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EXPLOSIVE GEL COMPOSITION CONTAINING UREA AND SODIUM CHLORIDE

John Anthony Arbie, Poland, Ohio, assignor to American Cyanamid Company, Stamford, Conn., a corporation of Maine

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This invention relates to new and improved aqueous gel explosive compositions. More particularly, it relates to gelled ammonium nitrate explosive compositions having outstanding "anti-freeze" properties.

Aqueous slurry-type explosive compositions comprising ammonium nitrate and an explosive sensitizer, such as trinitrotoluene, smokeless powder, dinitrotoluene, etc. have attained substantial commercial acceptance. It has been recognized, however, that these compositions, while highly useful, possess certain drawbacks. Thus, they tend to separate into layers, each containing different proportions of the various components. Because of this, these compositions are often-times not only difficult to handle, but their non-uniform consistency adversely affects their explosive characteristics and consequently their reliability in use.

Recently, it has been shown that the separation problem and difficulties attendant therewith can be counteracted to a substantial extent by the incorporation in the slurry compositions of various gel-forming materials which increase the viscosity of the compositions and thereby reduce the settling tendency of the solid components. Thus, the gelled compositions generally exhibit improved, uniform consistency and at the same time sufficient fluidity to permit easy handling and pouring.

It has been further recognized in the art with respect to explosive gel compositions that their stability is enhanced by the incorporation therein, along with the gelling agent, of a small amount of a "cross-linking" agent in the form of a polyvalent metal salt. Salts of aluminum, chromium, iron, tin, and the like have been used. The particular anion of the salt does not appear to be critical. Sulfates have been commonly used, particularly, aluminum sulfate. Nitrates and chlorides have also proved effective, particularly, chromium nitrate.

Of the various gelling agents which have been used in explosive compositions, one which has proved particularly advantageous is the cross-linked partially hydrolyzed polyacrylamide described in U.S. Patent No. 3,097,-120, issued July 9, 1963, to Bowkley et al. While the explosive gel compositions containing this material represent a substantial advance over the non-gelled, slurry-type compositions, they still possess a troublesome defect. Thus, the gels tend to harden considerably on standing, rather than remaining uniformly soft and pourable, particularly when exposed to temperatures in the order of 0° F. or below. A prime characteristic and advantage of the explosive gels is, of course, their pourability, by virtue of which they are readily and efficiently loaded into bore-holes. In the hardened or semi-hardened state, this advantage is, of course, greatly reduced or lost entirely. Accordingly, it is evident that the hardening of the gels at the aforesaid temperatures, which are not uncommon in northern mining operations during the winter, constitutes a serious drawback to their use.

Although the gels in the hardened or semi-hardened state are sometimes referred to as being "frozen," this is somewhat of a misnomer since the hardening of the gel is not the result of freezing in the conventional sense, but rather of the "salting out" of crystals from the saturated ammonium nitrate and/or sodium nitrate solution which is a component of the gel compositions. Thus,

the solidifying effect can occur at temperatures well above freezing, i.e., about 60° F. or higher, although as would be expected, it becomes more pronounced as the temperature to which the compositions are exposed becomes lower. On this basis, a gel composition which exhibits pronounced hardening tendencies particularly when exposed to relatively low temperatures is said to have poor "anti-freeze" properties.

It is the object of this invention to provide explosive gel compositions having markedly improved anti-freeze properties, said compositions being free of hardening tendencies, even when subjected to temperatures of 0° F., or lower, for prolonged periods. Other and further objects will become apparent from the following description of the invention.

In accordance with this invention, the aforesaid objects are accomplished by the incorporation in explosive gel compositions containing the aforesaid cross-linked partially hydrolyzed polyacrylamide gelling agent of minor proportions of urea and a metallic chloride, preferably sodium chloride.

