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FATTY ALCOHOL SULFATE MODIFIED WATER-BEARING EXPLOSIVES CONTAINING NITROGEN-BASE SALT

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11 Claims

ABSTRACT OF THE DISCLOSURE

Addition of fatty alcohol sulfates to water-bearing explosives having salts of oxidizing acids and nitrogen bases as the principal sensitizer.

BACKGROUND OF THE INVENTION

Blasting compositions of the type known as aqueous slurry or water gel compositions have attained wide acceptance in recent years. These products typically comprise an inorganic oxidizing component, usually predominantly an inorganic nitrate, particularly ammonium nitrate, and sensitizer and/or fuel components dispersed or dissolved in an aqueous medium which is normally thickened or gelled. Until recently, high strength, high velocity water-bearing explosives used where premium performance has been required contained a self-explosive sensitizer such as TNT, PETN, RDX, pentolite, smokeless powder or nitrostarch or a metallic fuel, usually aluminum, or combinations thereof as major part of the fuel. More recently, it has been found that economical, premium performance water-bearing blasting compositions can be obtained by incorporating in said compositions as the primary sensitizer component at least one salt of an inorganic oxidizing acid and a nitrogen base having no more than two hydrogen atoms bonded to the basic nitrogen and up to three carbon atoms per basic nitrogen. Preferred salts of nitrogen bases are salts of nitric acid with a base selected from the group consisting of (a) acyclic nitrogen base and (b) phenyl amines, said salts having an oxygen balance more positive than -150%. Particularly outstanding compositions of this type are discussed more completely in U.S. application Ser. No. 643,064, filed June 2, 1967, the teachings of which are included in this application by reference. The compositions of Ser. No. 643,064 provide products of premium performance at low cost and are readily formulated in the field. Further, especially the aforementioned preferred compositions give excellent blasting performance while eliminating the need for the relatively expensive and more difficultly handled self explosives or metal sensitizers. However, for some applications, it can be desirable to provide compositions of still increased performance strength and sensitivity to intentional initiation stimuli (primers) particularly at low temperatures. One effective index of performance is the velocity at which detonation is propagated through the mass of composition, the blasting effectiveness generally increasing with increasing velocity of detonation, other factors remaining constant.

SUMMARY OF THE INVENTION

In accordance with this invention, improved high performance water-bearing blasting compositions are provided which have surprisingly high detonation velocities and strength, even at low temperatures, and, thus, are particularly adapted for "hard shooting" conditions. These advantageous properties are obtained with the products of this invention over a wide range of densities, e.g., about from 1.0 to 1.7 g./cc. or higher.

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More specifically, this invention provides an improvement in water-bearing explosives comprising inorganic oxidizing agents, water and salts of inorganic oxidizing acid and nitrogen bases having no more than two hydrogen atoms bonded to the basic nitrogen and an oxygen balance more positive than -150% as the principal sensitizer, said improvement comprising including a fatty alcohol sulfate in the explosives.

"Oxidizing" and "fuel" components are referred to herein in their conventional sense to designate materials in the composition with high positive and negative oxygen balances, respectively. "Oxygen balance" as used herein refers to the percent excess or deficiency of oxygen required for complete combustion and is calculated as the molecular weight of oxygen required or given up in complete combustion divided by the molecular weight of the material in question. "Sensitizer" refers to a material which if removed from the composition in small, incremental amounts substantially reduces the sensitivity of the composition to initiation by a conventional stimuli, i.e., that of a primer, at a specified diameter at a given temperature of test.

