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3,523,841

AQUEOUS SLURRY TYPE BLASTING COMPOSITIONS CONTAINING A DENSIFIED NITROCELLULOSE SENSITIZER

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No Drawing. Continuation-in-part of application Ser. No. 694,097, Dec. 28, 1967. This application Dec. 16, 1968, Ser. No. 784,212

Int. Cl. C06b 7/00

U.S. Cl. 149—21

18 Claims

ABSTRACT OF THE DISCLOSURE

Inorganic oxidizer salt explosives of the aqueous slurry type are provided which contain a particulate densified nitrocellulose sensitizer component having a particle size of from 100 to 2000 microns and a density of from 1.2 to 1.5 grams per cc., and prepared in accordance with the selected series of steps described. When the proportion of densified nitrocellulose sensitizer component is less than about 8 percent, the composition contains a supplementary sensitizer.

This application is a continuation-in-part of my co-pending application Ser. No. 694,097 now U.S. Pat. No. 3,442,729, filed Dec. 28, 1967.

This invention relates to inorganic oxidizer salt explosive compositions of the aqueous slurry type containing a densified nitrocellulose sensitizer component.

Inorganic oxidizer salt explosive compositions of the aqueous slurry type have had extensive 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 any of the various ingredients.

Various sensitizer materials have been utilized in these compositions, including smokeless powder as described in U.S. 3,235,425, particulate metals and high explosives such as TNT and/or aluminum as described in U.S. 2,930,685, and selected hexamethylenetetramine nitrates as described in U.S. 3,318,740.

This invention is concerned with inorganic oxidizer salt explosives, above described, containing densified nitrocellulose of a limited class of particle size, particle density and manufacture, as an improved sensitizer component.

In accordance with the invention, inorganic oxidizer salt explosive compositions of the aqueous slurry type are provided which contain a sensitizing amount of at least 3 weight percent of a particulate densified nitrocellulose as a sensitizer component together with a supplementary sensitizer therefor when said amount is less than about 8 percent; said particles having a density of from about 1.2 to 1.5 grams per cc. and a maximum linear dimension of from 100–2000 microns, and having been prepared in accordance with the steps comprising forming a water slurry of fibrous nitrocellulose having a nitrogen content of 12.0 to 13.4 weight percent, and said slurry containing said water in an amount greater than that required for distillation of same from said slurry as a minimum boiling water-solvent azeotrope described hereinafter; maintaining the resulting water slurry under agitation at a temperature of at least 20° C., and concurrently adding thereto an active nitrocellulose solvent having limited solubility in water and capable of forming said minimum boiling azeotrope with said water, in an amount to soften and swell the nitrocellulose fibers without dissolving same; and continuing said agitation while

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substantially completely removing said solvent from said slurry by distillation as said azeotrope; whereby resulting residual water slurry contains solid product particles as said particulate densified nitrocellulose for recovery and incorporation into said explosive composition.

The slurry compositions of the invention generally contain (weight basis) from 8 to 35 percent water, from about 20 to 75 percent inorganic oxidizer salt, the above described sensitizer component, and from about 0.2 to 5 percent of a thickener. Now-preferred compositions of the invention contain (weight basis) from 12 to 30 percent water, any one, or combination of, ammonium nitrate, sodium nitrate and sodium perchlorate as the total oxidizer salt, from 8 to 50 percent of said densified nitrocellulose and from 0.2 to 2 percent of the 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.

Although as above described, a supplemental sensitizer is required when the total densified nitrocellulose content is less than about 8 percent, it is within the scope of the invention to supplement the densified nitrocellulose sensitizer whenever desired, the proportion of the supplemental sensitizer generally being from about 2 to about 20 weight percent of the finished slurry. Exemplary supplemental sensitizers are flake aluminum, DNT, crystalline high explosives such as PETN, tetryl, Pentolite, Composition B, smokeless powder, and the like.

One or more supplemental carbonaceous fuel components such as fuel oil and ground coal, and water-soluble organic compounds such as ethylene glycol, formamide and urea are often added to the formulation generally in an amount of from about 1 to 20 weight percent of the total composition. The total energy of the slurry explosive composition is often increased by the addition of one or more of various particulate metal energizers such as aluminum, ferrosilicon, ferrophosphorous, silicon, silicon alloys, and the like, generally in an amount of from about 1 to 20 weight percent of the total composition.

