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[54] EXPLOSIVE COMPOSITIONS CONTAINING CALCIUM NITRATE

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[56] **References Cited**

UNITED STATES PATENTS

3,180,768	4/1965	Scott, Jr.	149/46 X
3,645,809	2/1972	Stow, Jr.	149/44 X
3,660,181	5/1972	Clay et al.	149/44 X
3,713,917	1/1973	Cook et al.	149/61 X
3,303,073	2/1967	Graham et al.	149/61 X
3,397,097	8/1968	Atadan et al.	149/46
3,450,582	6/1969	Sheeran	149/2
3,465,675	9/1969	Bronstein, Jr.	149/44 X
3,523,048	8/1970	Hopler	149/109
3,522,117	7/1970	Atadan et al.	149/60

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[57] ABSTRACT

Water-containing explosive compositions, substantially stable against gravitational segregation of the ingredients and degasification, comprise a homogenous emulsion-like dispersion of (1) inorganic nitrate oxidizer, e.g., ammonium nitrate, (2) finely dispersed particles of liquid hydrocarbon fuel, e.g., fuel oil, (3) calcium nitrate and (4) an agent to sufficiently thicken said composition to substantially inhibit such gravitational segregation during formulation and/or use and improve the water resistance of the composition.

19 Claims, No Drawings

EXPLOSIVE COMPOSITIONS CONTAINING CALCIUM NITRATE

The present invention relates to improved explosive compositions containing calcium nitrate. In general, it concerns explosives employing a liquid hydrocarbon fuel in emulsion-like form and calcium nitrate.

BACKGROUND

Fuel-sensitized ammonium nitrate (AN) explosives have become significant factors in the field of commercially successful blasting agents. ANFO (ammonium nitrate prills oxygen balanced with fuel oil) explosive compositions, even though widely used and suitable for some uses, are not suitable, per se, for use in water-containing boreholes. Aqueous slurry blasting agents, e.g., so-called aluminized NCN slurries comprising a stable slurry of solid AN particles and aluminum metal sensitizer in an aqueous AN solution, (see for example U.S. Reissue Pat. No. 25,695), have been very successfully commercially employed even in water-containing boreholes. In addition, both solid and liquid hydrocarbon fuels, for example fuel oil, have also been successfully incorporated into NCN slurries, the liquid fuel by use of conventional emulsifying agents. These and other types of fuel sensitized AN explosives are discussed in "Explosives, a Survey of Technical Advances", M.A. Cook, *Industrial & Engineering Chemistry*, July, 1968, pages 44–55.

In prior art attempts to provide more economical explosive compositions by eliminating the metal sensitizer (e.g., aluminum) or high explosive sensitizer (e.g., TNT having a particle size greater than 30 mesh) compositions in various forms including aqueous slurries comprising essentially AN (or AN/sodium nitrate (SN) combinations) fuel oil, and water, have been suggested but these latter compositions have not detonated satisfactorily in dry or water-containing boreholes except by use of multiple boosters at high booster/slurry ratios, e.g. 1/25 or higher.

Calcium nitrate (CN) has heretofore been disclosed (e.g., U.S. Pat. Nos. 3,083,127, 3,147,163 and 3,236,180) as essentially equivalent to or as a partial substitute for AN (and/or SN) employed as inorganic oxidizers in various types of explosive compositions, including those containing liquid hydrocarbon fuels. The use of two or more inorganic oxidizers, one of which could be CN, has been disclosed in the prior art (e.g. U.S. Pat. Nos. 3,201,291, 3,249,476) as a means for reducing the fudge point or crystallization temperature, and thus permit higher salt concentration in water-containing explosives. The use of CN as a possible constituent of explosives is also disclosed in other references including U.S. Pat. Nos. 3,390,029, 3,450,582, 3,459,608, 3,475,238 and 3,496,040. Both AN and SN have found extensive commercial use, but CN has apparently not been in substantial commercial use in any explosive composition. CN is generally considered less effective as an oxidizer for explosives than AN, even though calcium is divalent and therefore, has two nitrate groups per calcium atom while AN has only one nitrate per ammonium ion. Moreover, industrial grade CN is also normally hydrated (e.g., $CN \cdot 4H_2O$), which further reduces its oxiding capacity. Thus, the prior art does not suggest that any other improvements in explosive compositions could be achieved by the use of CN.