DESCRIPTION OF PREFERRED EMBODIMENTS

"Fatty alcohol sulfate" refers to neutralized salts of sulfuric acid and aliphatic alcohols, preferably normal, saturated aliphatic primary alcohols of 8 to 22, and preferably 8 to 18 carbons soluble in the system. Preferably such sulfates are salts of alkali metals, preferably sodium and potassium, ammonia, aliphatic amines of up to 5 carbons, or alkanol amines of 2 to 6 carbons, inclusive. Such preferred sulfates can be represented by the formula $\text{CH}_3(\text{CH}_2)_n\text{OSO}_3\text{M}$, wherein M is one of the aforementioned cations, e.g., Na^+ , K^+ , etc., and n is 7 to 21. Alkali metal salts of the fatty alcohol sulfates, especially sodium salts with monoesters of sulfuric acid and an aliphatic alcohol of 8 to 14 carbon atoms, are particularly preferred. Examples of fatty alcohol sulfates which can be used include sodium octyl sulfate, sodium nonyl sulfate, sodium decyl sulfate, sodium lauryl sulfate, potassium lauryl sulfate, ammonium lauryl sulfate, the methylamine salt of lauryl sulfate, the diethanolamine salt of lauryl sulfate, sodium cetyl sulfate, ammonium cetyl sulfate, potassium cetyl sulfate, sodium oleyl sulfate, and potassium oleyl sulfate. Because of commercial availability at low cost and the excellent explosive properties of products of this invention formed therewith, sodium salts of octyl sulfate, decyl sulfate, oleyl sulfate and especially of lauryl sulfate (technical grade) are especially effective. Only small quantities of the salt of the fatty alcohol sulfate are required to provide the high performance blasting compositions, usually only about from 0.2 to 2% by weight, based on the total weight of the composition, is needed. Usually from about 0.25 to 1.0% is sufficient; use of greater amounts of the salt of a fatty alcohol sulfate can cause excess foaming and complicate formulation and mixing of the explosive compositions without benefiting explosive performance. The weight ratio between the fatty alcohol sulfate and the salt of the nitrogen base typically will be about from $\frac{1}{40}$ to $\frac{1}{4000}$, products of particularly noteworthy premium performance being provided when this weight ratio is about $\frac{1}{30}$ to $\frac{1}{150}$. The salt of the fatty alcohol sulfate usually is added to the blasting composition as an aqueous solution or paste-like dispersion and presents no problem in mixing of the composition.

The compositions of this invention are prepared similarly to those containing only a salt of a nitrogen base as sensitizer, e.g., preferably using the crude reaction product obtained by neutralizing the nitrogen base with oxidizing acid in aqueous medium. The salt of the alcohol sulfate preferably is added to a hot "neutral" solution of

oxidizing component, preferably ammonium nitrate before addition of the thickening of the thickening or gelling agent. Addition of the fatty alcohol sulfate to this hot solution prior to its cooling is particularly advantageous since salts of the alcohol sulfates, especially the particularly preferred sodium lauryl sulfate, tend to modify crystallization, particularly of the ammonium nitrate as the solution cools, reducing the size of the crystals formed and producing minute chunks of conchoidal or porous crystals. Increased sensitivity to detonators and primers at low temperatures is attributed, at least in part, to the homogenous entrapment of exceedingly small gas filled cavities, e.g., air bubbles, e.g., of about from 500 angstroms to 500 microns diameter, throughout the composition.

The nitrogen base salt used in this invention can be derived from inorganic bases such as hydrazine but preferably are derived from organic amines. Salts of aliphatic, cycloaliphatic, aromatic, and heterocyclic (including bridged heterocyclic) primary, secondary and tertiary amines meeting the aforementioned oxygen balance requirements can be used. Although the base moiety can bear substituents other than carbon, hydrogen and basic nitrogen that are inert in the system, those consisting of carbon, hydrogen and the basic nitrogen are preferred. Because of availability, low cost, ease of handling and manufacture as well as the excellent explosive characteristics of products made therefrom, salts of aliphatic, preferably saturated aliphatic, amines of up to three carbon atoms are preferred. The oxidizing inorganic acid moiety can be derived from any of the strong oxidizing acids, preferably mineral acids such as, for example, nitric, nitrous, chloric and perchloric acids. Those acids having an oxygen balance of at least about +10% are preferred. Nitrates are particularly preferred because of their ready availability and excellent sensitizing effect and since they introduce no foreign ions into the system.