As is well known, explosive gels ordinarily contain as essential components (a) ammonium nitrate either alone or in combination with a metal nitrate, such as sodium nitrate, (b) a sensitizer, (c) water, and (d) a suitable gelling agent. The sensitizer may be of the high explosive type such as TNT, smokeless powder, PETN, RDX, pentolite and other nitrated equivalents. These are available in commercial form both as such and in various admixtures such as the group of compositions commonly referred to as "tols." Also, the sensitizer may be the product of coating ammonium nitrate with a non-high explosive oil, such as dinitrotoluene, or fuel oil. Although the latter materials (dinitrotoluene and fuel oil) are not explosive per se they provide sensitizing action when combined with ammonium nitrate. Since they are utilized in this fashion in the compositions of this invention, the term "sensitizer" as used herein is meant to include them. Gels containing this type of sensitizer are known as nitro-carbo-nitrate, or "NCN," explosives.

The manner of preparation and the proportions of the several components of the explosive gel compositions will depend upon the nature of the composition, i.e., whether it is of the high explosive or NCN type, and also upon the particular explosive use for which the composition is intended. Generally, the gels employing a high explosive sensitizer will be composed of relatively lower amounts of ammonium nitrate or sodium nitrate than the NCN compositions. The principle of the invention can be advantageously applied to explosive gels, in general, whether they are of the high explosive or NCN type. Thus, in all cases the presence of the urea and the sodium chloride overcomes the tendency of the gel to harden on standing even when the gel is exposed to temperatures in the order of 0° F.

Various techniques used for the manufacture of aqueous explosive gels have been shown in the prior art. A common practice is to add all of the ammonium nitrate, sodium nitrate, sensitizer and thickening agent as dry ingredients to a mixing bowl for blending which, after completed, is followed by the addition of hot water with continued mixing in order to disperse and dissolve the polyacrylamide. Finally, the cross-linking agent is added with further mixing until the gelled product is obtained. Another technique involves preparation of a saturated solution comprising a portion of the ammonium nitrate component and all of the sodium nitrate component. This solution is then added to a dry mix of the remainder of the ammonium nitrate component, the sensitizer, the gelling agent and the cross-linking agent. However, this order of mixing is not always used. Thus, in some instances, it is advantageous to add either the gelling agent

or the cross-linking agent or both to the ammonium nitrate solution rather than to the dry mixture. Other variations in manufacturing technique will be apparent to those skilled in the art and, accordingly, are considered to be within the scope of this invention.

As aforeindicated, the gelling agents employed in the improved compositions of this invention are the polyacrylamides disclosed in U.S. Patent No. 3,097,120. These polyacrylamides have apparent molecular weights ranging from about 1 million to about 25 million. They are further characterized in that they have been partially hydrolyzed so as to contain a defined proportion of so-called "free acid" or "carboxy" groups. Thus, to be suitable they should contain from about 0.1% to about 8% of such groups, preferably from about 1% to about 2% thereof. Also, after the fashion of the patent, the compositions of this invention employ a polyvalent metal cross-linking agent in conjunction with the polyacrylamide gelling agent. As previously pointed out and as described in the patent, a number of polyvalent metal salts are suitable for this purpose. However, aluminum sulfate and chromium nitrate have been found particularly useful for the purpose of the present invention and these salts have been used in the illustrative examples given hereinbelow. The polyacrylamide used in the examples was a commercially available material having an apparent molecular weight of from about 5 million to about 7 million and which had been hydrolyzed to contain about 1.5% carboxylic acid groups.

The invention is illustrated by the following examples wherein the percentages given are by weight unless otherwise indicated.

Example 1

Five explosive gel compositions, A, B, C, D, and E were prepared having the following formulations:

	A	B	C	D	E
NH_4NO_3, uncoated whole prills	21.50	18.50	21.50	17.50	21.50
NaCl*	------	5.20	------	5.20	------
H_2O*	------	14.20	------	14.20	------
$NaNO_3$	17.78	17.78	17.78	16.78	17.78
Smokeless powder (20 mm.)	------	------	35.00	35.00	------
Trinitrotoluene	35.00	35.00	------	------	35.00
Polyacrylamide	0.62	0.62	0.62	0.62	0.62
Aluminum sulfate	0.10	0.10	0.10	0.10	0.10
Water	15.00	0.80	15.00	0.80	15.00
Urea	10.00	5.00	10.00	5.00	------
NaCl	------	2.80	------	4.80	10.00

*As saturated solution.