The inorganic oxidizer salt component, in preferred practice, is generally ammonium nitrate or sodium perchlorate or both, often together with sodium nitrate. Further exemplary of suitable inorganic oxidizer salts that can be used alone or with any one of the above inorganic oxidizer salts, are other alkali metal and alkaline earth metal nitrates and perchlorates (including ammonium) as for example magnesium nitrate, calcium nitrate, potassium nitrate, barium nitrate, ammonium perchlorate, potassium perchlorate, calcium perchlorate and magnesium perchlorate. When ammonium nitrate and sodium perchlorate constitute the inorganic salt component, they are utilized in any suitable relative proportions. Often, when either, or both, of ammonium nitrate and sodium perchlorate, is utilized with sodium nitrate, each is utilized in a weight ratio to the sodium nitrate within the range of from about 1:1 to 10:1.

Particle size and type of the oxidizer salt ingredient are not generally 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 amount of thickener is dependent upon the particular thickener and the desired consistency of the finished composition. Generally, a thickener content up to about 5 percent and more often not exceeding about 2 percent is sufficient. When the thickener content is within

the range of 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. When utilizing the now referred thickener component, which is a combination of polymers I and II described hereinbelow, the amount is generally from about 0.4 to 1.5, preferably from 0.8 to 1.2, percent. Exemplary thickeners are sodium carboxymethylcellulose, karaya gum, water-soluble starches, locus bean meal, cereal products, mannogalactans, often guar gum particularly in cross-linked form, polyacrylamide systems, and the like.

The slurry compositions of the invention are characterized by improved sensitivity imparted by the densified nitrocellulose sensitizer component. In some embodiments of the invention they are cap-sensitive by which term it is meant sensitive to detonating action of a No. 8 commercial blasting cap. In all events, they exhibit improved sensitivity and are detonatable by conventional "booster" type charges of PETN (pentaerythritol tetrani- 5 tritate), RDX (cyclotrimethylenetrinitramine), Pentolite (PETN-TNT, 50/50), tetryl, 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 TDX is a plastic carrier such as described in U.S. 2,965,466, and which is detonated 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.

Now preferred, as a thickener component of the slurry composition of the invention, is the polyacrylamide system disclosed and claimed in my parent application Ser. No. 694,097, above referred to, which is a combination of polymers I and II in a polymer I to polymer II weight ratio within the range of 10:1 to 1:1. The polymer I is a partially hydrolyzed acrylamide polymer having a degree of hydrolysis such that 15-40 percent of the monomeric units therein have been converted to the hydrolyzed form, and the polymer having a molecular weight such that a 1 percent solution of the polymer in distilled water will have a viscosity in the range of 1500-1700 centipoises at 25° C.; and said polymer II being formed by copolymerizing acrylamide with at least one acrylate of the group consisting of ammonium and alkali metal acrylates, in an acrylamide to total acrylate weight ratio within the range of 40:1 to 2:1 in an aqueous solvent medium containing from 30-65 weight percent water and selected from the group consisting of water-tertiary butanol, water-acetone, and water-tertiarybutanolacetone, at a temperature of 0-60° C., and cross-linking the resulting polymer as an ingredient of the thickener component, preferably during formation of the slurry explosive, by action of from 0.001 to 0.1 percent of a polyvalent metal salt-cross-linking agent therefor based on the weight of the finished slurry explosive. The polymeric I ingredient above described is that set forth in U.S. Pat. 3,341,383, above referred to, granted Sept. 12, 1967 and in preferred practice contains from about 20 to 35 percent of the monomeric units therein compared to the hydrolyzed form, often in the order of about 22 percent together with a polymer viscosity of about 4000 centipoises.

The polymeric II copolymer ingredient, above described, is disclosed in most of the monomeric unit proportions contemplated in practice of this invention in the copending application of Harrison et al., U.S. Ser. 594,500, filed Nov. 15, 1966; and in preferred practices has an acrylamide to total acrylate weight ratio not exceeding 20:1 and often within the range of about 6:1 to

12:1, a weight ratio of about 9:1 being advantageously employed in many instances.

The polymeric II ingredient is a copolymer and is prepared by only one known process, i.e., which will produce the polymeric II ingredient having the properties applicable in the present invention. This process is referred to as a precipitation polymerization and comprises polymerizing a solution of acrylamide and acrylate monomers in aqueous tertiary butanol, aqueous acetone or aqueous tertiary butanol-acetone in the substantial absence of air while agitating the solution to give a copolymer product that can be isolated by filtration, the aqueous tertiary butanol and aqueous acetone being solvents for the monomers but nonsolvents for the copolymer product.