Examples of salts of nitrogen bases which can be used in conjunction with fatty alcohol sulfates in accordance with this invention include inorganic salts such as hydrazine mono- and dinitrate and perchlorate, salts of aliphatic amines such as monomethylamine nitrate, nitrite, chlorate and perchlorate, ethylenediamine dinitrate and diperchlorate, dimethylamine nitrate, propylamine nitrate, trimethylamine nitrate, guanidine nitrate and urea nitrate; cycloaliphatic salts such as cyclohexylenediamine dinitrate; salts of monocarbocyclic aryl amines such as aniline nitrate, chlorate and perchlorate, p-chloroaniline nitrate and phenylenediamine dinitrate; salts of bridged heterocyclic amines including bridged heterocyclic amines such as hexamethylene tetramine mono- or dinitrate, as well as those such as piperazine nitrate, piperidine nitrate and pyridine nitrate. Of the aforementioned salts, monomethylamine nitrate, trimethylamine nitrate and ethylenediamine dinitrate are particularly preferred because of ease of formulation of blasting compositions therewith and the outstanding explosive properties of the resulting products. Mixtures of the aforementioned salts can be used as well as mixtures of one or more of such salts with other, similar salts having an oxygen balance more negative than -150%, for example, cyclohexylamine nitrate and diethylamine dinitrate. Usually, in employing mixtures of such salts the overall oxygen balance of the mixture should be more positive than -150%. As a group, those nitrogen base salts and compositions described in aforementioned Ser. No. 643,064 are particularly unique and preferred for their explosive properties.

The nitrogen base salt can be incorporated into the blasting composition in substantially pure form; however it can be and preferably is provided as the crude reaction mixture either formed separately or in situ in the blasting composition. When such is the case, water content in the product can be controlled by the concentration of oxidizing agent employed to neutralize the nitrogen base.

A characteristic feature of the explosives of this inven-

tion is that they require none of the conventional high explosive sensitizers or metallic-fuels characteristically required for premium performance in high velocity, high strength water-bearing explosives. Thus, although metals such as finely divided aluminum or high explosives such as TNT, PETN, RDX, HMX, smokeless powder or mixtures thereof such as pentolite (PETN/TNT) and Composition B (TNT/RDX) can be used as a minor part of the sensitizer component, they are not required and, in the preferred case, are avoided. If such conventional high explosives are employed, they constitute less than about 50% of the total weight of sensitizer. Some of the amine salts used in the compositions of this invention are high explosives, i.e., detonating explosives per se. However, both high explosive salts as well as those that are not explosives per se, so long as they meet the aforementioned criteria, can be used alone or in combination in the sensitizer component of the subject products.

The total amount of nitrogen-base salt used varies with the particular composition and can range from 5 to 90% by weight of the total composition. In general, the amount of salt decreases as the amount of water used is reduced and as the amount, if any, of auxiliary sensitizer is increased or as a lower strength product is desired. Preferably, about 10 to 50% of the salt sensitizer is used. Depending on its oxygen balance, the amine salts in addition to being the primary sensitizer, are a part of the oxidizing or fuel component, normally the latter.

The addition of the salt of a fatty alcohol sulfate sensitizes the compositions to a degree greater than that observed when the salt of a nitrogen base alone is present and makes possible their reliable detonation in even smaller diameters and at lower temperatures. The marked increase in detonation velocity is another characteristic of note in the products of this invention over those which contain only the salt of a nitrogen base.

In its broad aspects the explosives of this invention can contain the conventional ingredients normally employed in such water-bearing explosives in the amounts generally used therein. As the primary oxidizing ingredients, the compositions of this invention usually contain at least about 20% by weight of inorganic oxidizing salt. Examples of inorganic oxidizing salts include ammonium, alkali metal and alkaline earth metal nitrates and perchlorates as well as mixtures of two or more such salts. Examples of such salts are ammonium nitrate, ammonium perchlorate, sodium nitrate, sodium perchlorate, potassium nitrate, potassium perchlorate, magnesium nitrate, magnesium perchlorate and calcium nitrate. Preferably, when an inorganic oxidizing salt is used as the oxidizing component, such component contains at least 45% of at least one salt which is highly soluble in water at room temperature, that is, at least as soluble as ammonium nitrate, and preferably, the aqueous phase in the compositions contains a substantial proportion of oxidizing salt, for example, 40 to 70% by weight thereof at room temperature. Inorganic oxidizing salt mixtures containing at least about 50% by weight of ammonium nitrate and at least 5% by weight of sodium nitrate are particularly preferred.