It has been found, however, that the incorporation of CN slurry blasting compositions comprising solid particles of AN or mixtures of AN or SN (sodium nitrate) dispersed in a thickened or gelled solution of AN which solution also contains a low molecular weight alkylene glycol, e.g., ethylene glycol does enhance the effectiveness of such compositions. The use of CN (a) permits the use of less aqueous solvent to obtain a pourable, pumpable (though viscous) slurry; (b) reduces the fudge point (congelation temperature) and thereby avoids unnecessary heating of the solution to obtain a desired concentration of oxidizer salt; and (c) accelerates the firming up or rigidification of the slurry after it is delivered or packaged thereby preventing the segregation and separation of suspended particles in the slurry, improving water resistance and sensitivity by fixing previously entrapped or otherwise incorporated gas bubbles against migration and escape. This invention is disclosed and claimed in U.S. patent application Ser. No. 90,005 filed Nov. 16, 1970. The compositions described therein preferably contain solid particulate fuels or sensitizers such as aluminum, gilsonite, sulfur, TNT, etc.

It has been further found that CN can be used according to the present invention to provide a fuel-sensitized AN base explosive composition having unique and useful characteristics. The water-containing explosives such as slurry blasting agents which have achieved commercial importance have employed solid fuels such as aluminum, TNT, sulfur, smokeless powder, solid hydrocarbons and others dispersed with solid oxidizers in a continuous fluid phase which generally consists of a thickened or gelled solution of an oxidizer. While economies can be effected by the use of less expensive fuels such as liquid petroleum fractions, e.g., fuel oils, stably dispersing the fuel oil in the water-containing phase of the explosive composition is difficult. In accordance with this invention it has been found that owing to a tendency of CN to produce an emulsion-like composition of finely-dispersed liquid hydrocarbon fuel particles, CN may be employed in proper proportions in a liquid hydrocarbon fuel sensitized, AN containing explosive in which the fuel and (the solid) part of the AN with or without other oxidizers such as SN uniformly dispersed in a continuous aqueous fluid phase generally consisting of a thickened or gelled oxidizer solution. Such compositions have extraordinary sensitivity to detonation, and can be detonated even at relatively low temperatures, e.g., 5°C and lower.

This tendency of CN to form an emulsion-like dispersion of liquid hydrocarbon fuel is not thoroughly understood. The CN however cannot be considered to function as a conventional emulsifier in dispersing the liquid hydrocarbon fuel. Conventional emulsifying agents or emulsifiers are commonly employed in very small amounts and are surface-acting agents which allow the formation of a stable, non-coalescing emulsion of liquid particles in another liquid phase. CN in the present invention is distinguished from these conventional emulsifiers in that (1) CN must be used in a greater proportion (5 percent or more based on the total weight of the composition) before it will produce an emulsion-like dispersion, (2) CN will not by itself form a stable emulsion and a thickening agent must be employed following the emulsion-like dispersion by the CN to prevent coalescence and subsequent loss of the emulsion-like form and (3) CN functions not only to form an emulsion-like dispersion but also as an oxidizer for functional component of the explosive, an effect not produced with conventional emulsifiers.

In the following description unless otherwise specifically indicated all references to percentages (%) or parts mean weight percentages and parts by weight based upon the total weight of the composition.

ESSENTIAL INGREDIENTS

The essential ingredients of the explosive compositions of the present invention are CN; a liquid hydrocarbon fuel, an inorganic oxidizer salt other than CN, for example AN with or without other oxidizers, sufficient water to form a pumpable composition at the preparation or mixing temperature, the water being either from hydrated CN or added water or both; and a suitable thickening agent.

The CN used in the present invention functions primarily as an oxidizer and an emulsion-producing agent. It also provides a means of reducing the total water content by forming a beneficially eutectic solution when combined with certain other salts in solution. The CN preferred for use is the commercially available "fertilizer grade" CN. A typical analysis of a commercially available CN is shown in Table I.