Solvent and temperature conditions of this precipitation polymerization process are critical. Thus, the solvent for the monomers must be aqueous tertiary butanol, aqueous acetone, or aqueous tertiary butanol-acetone (i.e., mixtures of water with tertiary butanol or acetone alone or with both). The concentrations of water in said mixtures must be 30 to 65 percent, preferably 45 to 60 percent, by weight of said mixtures. The polymerization reaction temperature must be 0° C. to 60° C., preferably 0° C. to 40° C.

The polymerization may be carried out either in the presence or absence of a polymerization catalyst (initiator), but preferably a polymerization initiator is used. Both the types and amounts of free radical initiator applicable are well known in this art. Peroxygen compounds are quite suitable, including e.g., ammonium persulfate, potassium persulfate and hydrogen peroxide. Other free radical initiators include, e.g., a, a'-azo-bis-isobutyronitrile. The peroxygen initiators may be used alone or in combination with activators (also well-known in this art) including, e.g., sodium bisulfite, sodium thiosulfate, tetramethylethylenediamine, thiourea and ferrous chloride, said combination forming a redox system. The amount of initiator usually will not exceed 0.5 percent, preferably is 0.05 to 0.2 percent, 0.05 percent being specifically preferred, by weight of the combined weight of monomers.

Although not necessary, preferably the precipitation polymerization is carried out in the presence of a salt dissolved in the polymerization reaction mixture. By polymerizing in the presence of a salt, or a buffer system comprising one or more salts in combination with another material to complete the buffer system, recovery of the copolymer product is substantially facilitated. These salts and buffer systems include, e.g. (1) alkali metal and ammonium acetates, carbonates, bicarbonates, chlorides, phosphates, sulfates, bisulfates, borates; (2) buffer systems comprising (a) mixture of weak acid or weak base and their salts including (b) phthalates, citrates, borates, phosphates, acetates, ammonium hydroxide, ammonium acetate, ammonium chloride, (c) specific combinations including mixtures of boric acid-borax, citric acid-sodium acid phosphate, sodium carbonate-sodium bicarbonate, ammonium-ammonium hydroxide, ammonium acetate-ammonium hydroxide; or (3) and combination of (1) and (2).

The amount of salt which may be used is about 0.1 to 2.0 percent, preferably about 0.2 to 0.7 percent, by weight of the reaction mixture. If the amount of salt exceeds about 2.0 percent, usually there is a tendency for the granules of the polymeric product to agglomerate in the polymerization reaction mixture. The manner of adding the salt and the point at which it is added are not critical.

Any suitable procedure can be utilized in the manufacture of the slurry type compositions of the invention. In accordance with one such procedure, which is directed to preparation of now-preferred slurry compositions containing the above-described combination of polymers I and II as the thickener component, the required mixture of polymeric I and II ingredients is dispersed in a non-

aqueous liquid, generally ethylene glycol and then added to a hot aqueous solution of the inorganic oxidizer salt in an amount to permit sufficient thickening to retain subsequently added ingredients in suspension. After the addition of all ingredients, during which time the mixture is under constant agitation, a suitable cross-linking agent is added such as polyvalent metal salt. Although the cross-linking agent is preferably the last added ingredient, it can be added at any time during formation of explosive slurry after a portion of each of polymer I and polymer II ingredients is added, preferably after the polymer I and polymer II ingredients are added in their entirety.

Further exemplary of well-known polyvalent metal salt cross-linking agents for the formation of the polymer II ingredient are alum, chromium acetate and ferric citrate. Trivalent metal salt cross-linking agents are generally preferred.

Other polyacrylamide type thickener systems for the aqueous slurries are well known in the art and are described in several U.S. patents, viz. U.S. Pat. Nos. 3,097,120, 3,097,121, 3,321,344, 3,341,383 and 3,355,336. These type thickeners, including the above-described system of polymers I and II, are advantageously employed in the manufacture of inorganic oxidizer salt compositions of the invention exhibiting pourability at temperatures below -20° F. and often below 0° F.

Often, when the slurry product is to be packaged, a paraffin oil, or other suitable agent is added to the packaged slurry product, either as an ingredient of the slurry product or to the container inner wall, to serve as a release agent to facilitate removal of the product from the package for field use, as disclosed and claimed in my copending application.

The densified nitrocellulose sensitizer component of the compositions of the invention is manufactured in accordance with selected process steps disclosed in U.S. Pats. 2,948,601 and 3,346,675. The manufacture involves formation of a water-fibrous nitrocellulose slurry, addition of an active nitrocellulose solvent to the slurry, and azeotropic distillation of the solvent from the slurry, all under agitation conditions.