The nitrogen base salt sensitizer can provide substantially all of the fuel component. Often, however, it is desirable to include one or more of the conventional fuels as auxiliary fuels. Auxiliary fuel or fuels used in the compositions of this invention can be varied widely, provided that in the composition in which any particular fuel is used, the fuel is stable, that is, prior to detonation, during preparation and storage, the fuel is chemically inert with the system. In addition to the aforementioned high-explosive auxiliary sensitizers examples of auxiliary fuels are sulfur and carbonaceous nonexplosive fuels such as finely-divided coal and other forms of finely-divided carbon and solid carbonaceous vegetable products such as cornstarch, wood-pulp, sugar, ivory nut meal and bagasse. Examples of auxiliary metallic fuels are aluminum and iron, and alloys of such metals as aluminum-

magnesium alloys, ferrosilicon, ferrophosphorus, as well as mixtures of the aforementioned metals and alloys. Sulfur, ferrophosphorus and ferrosilicon are particularly valuable auxiliary fuels for use in compositions of this invention. Preferably, the total amount of fuel is adjusted so that the total composition has an oxygen balance of about from -25 to +10% and, except for those compositions containing the aforementioned heavier metallic fuels such as ferrophosphorus and ferrosilicon, preferably the oxygen balance is between about -10 and +10%.

As is conventional in water-bearing explosives, the compositions of this invention contain at least about 5% by weight of water. The water-bearing compositions to which this invention is directed generally contain less than about 50% by weight of water and, preferably, on the order of about 10 to 30% by weight of water based on the total composition.

Conventional materials also can be used to thicken or gel the aqueous phase. Of such materials, galactomannans, especially guar gum, are particularly preferred. Usually about from 0.1 to 5% of such galactomannan based on the total weight of composition is employed. Galactomannans also preferably are crosslinked with an oxidizing agent such as an alkali metal dichromate either alone or in combination with a soluble antimony compound such as potassium antimonyl tartrate. Crosslinked combinations of guar gum and acrylic polymer, especially polyacrylamide are often preferred for cohesive yet pourable explosives.

As previously mentioned, the compositions of this invention can be prepared conveniently by blending into a hot (120-180° F.) substantially saturated solution of the inorganic oxidizing salt component, the fatty alcohol sulfate, the nitrogen base salt, and other additives such as gelling and thickening agent, then cooling the resulting product. As prepared initially a substantially large proportion of the oxidizing salt is in solution. As the product cools, part of the salt crystallizes therein so that at ambient temperature 10 to 20% of the salt may be undissolved, i.e., crystallized from solution, whereas at 40° F. as much as 50% or more of the salt may be crystallized. Auxiliary fuels, if desired, and any other additives such as fluidizing agents, buffering agents, e.g., fumaric acid and sensitizing amounts of gas-filled cavities can be added either to the hot solution or to the cooled product to modify the characteristics of the composition. Crosslinking agents for the gelling system are usually the last-added ingredient, this agent being incorporated into the composition just prior to discharging the container for packaged products or just prior to loading into the borehole in the case of mobile, pump-truck products.

In the following examples which further illustrate this invention parts and percentages are by weight unless otherwise indicated.

Examples 1-3

Water-bearing explosive compositions comprising the ingredients shown in the table are prepared in a rotary mixer by the following sequence of steps:

(1) Ammonium nitrate liquor (about 80% ammonium nitrate), solid ammonium nitrate, and an aqueous solution of the salt of a nitrogen base, i.e., an amine nitrate of 70 to 90% concentration are combined, and the mixture heated to 120 to 140° F. (50-60° C.);

(2) The fatty alcohol sulfate is added as a dry powder commercially available as "Dupanol" Me to give a sodium lauryl sulfate content as indicated in the table and thoroughly blended into the composition;

(3) A premixed blend of sodium nitrate and guar gum is added and blended into the contents of the mixer until thickening is observed, about 3 to 5 minutes;

(4) The auxiliary fuels are uniformly incorporated into the blend;

(5) Crosslinking agents for the guar gum are added; the composition is mixed for several more minutes then

discharged into polyethylene bags 6 inches in diameter and cools to ambient temperature to crystallize a portion of the dissolved ammonium nitrate therefrom in the presence of the fatty alcohol sulfate.