Table I — Typical Analysis of "Fertilizer Grade" CN

Component	Wt. %
$Ca(NO_3)_2$ (anhydrous basis)	80.4-81.4%
H_2O (of hydration)	13-14%
$NH_4(NO_3)$	4.8-5.4%
$Mg(NO_3)_2$	0.5-1.0%

U.S. Sieve No. (mesh)	
+10	4.5%
+20	78.0%
+40	97.0%
+60	99.7%

Although the above fertilizer grade CN is a hydrated and prilled product, having the particle size distribution set forth, the CN can also be ground or otherwise treated to provide different physical forms and/or particle size distributions. Moreover, pure anhydrous CN or other hydrates of CN can also be used. If other than hydrated CN is used, generally a small amount of added water as distinguished from that present as water of crystallization in the CN is also employed as more fully described hereafter, the amount of water being directly proportional to the state of hydration of the CN used and total amount of water required to provide a composition which is pumpable in the course of preparing the composition. The CN is generally dissolved or put into solution in preparing the explosive compositions; however, under service conditions (i.e., time of use, temperature, pressure, and other conditions of use of the explosive composition) from a small proportion to substantially all of the CN is in a solid hydrated form.

In the explosive compositions of the present invention the liquid hydrocarbon fuel is the primary fuel and is present in the form of a uniform and homogeneous dispersion of discrete liquid droplets. Under service conditions, the dispersed liquid particles are approximately 0.001 cm. or smaller in diameter, which, because of the combined effect of the CN and the thickening agent, do not rapidly settle out of or coalesce in the medium in which such particles are suspended. Preferably, the dispersed liquid hydrocarbon fuel particles are of colloidal size, i.e., about 5 to about 5,000 Angstroms.

The hydrocarbon fuels can be aliphatic, alicyclic and/or aromatic. Suitable fuels can be either saturated and/or unsaturated. For example, benzene, toluene, and the zylenes can be employed. Preferred fuels include mixtures of normally liquid hydrocarbons generally referred to as petroleum distillates such as gasoline, kerosene, and diesel fuels. A particularly preferred liquid fuel is No. 2 fuel oil.

One or more conventional thickening agents are employed in the course of preparing the explosive compositions of the present invention in order to regulate the viscosity of the composition so as to permit pumping of the composition while at the same time holding in place finely divided sensitizing gas bubbles and also preventing any substantial segregation and/or coalescence of the ingredients. The thickening agents also improve the water resistance of the composition. Conventional thickening agents known in the art including guar gums, starches and synthetic polymeric products such as the anionic heteropoly-saccharide polymer identified as "Biopolymer XB-23" can be employed, the solution of which depends upon the rheology of the composition.

In addition to CN, water, a liquid hydrocarbon fuel and a suitable thickening agent, the explosive compositions of the present invention contain at least one inorganic oxidizer salt other than CN. Such inorganic oxidizer salts are well known in the art and include inorganic nitrates such as AN and SN, as well as inorganic chlorates, perchlorates such as sodium perchlorate. AN employed in the present invention can be a fertilizer grade and/or an explosive grade. Both granular and prilled forms are suitable. In preparing the composition of the present invention the inorganic ozidizer salt can be used in solution, or it can be used as a solid. In one preferred embodiment, a part of the salt used as AN in aqueous solution and another part of the salt is used as solid AN.

The relative amounts of the ingredients employed in the explosive compositions of the invention will, of course, depend upon various factors such as the desired explosive strength, sensitivity, and the like; and those skilled in the art will no doubt be able, by routine experimentation, to obtain desired optimum effects. In general, detonable compositions have been employed wherein the amount of inorganic oxidizer salt other than CN ranges from about 25 percent to about 75 percent, preferably about 60 percent to about 70 percent of the composition, and the amount of CN used being at least sufficient to effect dispersion of the liquid hydrocarbon fuel in the composition during its preparation. Satisfactory compositions have been prepared wherein the CN content has been as low as about 5 percent or as high as about 60 percent. Preferred compositions will usually contain about 15 percent to about 30 percent of CN.