In carrying out the manufacture of the densified nitrocellulose particle product, the active nitrocellulose solvent is added to the water-nitrocellulose slurry under agitation conditions in an amount sufficient to soften and swell the nitrocellulose fibers without dissolving the same; and is then substantially completely removed from the slurry as a water-solvent azeotrope to form residual hard densified particles of nitrocellulose. Although after boiling off substantially all the solvent (the azeotropic distillation) the residual product particles are generally sufficiently hardened for use in practice of the invention, it is often advantageous to continue heating the residual water-particle mixture, e.g. under continued reflux for a few minutes, to remove any trace amounts of residual solvent and hence to obtain a corresponding further degree of hardening of the product particles. Vigorous agitation is required during the entire period of time extending from initial contact of the nitrocellulose with the active solvent, to final solvent removal, for prevention of substantial agglomeration of the softened nitrocellulose particles into lumps.

Any organic liquid solvent having active solvent power for nitrocellulose can be employed. Preferred solvents are those having an appreciable vapor pressure at or below the boiling point of water, which have limited solubility in water, and which form a minimum boiling azeotrope mixture with water. Suitable solvents include by way of illustration ketones such as methyl ethyl ketone, methyl propyl ketone, methyl isobutyl ketone, methyl butyl ketone, and the like, and esters such as ethyl acetate, propyl acetate, butyl acetate, ethyl butyrate, isopropyl butyrate, ethyl propionate, β -ethoxyethyl acetate, and the like. Methyl isobutyl ketone (MIBK) and butyl acetate are preferred solvents.

Generally, the water-nitrocellulose slurry before solvent addition, contains from 3 to 15 weight percent nitrocellulose, more often from about 7 to 12 percent, although the upper practical limit is governed by the ability to agitate the slurry efficiently.

The ratio of active nitrocellulose solvent to water is regulated to within a range permitting sufficient partitioning of solvent without dissolving any appreciable proportion of nitrocellulose. The desired degree of alteration of physical structure of the nitrocellulose is to obtain particle product, which, after solvent removal, has a particle density of from 1.2 to 1.5 grams per cc., and which in turn generally has a bulk density of from about 25 to 45 lbs./ft.³. Dependent on choice of solvent, the solvent requirement to obtain particulate product of those characteristics will vary. However, regardless of the solvent employed for densification purposes, it is a simple expedient to carry out a preliminary densification trial, to accomplish the required degree of densification. It will be apparent, of course, that densification will improve with increasing quantity of active nitrocellulose solvent employed, until that point is reached where the softened particles begin to agglomerate into large lumps.

Although any suitable agitation means can be utilized in preparation of the densified nitrocellulose sensitizer component, it is necessary that the agitation be vigorous, and accordingly a standard turbo- or high shear-type agitation system is preferred.

Although the temperature of the solvent water-nitrocellulose system can be regulated in any suitable manner, it does not exceed the boiling point of the water component, and it is required that the solvent be removed by distillation as a solvent-water azeotrope. In accordance with one procedure consonant with disclosure in U.S. 2,948,601, the water-nitrocellulose slurry can be heated to a temperature above that of the boiling point of the minimum boiling azeotrope to be formed under reflux, with subsequent addition of the solvent which in turn, by the azeotrope formation, lowers the system temperature with gradual temperature increase as azeotrope removal progresses. After removal of the solvent, the temperature of the slurry is at about the boiling point of the residual water, and that temperature level is retained for a suitable period, say in the order of from about 2 minutes to an hour, to facilitate removal of any last traces of solvent and final hardening of the residual densified particles as mentioned above. In accordance with preferred practice, the temperature of the water-nitrocellulose slurry is maintained at a level within the range of about 20 to 50° C., under high shear agitation, during addition of the nitrocellulose solvent, and the resulting solvent-containing slurry is then held under reflux with gradual temperature increase as removal of the azeotrope progresses. Subsequent heating, i.e. after solvent removal, is continued to accomplish a final hardening of the particles as above described.

The densified nitrocellulose particles are recovered from the residual slurry mixture by any suitable means such as by filtration, or decantation, with recovery of water-wet particles for incorporation into the explosive product. If desired, a predetermined portion of the residual water can be recovered along with particulate densified nitrocellulose product to constitute part or all of the formula weight water of the explosive composition contemplated. Densified particulate product, for the explosive compositions, on the other hand, can be separated from the residual slurry and subjected to solvent extraction for water removal and subsequently dried, utilizing an alcohol as the extraction solvent, as for example, ethanol, isopropanol, butanol, and the like.

