaffin is mononitroethane.

Any suitable method can be utilized in the manufacture of the slurry compositions of the invention. One such method comprises the steps of forming a "premix" of initial portions of guar gum and the oxidizer salt, partially gelling the nitroparaffin (a liquid), mixing the partially gelled nitroparaffin with a sufficient amount of an additional portion of the oxidizer salt to form a slurry, mixing the remaining portion of the guar gum with the remaining portion of oxidizer salt, adding the premix to the water ingredient at a temperature of about 120-150° F. to permit initial thickening action of the guar gum, adding the subsequently formed oxidizer salt-guar gum mixture to the initially thickened aqueous mixture and then as the final ingredient, adding the nitroparaffin slurry formed as above described. When a supplemental sensitizer is to be included, it is advantageously the last added ingredient.

The guar gum ingredient of the premix is generally in the order of about one-half of the total amount contemplated and is hydratable only, i.e. it is not cross-linkable, or, in any event, does cross-link at an insignificantly low rate. It is present in the premix in a salt-to-guar gum weight ratio of from about 3:1 to 5:1. The amount of oxidizer salt utilized in slurring the gelled nitroparaffin is generally in an amount up to about 20 percent of the nitroparaffin, often in the order of about 10 to 15 percent. The remaining portion of the guar gum, i.e. admixed with the remaining portion of the oxidizer salt, is cross-linkable and undergoes cross-linking in the final product mixture to provide the desired plastic product consistency, completed during storage.

The initial thickening action, i.e. of the hydratable (only) guar gum, provides sufficient increase in consistency to prevent settling of ingredients during the mixing steps but short of that which would preclude uniform mixing of all ingredients. The cross-linkable guar gum, subsequently added, imparts, through cross-linking, the requisite plasticity of the final slurry product.

Various agents contained in the guar gum, and associated conditions for providing the cross-linking action

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11. A composition of claim 3 when said nitroparaffin is 2,2-dinitropropane.

12. A composition of claim 7 containing a mixture of from 40 to 60 percent ammonium nitrate and from 5 to 20 percent sodium nitrate as said oxidizer salt, from 12 to 20 percent water, from 5 to 35 percent of said nitroparaffin component, and from 3 to 17 percent particulate aluminum when the total amount of said nitroparaffin sensitizer component of said slurry is below about 9 percent.

13. A composition of claim 12 wherein said aluminum is in flake form.

14. A method for the manufacture of an inorganic oxidizer salt explosive of the aqueous slurry type containing from 3 to 40 weight percent of a nitroparaffin component, as a sensitizer, selected from the group consisting of nitroparaffins containing from 1 to 3 carbon atoms in the molecule, and mixtures thereof, and guar gum as a thickener, which comprises the steps of forming a premix of a hydratable portion of the said guar gum and a portion of the contemplated oxidizer salt component, in a ratio of said salt to said gum of about 3:1 to 5:1, and the said portion of guar gum not exceeding about 1 percent of the finished slurry product; partially gelling said nitroparaffin sensitizer and mixing the resulting partial gel with not more than 20 percent of its weight, of another portion of the said oxidizer salt, to form a resulting nitroparaffin slurry; admixing the premix, formed as above described, with the total contemplated water component of said slurry to permit hydration of the said guar gum portion; admixing the remaining of the said oxidizer salt and guar gum ingredients with the thus thickened aqueous mixture, and the last said added guar gum being cross-

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linkable; admixing the above-described nitroparaffin slurry with the resulting aqueous mixture, and also admixing a supplemental sensitizer selected from the group consisting of particulate aluminum, powdered coal, dinitrotoluene, and a hydrocarbon oil, with said resulting aqueous mixture, as the last added ingredient, when the total amount of said nitroparaffin sensitizer component of the resulting slurry explosive product is below about 9 percent; and retaining the resulting slurry mixture under conditions for effecting cross-linking of guar gum therein to regulate consistency of same to a predetermined degree.

15. A method of claim 14 wherein particulate aluminum is added to said slurry as a supplemental sensitizer, after the step of adding said nitroparaffin slurry to the said aqueous mixture.

16. A method of claim 14 wherein nitrocellulose in an amount of from 3 to 5 weight percent of the total nitroparaffin is utilized as the partial gelling agent therefor.

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