The amount of liquid hydrcarbon fuel dispersed in any particular composition of the invention should generally be determined from oxygen balance considerations, such that the explosive composition is oxygen balanced to within about +10 percent to about −20 percent of the oxygen necessary to balance the composition. Preferred compositions will contain about 6 percent to about 12 percent hydrocarbon in emulsion-like form.

While the compositions of the invention can be prepared without any added water (e.g., water added in addition to the water of crystallization of CN), generally about 1–10 percent, and preferably 3 percent to about 6 percent added water is used in the preparation. Generally, about 0.05 percent to about 0.50 percent, preferably about 0.1 percent, of a conventional thickening agent is used.

Preferred Ingredients

In addition to essential ingredients, the explosive compositions of the present invention generally contain, as preferred ingredients in the preparation of the composition, a density lowering or gassing agent such as sodium nitrite, a cross-linking agent to effect the gelation of the selected cross-linkable thickening agent, and a fudge point or crystallization temperature depressant such as sodium nitrite.

As is well known in the art, gassing agents such as sodium nitrite and hydrogen peroxide have been employed heretofore to lower the density and thereby in part control the sensitivity of explosive slurry compositions. The compositions of the present invention preferably employ a small amount, e.g., about 0.01 percent to about 0.2 percent or more, most preferably about 0.05 percent of such gassing agent in order to obtain a density under service conditions of about 1.0 gms/cc to about 1.3 gms/cc.

Cross-linking agents in combination with suitable cross-linkable thickening agents are also preferably employed, if it is desired to gelatinize the composition during preparation, in order to stabilize the fine dispersion or distribution of the emulsion-like particles of liquid hydrocarbon fuel as well as prevent the undesired escape of gas bubbles and thus maintain the sensitivity to detonation resulting from the fine dispersion. Cross-linking agents are especially useful where the stability or integrity of the composition must be maintained in the presence of water-containing boreholes. If guar gum is employed, for example, the calcium ion resulting from the solution of CN functions, in part, as a cross-linking agent. In addition, it has been found that excellent cross-linking of guar gum can be obtained using a small amount, e.g., about 0.05 percent to about 0.2 percent of an aqueous solution of ferric nitrate and sodium dichromate. Other cross-linking systems will also be apparent to those who are skilled in the art.

Other Desirable Ingredients

SN is known in the art (e.g., U. S. Pat. No. 3,249,476) to be useful as an inorganic oxidizer salt component which lowers the crystallization temperature, or fudge point, of compositions containing AN. It is desirable in the compositions of the present invention to be able to control the fudge point and the inclusion of SN as a component of the inorganic oxidizer salt solution permits a degree of control over the fudge point. In one embodiment of the invention the composition contains about 3 percent to about 5 percent SN.

Optional Ingredients

Various optional ingredients can also be included in the compositions of the present invention. For example, supplemental solid fuels such as particulate aluminum, magnesium alloys, normally solid hydrocarbons, and the like may be added to increase the strength of the compositions. Thiourea may also be employed in very small amounts, e.g., about 0.05 percent, to control the rate at which sodium nitrite gassing agent functions. Ethylene glycol, formamide, and other mutually dispersible ingredients may also be included in small amounts which do not change the essential character of the basic composition.

Preparation of CN Containing Explosives

The explosive compositions of the present invention are preferably prepared by finely dispersing or distributing a liquid hydrocarbon fuel in an emulsion-like form in an aqueous solution of the oxidizer salt, e.g., AN and/or AN and SN, in which is also incorporated the CN. The thickening agent is then added. The resultant dynamically stable dispersion is either pumped into suitable containers for use as packaged explosives or pumped by means of pump trucks similar to those described in U.S. Pat. No. 3,303,738 in an on-site mixing and pumping operation used for the direct loading of boreholes. In a typical prepartion, an oxidizer salt solution having a fudge point of about 50°C. is prepared by mixing about 3 percent SN, 30 percent fertilizer grade CN (typical analysis of Table I), 30 percent AN and 3 percent added water. The solution as used is at about 60°C., or about 10°C. higher than the fudge point. The preparation of the solution may be facilitated if the SN is first dissolved in the added water followed by the addition of a part of the AN and then by the addition of the CN and the remainder of the AN. Small amounts of a conventional thickening agent, e.g., 0.1–0.2 percent are then added. The resulting ozidizer salt solution is then combined with a liquid hydrocarbon fuel in emulsion-like form, e.g., about 7 percent No. 2 fuel oil, by injecting fine size particles or droplets of the fuel oil through one or more spray nozzles into a moving stream of the solution to obtain a substantially homogeneous and fine dispersion. To this resulting stable dispersion one or more of the above described preferred, desirable and/or optional ingredients may be added, such as cross-linking agents and/or additional amounts of solid AN and particulate aluminum with or without a conventional gassing agent. Conventional equipment such as mixing funnels, pumps, solids eductors and the like can be employed, provided that the resulting composition consists essentially of a substantially homogeneous fine dispersion which is gasified to the desired bulk density by stirring in air, for example, or by incorporating a gassing agent.