The densified nitrocellulose product particles have smooth dense surfaces and porous interior structures. They are optionally rendered further stable as sensitizer components in the compositions of the invention, by the incorporation of a suitable stabilizer material, such as

DPA (diphenylamine) into the nitrocellulose prior to the densification.

The densified nitrocellulose particles formed as dis-

The invention is illustrated with reference to the formulations of the following examples, all on a weight percent basis:

TABLE 1.—FORMULATIONS AND ASSOCIATED SENSITIVITY TEST DATA

Example No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Formulation, weight percent:															
Water	18.0	18.0	18.0	18.0	18.0	20.0	20.0	18.0	18.0	31.2	22.0	18.0	10.9	18.0	16.0
Densified Nitrocellulose: ¹															
Within Scope of the Invention	35.0	30.0	25.0			15.0		10.0		19.5		20.0	20.0	20.0	
Outside Scope of the Invention							15.0								
Smokeless Powder ²															31.6
TNT, pelleted				35.0	33.0				10.0		35.0				
Ammonium Nitrate	25.4	28.0	32.4	26.0	28.0	38.0	38.0	43.6	43.6			30.9	30.7	30.7	37.8
Sodium Nitrate	15.0	17.4	18.0	16.4	18.0	18.0	18.0					15.3	14.7	14.7	9.7
Sodium Perchlorate								15.0	15.0	38.5	30.0				
Hexamethylenetetramine Mononitrate								7.5	7.5						
Ethylene Glycol	5.0		5.0	3.0		7.5	7.5	4.4	4.4	9.3	6.5	6.0	1.8	1.8	3.7
Formamide		5.0			1.9										
Ammonium Sulfamate															0.4
Aluminum ³											5.0		14.0		
Ferrosilicon ⁴														14.0	
Pine Oil	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Thickener ⁵	1.0	1.0	1.0	1.0	1.0	0.9	0.9	0.9	0.9	0.9	0.9	0.7	0.7	0.7	0.7
Paraffin Oil	0.5	0.5	0.5	0.5		0.5	0.5	0.5	0.5	0.5	0.5				
Specific Gravity	1.29	1.30	1.36	1.26	1.36	1.40	1.37	1.41	1.42	1.40	1.42	1.33	1.37	1.51	1.42

Sensitivity Test Data, Detonation Rate, Meters per second:⁶

Unconfined:	Initiator Charge, grams: ⁷														
4"	Titan 225					4,100	(⁸)			4,650	4,650	4,750			
4"	160														5,150
3"	Titan 500				4,650										(⁸)
3"	Titan 225			4,000				3,650		4,750	4,750	4,450	4,450	4,450	
2 1/4"	Titan 225			3,550		4,750	(⁸)			4,650	4,650				
2"	Titan 225				(⁸)	4,550	(⁸)			4,750	(⁸)				
2"	160				(⁸)										
2"	Titan 25	5,250	4,650	4,900											
1 1/2"	Titan 225									4,550	(⁸)				
1 1/2"	5	5,000	4,650	4,650											
1"	Titan 25	5,250	4,650	4,650											
Confined:															
4"	Titan 225								(⁸)						
1 1/2"	40														
1 1/4"	No. 6 cap	5,250													

¹ Particulate Densified Nitrocellulose: Preparation:

Examples 1-3.—Forming a slurry of 100 parts of fibrous nitrocellulose (13.2% N) and 800 parts water; subjecting the resulting water slurry to high shear agitation (900 r.p.m.) while heating the slurry to 50° C.; continuing the high shear agitation at the 50° C. level concurrently with addition to the slurry of 220 parts methyl isobutyl ketone (MIBK) solvent with one part DPA (diphenylamine) dissolved therein; raising the temperature of the resulting MIBK-containing slurry with continued high shear agitation up to the boiling point of the water-MIBK azeotrope; removing MIBK from the slurry by distillation under the continued high shear agitation as the water-MIBK azeotrope; continuing said agitation with heating of the residual slurry under reflux, which was at about 100° C., for five minutes; and recovering from the residual slurry, water-wet solid product particles as the particulate densified nitrocellulose incorporated into the formulations as shown.