TABLE

Example	1	2	3	Control
Water	15.0	15.0	15.0	15.0
NH ₄ NO ₃	36.75	36.60	31.50	37.00
NaNO ₃	15.0	15.0	15.0	15.0
MMAN ¹	30.0	30.0	15.0	30.0
Ethylene diamine dinitrate			20.0	
Sulfur	2.0	2.0	2.0	2.0
Sodium lauryl sulfate	0.25	0.50	0.50	
Guar gum	1.0	1.0	1.0	1.0
Velocity, m./sec.	3,000	5,700	4,950	2,800
Temp., ° F.	33	33	50	33
Density, g./cc.	1.40	1.40	1.40	1.40

¹ Monomethylamine nitrate.

The compositions also contain, in addition to the ingredients listed above, crosslinking agents for the guar gum and inerts added as a part of the commercially available sodium lauryl sulfate.

When equivalent weight of potassium lauryl sulfate, the monomethylamine salt of lauryl sulfate, the ethanolamine salt of lauryl sulfate or sodium decyl sulfate are substituted for sodium lauryl sulfate in Example 2, similar improved results are obtained. Likewise, ethylene diamine dinitrate or aniline nitrate can be substituted for monomethylamine nitrate to give explosive compositions which are essentially oxygen balanced.

I claim:

1. In water-bearing explosives comprising inorganic oxidizing salts, water and nitrogen-base salts of (a) oxidizing acids and (b) nitrogen bases having no more than two hydrogen atoms bonded to the basic nitrogen and an oxygen balance more positive than -150%, the improvement which comprises including a fatty alcohol sulfate in said explosives.

2. A composition of claim 1 wherein said fatty alcohol sulfate is about from 0.2 to 2% based on the total weight of composition of at least one salt of fatty alcohol sulfate of the formula CH₃(CH₂)_nOSO₃M wherein M is an alkali metal cation, an alkamine cation of 1 to 5 carbons or an alkanolamine cation of 2 to 6 carbons, inclusive, and n is 7 to 21 inclusive.

3. A composition of claim 2 wherein said fatty alcohol sulfate is at least one sodium or potassium salt of an 8 to 18 carbon alkanol sulfate.

4. A composition of claim 3 wherein said fatty alcohol sulfate is sodium lauryl sulfate.

5. A composition of claim 2 wherein said nitrogen-base salt is at least one phenyl amine nitrate.

6. A composition of claim 2 wherein said nitrogen base salt is at least one aliphatic amine nitrate.

7. A composition of claim 6 wherein said aliphatic amine nitrate is nitrate of 1 to 3 carbon aliphatic amine.

8. A composition of claim 7 comprising inorganic oxidizing salt at least 50% by weight of which is ammonium nitrate, about from 10 to 30% water, about from 10 to 50% by weight of said aliphatic amine nitrate and about from 0.25 to 1% of sodium lauryl sulfate.

9. A composition of claim 8 wherein said aliphatic amine nitrate is monomethylamine nitrate.

10. A composition of claim 8 wherein said aliphatic amine nitrate is a mixture of monomethylamine nitrate and ethylene diamine dinitrate.

11. In the process for preparing water-bearing explosives which comprises blending together inorganic oxidizing salts, water and nitrogen-base salts of (a) oxidizing acids and (b) nitrogen bases having no more than two hydrogen atoms bonded to basic nitrogen and an oxygen balance more positive than -150%, the improvement which comprises blending said ingredients at a temperature at least sufficient to dissolve a major proportion of said inorganic oxidizing salt and cooling said explosive in

the presence of a dissolved fatty alcohol sulfate to crystal-
lize inorganic oxidizing salt therefrom.

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