If the above-described preparation technique is used, the resultant stable dispersion of normally liquid hydrocarbon fuel droplets intimately and homogeneously associated with the oxidizer components and other additives if placed directly in a borehole can be shot promptly. When gassing agents are used generally the composition can be shot after about 10 minutes. As the composition gradually cools, the soluble oxidizer salts begin crystallizing out of the solution. After about 10–14 hours, depending upon amounts, heat transfer conditions, etc., the composition becomes firm but pliable. In about 24 hours under normal conditions, the composition will become hard and be substantially devoid of free water as distinguished from any bound water which may be present as water of crystallization, water of hydration and the like. During the entire cooling period, the liquid hydrocarbon fuel droplets remain dispersed uniformly and homogeneously throughout the composition in a free state. If one's finger were rubbed across a transverse cross section of a fully hardened composition of this invention small amounts of the liquid hydrocarbon fuel would be transferred to the finger.

The effectiveness of the composition of this invention is generally not effected by the changing state of the composition during cooling. The composition will be more sensitive at the higher temperatures occurring during the cooling process.

Although the above-described method is illustrative of the preferred embodiment, other formulation techniques which will achieve the objectives of this invention will be apparent to those skilled in this art. Accordingly, this invention is not to be limited except as may be set forth in the appended claims by any manipulative formulation techniques.

The present invention can be further understood by reference to the following illustrative examples.

Example 1

In this example, compositions of the present invention having the ingredients and characteristics set forth in Table II were prepared and successfully detonated as indicated in Table II.

Table II

Composition	A	B	C
Ingredients, (wt.%)			
Solution Containing:			
AN	29.4	35.5	35.5
CN (Table I Analysis)	23.5	28.4	28.4
SN	3.5	4.3	4.3
H_2O	3.5	5.3	5.3
Thickening Agents$_1$	0.12	0.14	0.14
Thiourea	0.06	0.07	0.07
Fuel Oil, No. 2	7.0	7.5	7.5
Dry Solid AN	33.0	20.0	20.0
Gassing Agent$_2$	0.2	0.2	0.2
Cross-linking Agent$_3$	0.2	0.1	0.05
Properties			
Solution Temperature	70°C	70°C	70°C
Fuel Oil Temperature	10°C	10°C	10°C
Density (gm/cc) at Loading$_4$	1.20	1.19	1.19
Consistency (about 12 hrs after loading)	Hard-Solid	Hard-Solid	Hard-Solid
Shooting Results [in cardboard tubes (length = 6× diameter), with 3 in. dia. × 2 in. long cast booster]			
at 20°C, 3" diameter	F	D	D
at 5°C, 4" diameter	F	F	F
5" diameter	D	D	D

1 — Thickening agents = 4 parts Stein-Hall "J-100" guar gum/1 part General Mills "XB-23", a commercially available anionic heteropoly saccharide produced by the fermentation of a carbohydrate by the bacterium, Xanthomonas compositions.

2 — Gassing agent = 1 part $NaNO_2$/4 parts H_2O

3 — Cross-linking agent = 1 part $Na_2Cr_2O_7 \cdot 2H_2O$/1 part H_2O/1 part $Fe(NO_3)_3 \cdot 9H_2O$

4 — Bulk density at atmospheric pressure

F — Failed

D — Detonated

The results in Table II indicate that compositions of the present invention successfully detonated at temperatures as low as 5°C. when fired in 5 inch diameter unconfined charges.