Examples 6, 8, 10, 12, 13, 14.—Forming a slurry of 2000 parts of fibrous nitrocellulose (12.4% N) in 20,500 parts of water; subjecting the resulting water slurry to agitation (turbo-type agitator, peripheral speed 1,125 feet per minute) while heating the slurry to 75° C.; continuing the agitation at the 75° C. level concurrently with addition to the slurry of 1,840 parts of MIBK solvent containing 20 parts DPA dissolved therein; raising the temperature of the resulting MIBK-containing slurry with continued turbo-type agitation (1,125 ft./sec.), up to the boiling point of the water-MIBK azeotrope; removing the MIBK from the slurry by distillation, while continuing said agitation, as a water-MIBK azeotrope; continuing said agitation, with heating the residual slurry at about 95° C., for 1/2 hour; and recovering from the slurry, water-wet solid product particles as the particulate densified nitrocellulose incorporated into the formulations as shown.

Example 7.—A commercially available particulate densified nitrocellulose prepared by forming a solution of fibrous nitro-

cellulose in a nitrocellulose solvent and precipitation of particle product from the solution by addition of water thereto.

Particle Properties:

Examples 1-3.—Particle size range, 150 to 140 microns; bulk density, 45 lbs./ft.³; distribution (Standard Sieve Size, percent on mesh per inch), 0 on 20, 70 on 40, 20 on 60, 60 on 80, 2 on 100, 2 on 200 (and trace through 200).

Examples 6, 8, 10, 12, 13, 14.—Particle size range, 100 to 1,000 microns; bulk density, 35* lbs./ft.³; distribution (Standard Sieve Size, percent* on mesh per inch) 40 on 20, 35 on 40, 10 on 60, 5 on 80, 3 on 100, and 7 on 200.

² 40 mm. ground smokeless powder (single base).

³ Particulate aluminum, 90 percent through 30 mesh (nonflake).

⁴ Particulate ferrosilicon alloy—50 percent iron, 50 percent silicon.

⁵ The thickener in each of the formulations of Examples 1-11 inclusive was formed from polymer I and polymer II as described herein; and the polymer II was a copolymer of acrylamide and sodium acrylate, in a weight ratio of acrylamide to sodium acrylate of 9:1; basic aluminum acetate utilized as cross-linking agent for polymer II—0.003 weight percent for each formulation of Examples 1-5, and 0.002 weight percent for each formulation of Examples 6-11. In each of Examples 12-15, the thickener was guar gum cross-linked with potassium pyroantimonate (0.04 percent) as cross-linking agent utilizing fumaric acid (0.04 percent) for regulation of pH for cross-linking.

⁶ Measured as average detonation velocity over a 20 cm. length, at the end of a 28" long column of explosive. The time for detonation to proceed across the 20 cm. length of explosive was measured electronically with a counter-chronograph. m/s=meters per second.

⁷ All "Titans" are standard Pentolite boosters of grams weight shown. Thus Titans 500, 225 and 25 contain about 475, 200, and 20 grams Pentolite, resp. Except for No. 6 cap, 1 1/4" confined, Ex. 1, all other initiator charges are shown as grams Pentolite.

⁸ Failed.

*Based on average of several batches prepared as above described.

closed and claimed herein differ from conventional single base smokeless powder particles, particularly inas- 60
much as the densified nitrocellulose particles contain porous structure and air voids and are not completely colloidized; they accordingly contain some uncolloidized nitrocellulose which although substantially free from fibrous structure is nevertheless in a unique agglomerated form in contrast to single base smokeless powder particles which are dense, completely colloidized and are substantially free from porous structure.

Although the mechanism by which the densified nitrocellulose product particles impart improved sensitivity to the slurry explosive in practice of the invention, is not clearly understood, it appears to involve the particular porous and incompletely colloidized particle structure, unique to their manufacture, as disclosed and claimed herein.

Examples 1-3 inclusive illustrate compositions of the invention containing from 25 to 35 percent of the densified nitrocellulose sensitizer component, and associated sensitivity properties. These examples show sensitivities at small diameters, unconfined, with high detonation rates in response to action of small initiator charges, including cap sensitivity at a diameter of 1 1/4 inch, confined (Ex- 65
ample 1).

Examples 4 and 5 illustrate formulations substantially the same as those of Examples 1-3 except that TNT is the sensitizer component in lieu of the densified nitrocellulose. As shown, the formulations of Examples 4 and 5 failed at a 2 inch diameter, unconfined, in response to action of a 160-gram charge and a Titan 225 of Exam- 70
ples 4 and 5 respectively. In contrast, the formulations of Examples 4 and 5 respectively. In contrast, the formu- 75
lations of Examples 1, 2 and 3 shot at the same unconfined

diameters in response to detonating action of charges as small as 25 grams.