EXAMPLE II

In this example, liquid hydrocarbon fuels other than No. 2 fuel oil were used to prepare and successfully detonate compositions of the present invention. The compositions and results are shown in Table III.

EXAMPLE III

In this example, aluminum metal was added as an additional or secondary, fuel to a composition of the invention and the resulting composition, shown in Table IV was successfully detonated.

TABLE III

Composition	D	E	F	G	H
SN	4.2	4.2	4.2	4.2	4.2
H$_{20}$	2.8	2.8	2.8	2.8	2.8
CN (Table I Analysis)	30.8	30.8	30.8	30.8	30.8
AN	32.2	32.2	32.2	32.2	32.2
Thiourea	0.1	0.1	0.1	0.1	0.1
Thickening Agent*	0.1	0.1	0.1	0.1	0.1
Ethylene Glycol	0.2	0.2	0.2	0.2	0.2
Dry AN	22.0	22.0	22.0	22.0	22.0
Gassing Agent**	0.004	0.4	0.4	0.4	0.4
Cross-linking Agent***	0.3	0.3	0.3	0.3	0.3
No. 2 Fuel Oil	7.8	2.6			
No. 6 Fuel Oil		5.2			
Toluene			7.8		
Benzene				7.8	
Xylene					7.8
Density at 20°C (g/cc)****	1.17	1.12	1.15	1.17	1.18
Shooting Results (3 in. dia. × 2 in. long cast booster)					
at 20°C – 3" dia.	failed	failed	failed	failed	failed
– 4" dia.	detonated	detonated	detonated	detnotated	detonated
at 5°C – 3" dia.	failed				
– 4" dia.	detonated		failed	failed	failed
– 5" dia.		failed	detonated	detonated	detonated
– 6" dia.		detonated			

*Stein Hall J-100 Guar Gum.

**Gassing Agent same as employed in Example I.

***Cross-linking Agent = 9 parts dimethyl formamide/1 part $TiCl_4$.

****Bulk Density at atmospheric pressure.

Table IV

Compositions	Wt.%
SN	3.6
H_2O	2.4
CN (Table I Analysis)	23.8
AN	29.7
Thiourea	0.12
Thickening Agent*	0.12
Ethylene Glycol	0.24
Dry AN	25.3
Gassing Agent**	0.05
Cross-linking Agent ***	0.3
No. 2 Fuel Oil	4.4
Aluminum metal (LSA-123 coated atomized aluminum)	10.0
Density at 20°C (g/cc)****	1.20
Shooting Results (3 in. dia. × 2 in. long cast booster)	
at 5°C — 3" dia.	failed
— 4" dia.	detonated
at 0°C — 6" dia.	detonated

* See Table III

** See Table III

*** See Table III

**** See Table III

Characteristics and Use of CN Containing Explosives

In general, the explosive compositions of the present invention will find particular utility as blasting agents for use in boreholes having a diameter conventionally employed in open pit blasting operations or the like. In such applications, it is generally desirable to prepare a dynamically stable slurry of the ingredients either at the site of the borehole or at a location remote from the borehole and then pump the resulting composition through a hose and into the borehole.

During such preparation and at least until placing into a borehole, the compositions of the invention are generally maintained in a pumpable, dynamically stable slurry form, the consistency of which may of course vary depending in part upon the temperature of the composition, and the particular ingredients and amounts thereof.

It is common practice in borehole blasting operations to encounter some delay, which may be as short as minutes or as long as many days, between placing an explosive composition in the borehole and detonation. During this time period, the explosive composition is often subjected to the leaching effects of borehole water, and also gravitational segregation effects.

While the explosive compositions of the invention may, if desired, be used, i.e., detonated, immediately after being placed into a borehole, they also remain stable and thus may be detonated even encountering water in the borehole and/or being allowed to remain in the borehole for many days. In large part, this desired stability of the explosive compositions of the present invention is a result of the relatively non-fluid characteristics which the compositions develop within minutes after being placed into the borehole and the hard rigid characteristics which the compositions thereafter develop generally within 24 hours after placement in the borehole. As a result of these characteristics, the compositions at all times prior to detonation remain a substantially homogeneous dispersion of very good sensitivity.