Examples 6 and 7 illustrate criticalness of the densified nitrocellulose sensitizer component, on which the invention is based. Thus, the formulation ingredients, and ingredient proportions, of Examples 6 and 7 are exactly the same including the presence of a densified nitrocellulose sensitizer component. However, the densified nitrocellulose sensitizer component of Example 6 was that prepared in accordance with method contemplated by the invention whereas the densified nitrocellulose component of Example 7 was formed in accordance with method outside the scope of that contemplated by the invention, see footnote 1 of the table. As further shown, the formulation of Example 7, containing the densified nitrocellulose component outside the scope of the invention, failed to shoot at 2 inch and 2½ inch diameters unconfined, in response to action of a Titan 225 whereas the formulation of Example 6 containing a densified nitrocellulose sensitizer component in accordance with the invention shot at both diameters under the same conditions at high detonation rates.

Examples 8 and 9 illustrate formulations containing high energy fuels and oxidizers, i.e. with reference to hexamethylenetetramine mononitrate and sodium perchlorate. Each formulation contains 10 percent sensitizer component except that that of Example 8 is a densified nitrocellulose in accordance with the invention and that Example 9 is pelleted TNT. These examples show a significantly higher sensitivity imparted by the densified nitrocellulose than by the same content of TNT. Thus, the formulation of Example 8 shot at a rate of 4100 meters per second at a diameter of 4 inches unconfined in response to action of a Titan 225 whereas the formulation of Example 9, containing TNT in lieu of the densified nitrocellulose, failed under those conditions and also at a 4-inch diameter confined.

Examples 10 and 11 illustrate compositions of the invention containing sodium perchlorate as the only oxidizer salt, the formulation of Example 10 containing a densified nitrocellulose sensitizer component in accordance with the invention and the formulation of Example 11 containing TNT in lieu thereof. As shown, the formulation of Example 10, although containing only 19.5 percent densified nitrocellulose, shot at a high rate at unconfined diameters of 1½ and 2 inches, each in response to action of a Titan 225, whereas the formulation of Example 11 containing 35 percent TNT as a sensitizer failed under the same firing conditions.

Examples 12 through 14 are further illustrative of compositions of the invention, Example 13 and 14 being particularly illustrative of metallic energizer ingredients, i.e. with reference to particulate aluminum.

Example 15 shows a formulation containing 31.6 percent 40 mm. ground single base smokeless powder as a sensitizer component in lieu of a particulate densified nitrocellulose. Although the formulation of Example 15 differs somewhat from that of Example 2 in ammonium nitrate to sodium nitrate ratio, the sensitizer proportions are closely comparable, i.e. 31.6 vs. 30.0. As shown, the single base smokeless powder sensitized formulation of Example 15 failed to detonate at a 3-inch unconfined diameter in response to action of a Titan 500 booster whereas the formulation of Example 2 detonated at lower diameters, in response to action of a Titan 25. Accordingly, a comparison of Examples 15 and 2 shows a significantly greater sensitivity imparted by a densified nitrocellulose sensitizer component in practice of the invention than by a conventional single base smokeless powder type sensitizer.

As will be evident to those skilled in the art, various modifications can be made or followed, in the 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 I 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 a sensitizing amount of at least 3 weight percent of a particulate densified nitrocellulose as a sensitizer component together with a supplemental sensitizer therefor when said amount is less than about 8 percent; said densified nitrocellulose having a particle density of from about 1.2 to 1.5 grams per cc. and a maximum linear dimension of from 100 to 2000 microns, and having been prepared in accordance with the steps comprising forming a water slurry of fibrous nitrocellulose having a nitrogen content of 12.0 to 13.4 weight percent, and said slurry containing said water in an amount greater than that required for distillation of same from said slurry as a minimum boiling water-solvent azeotrope described hereinafter; maintaining the resulting water slurry under agitation at a temperature of at least 20° C., and concurrently adding thereto an active nitrocellulose solvent having limited solubility in water and capable of forming said minimum boiling azeotrope with said water, in an amount to soften and swell the nitrocellulose fibers without dissolving same; and continuing said agitation while substantially completely removing said solvent from said slurry by distillation as said azeotrope; whereby resulting residual water slurry contains solid product particles as said particulate densified nitrocellulose for recovery and incorporation into said explosive composition.

2. An aqueous slurry composition of claim 1 containing, on a weight basis, from about 8 to 35 percent water, from about 20 to 75 percent inorganic oxidizer salt, and from about 0.2 to 5 percent of a thickener.

3. An aqueous slurry composition of claim 2 containing from 8 to 50 percent of said sensitizer component.

4. An aqueous slurry composition of claim 2 containing less than 8 percent of said particulate densified nitrocellulose together with from 2 to 20 weight percent of said supplemental sensitizer therefor.

5. An aqueous slurry composition of claim 2 containing a particulate metal energizer.

6. An aqueous slurry explosive composition of claim 2 wherein, during preparation of said densified nitrocellulose, said slurry of water and nitrocellulose is maintained under high shear agitation at a temperature of from about 20 to 50° C. during the entire time that said solvent is added thereto.

7. An aqueous slurry composition of claim 6 wherein after removal of said solvent from said slurry, the residual distillation product is maintained under reflux for a period sufficiently long to effect removal of any residual solvent and, concomitantly, any further hardening of said product particles therein.

8. An aqueous slurry explosive composition of claim 2 wherein during preparation of said densified nitrocellulose, said slurry of water and nitrocellulose is maintained at a temperature up to about 75° C. under turbo-type agitation conditions during the entire time that said solvent is added thereto.

9. An aqueous slurry composition of claim 8 wherein after removal of said solvent from said slurry, the residual distillation product is maintained under reflux for a period sufficiently long to effect removal of any residual solvent and, concomitantly, and further hardening of solid product particles therein.

10. An aqueous slurry composition of claim 2 at least one salt of the group consisting of ammonium nitrate and sodium perchlorate, together with sodium nitrate in a weight ratio to said sodium nitrate of from 1:1 to 10:1.

11. An aqueous slurry composition of claim 2 wherein said thickener is guar gum in cross-linked form.

12. An aqueous slurry explosive composition of claim 2 containing a polyacrylamide thickener system as said thickener.

13. An aqueous slurry explosive composition of claim 12 wherein said thickener component is a combination

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of polymers I and II in a polymer I to polymer II weight ratio within the range of from 10:1 to 1:1, as a thickener component imparting thickening action to said slurry while maintaining same pourable; said polymer I being a partially hydrolyzed acrylamide polymer having a degree of hydrolysis such that 15-40 percent of the monomeric units therein have been converted to the hydrolyzed form, and the polymer having a molecular weight such that a 1 percent solution of the polymer in distilled water will have a viscosity in the range of 1500-7000 centipoises at 25° C., and said polymer II being a cross-linked product formed by copolymerizing acrylamide with at least one acrylate selected from the group consisting of ammonium and alkali metal acrylates in an acrylamide to total acrylate weight ratio within the range of from 40:1 to 2:1 in an aqueous solvent medium containing from 30-65 weight percent water and selected from the group consisting of water-tertiary butanol, water-acetone, and water-tertiary butanol-acetone, at a temperature of from 0-60° C., and cross-linking the resulting copolymer as an ingredient of said thickener component during the formation of said explosive composition by action of from 0.001 to 0.1 percent of a polyvalent metal salt cross-linking agent therefor, based on the weight of said explosive.

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14. An aqueous slurry composition of claim 13 wherein said inorganic oxidizer salt comprises sodium perchlorate.

15. An aqueous slurry composition of claim 14 containing from 1 to 20 weight percent of a water soluble carbonaceous fuel.

16. In an aqueous slurry composition of claim 14 ethylene glycol and hexamethylenetetramine mononitrate as said water-soluble fuel.

17. An aqueous slurry composition of claim 14 containing from 1 to 20 weight percent of a water-insoluble carbonaceous fuel.

18. An aqueous slurry composition of claim 13 containing from 0.4 to 1.5 weight percent of said thickener formed from said polymers I and II.

References Cited

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U.S. Cl. X.R.

149-2, 41, 44, 45, 48, 49, 63, 76, 78, 79, 92, 94, 96, 100

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. U.S.P. 3,523,841 . Dated August 11, 1970

Inventor(s) Herbert G. Knight, Jr. (Case 1-4

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Col. 3, line 47 of p.p.; Page 6, line 16 of spec.
"1500-1700" --should read-- "1500-7000"

Table 1, Example 13 (Water) - Page 15 of spec.
"10.9" --should read-- "18.0"

Col. 8, of pp; page 17 of spec.; footnote 1 under Particle Properties, Example 1-3
"60 on 80" --should read-- " 6 on 80"

Col. 8, line 73 to 74 of p.p.; Page 19, line 13 of spec.
"In contrast, the formulations of Examples 4 and 5 respectively." should be deleted.

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Attest:

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