In addition to being used in bulk amounts in conventional blasting operations, the compositions may also be packaged in any suitable container, for example, plastic bags or cardboard tubes and thereafter detonated at the blasting site.

The critical diameter of a composition of the invention can be controlled within a practical range so that such compositions can be safely pumped through a subcritical diameter hose. For example, one can pump such a composition with a five-inch critical diameter through a hose less than about four inches in diameter into a borehole of six inches or greater in diameter.

The explosive compositions of the present invention preferably are gasified by incorporation of small gas bubbles to a bulk density value less than the theoretical maximum density in order to thereby increase the sensitivity of the composition. Gasification techniques are well known in the art and any such techniques can be employed to obtain a bulk density under service conditions regardless of the state of the composition of about 1.0 gms/cc or less to about 1.3 gms/cc, preferably about 1.2 gms/cc.

While the present invention has been described with reference to certain illustrative examples and preferred embodiments, various modifications will be apparent to those skilled in the art and any such modifications are intended to be within the scope of the invention as set forth in the appended claims.

What is claimed is:

1. A water-containing explosive composition gasified to a predetermined density and comprising a homogeneous dispersion of (a) at least one inorganic nitrate oxidizer other than calcium nitrate, (b) a water-immiscible liquid hydrocarbon in emulsion-like form as the primary fuel, (c) hydrated calcium nitrate in an amount greater than about 5 percent to prevent substantial coalescence of said hydrcarbon, (d) added water in amount less than about 10 percent to form a dynamically stable slurry of said composition under formulating and pumping conditions and (e) a thickening agent, said composition being further characterized by being substantially stable against gravitational segregation of the ingredients and degasification.

2. A composition as defined by claim **1** wherein said inorganic nitrate oxidizer is ammonium nitrate.

3. A composition as defined by claim **1** wherein said inorganic nitrate oxidizer comprises ammonium nitrate and sodium nitrate.

4. A composition as defined by claim **1** wherein said liquid hydrocarbon fuel comprises an aromatic hydrocarbon.

5. A composition as defined by claim **1** wherein said liquid hydrocarbon fuel comprises a petroleum distillate.

6. A composition as defined by claim **1** wherein said liquid hydrocarbon fuel comprises No. 2 fuel oil.

7. A composition as defined by claim **1** wherein the composition contains a minor amount of a cross-linkable thickening agent.

8. A composition as defined by claim **7** wherein the composition contains a minor amount of a cross-linking agent.

9. A composition as defined by claim **8** wherein said cross-linking agent comprises about equal parts of water, sodium dichromate, and ferric nitrate.

10. A composition as defined by claim **1** wherein the composition is gasified by use of a minor amount of sodium nitrite gassing agent.

11. A composition as defined by claim **1** wherein the composition contains a minor amount of a cross-linkable guar gum.

12. A composition as defined by claim **1** wherein the compositions contains about 5 percent to about 60 percent solid hydrated CN.

13. A composition as defined by claim **1** wherein said added water is present in an amount of about 1 percent to about 10 percent.

14. A composition as defined by claim **1** wherein said added water is present in an amount of about 3 percent to about 6 percent.

15. A composition as defined by claim **1** wherein said hydrated calcium nitrate is fertilizer grade.

16. A substantially oxygen balanced explosive composition having a bulk density of about 1.0 gm/cc to about 1.3 gms/cc consisting essentially of about 20 percent to about 30 percent calcium nitrate; at least about 3 percent total water; about 60 percent to about 70 percent ammonium nitrate; about 3 percent to about 5 percent sodium nitrate; about 6 percent to about 12 percent of a normally liquid, water-immiscible hydrocarbon fuel in emulsion-like form and at least about 0.1 percent of a cross-linkable guar gum thickening agent.

17. A composition as defined by claim **16** which is further characterized as having a solid, cast-like consistency at the time of use.

18. A composition as defined by claim **16** which is further characterized as having a plastic consistency at the time of use.

19. A composition as defined by claim **16** which is further characterized as having a pourable fluid-like consistency at the time of placing in the container or location of use.

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