Compositions A–E were prepared as described below (the percentages of water and sodium chloride stated being based on the final gel composition).

Composition A—To the dry ingredients, i.e., ammonium nitrate, sodium nitrate and urea, in a gel mix bowl, the trinitrotoluene and the polyacrylamide were added and the whole mixed for 2 minutes. 14.2% of water was then added and the whole mixed for 5 minutes. The aluminum sulfate, dissolved in 0.8% of water, was then added to the mixture in the bowl and mixing was continued for 2 minutes to provide the final gelled product.

Composition B—To the dry ingredients, viz., ammonium nitrate, sodium nitrate, urea and 2.8% of sodium chloride, in a gel mix bowl, the trinitrotoluene and the polyacrylamide were added and the whole mixed for 2 minutes. A sodium chloride solution containing 5.2% of sodium chloride in 14.2% of hot (150° C.) water was then added and mixing continued for 5 minutes. The aluminum sulfate, dissolved in 0.8% of water, was then added and the whole mixed for 2 minutes to provide the final gel product.

Composition C—This composition was prepared in the same way as Composition A, except that smokeless powder was used in place of trinitrotoluene.

Composition D—This composition was prepared in the same fashion as Composition B, except that smokeless powder was used in place of trinitrotoluene and 4.8% of sodium chloride was added with the dry ingredients.

Composition E—This composition was prepared in the same way as Composition A, except that sodium chloride was substituted for urea in the dry ingredients.

The anti-freeze properties of the five compositions, A, B, C, D, and E, were tested by placing samples of each in low temperature storage and observing their hardening tendencies periodically. The results of the tests are presented in Table I.

TABLE I.—LOW TEMPERATURE STORAGE TEST

Composition	A	B	C	D	E
Temperature, ° F	−10	−15	−10	−10	−10
Days Gel Remained Fluid	½	−60	½	−60	½

As will be observed from Table I, Compositions A and C which contained urea but no sodium chloride and Composition E which contained sodium chloride but no urea became hard within half a day, whereas Compositions B and D, which contained both urea and sodium chloride, remained soft and fluid after 60 days. It is seen then that the outstanding anti-freeze properties of Compositions B and D derives from the presence therein of both urea and sodium chloride.

The foregoing examples are, of course, merely illustrative of the invention. Obviously, other known sensitizers can be substituted for those shown in the examples with the benefits of the invention still being attained. Also, compositions containing different proportions of ammonium nitrate, sodium nitrate and sensitizer as pointed out herein can be used without diminishing the benefits of the invention. Compositions containing such other sensitizers or proportions of ingredients, or which are prepared differently (such as by supplying the ammonium nitrate, sodium nitrate or urea in the form of a saturated solution) are, therefore, considered to be within the scope of the invention.

As indicated at the outset, explosive gel compositions vary widely in the proportions of ammonium nitrate and sensitizer employed therein. Thus, in NCN type compositions the proportion of ammonium nitrate is relatively high and the proportion of sensitizer relatively low as compared to compositions employing a high-explosive sensitizer such as TNT or smokeless powder. Thus, in NCN type compositions the ammonium nitrate is ordinarily present in amounts ranging from about 50 to about 80 weight percent, preferably about 60–75 weight percent, with the sensitizer being present in amounts of from about 2 to about 20, preferably about 6–12 weight percent. Also, the composition may contain an oxidizer in the form of a metal nitrate, such as sodium nitrate in amounts up to about 25 percent, preferably about 5–15 percent. The remainder of these compositions is, of course, comprised of water, usually from about 5 to about 25 weight percent, preferably 8–15 percent, and a small proportion, from about 0.05 to about 2 percent, of gelling agent. Gel compositions employing a high explosive sensitizer, on the other hand, contain ammonium nitrate in amounts generally ranging from about 15 to about 50 and preferably about 20 to about 35 weight percent with the sensitizer being present in amounts of from about 20 to about 50 and preferably about 30 to about 40 weight percent. Also, a metal nitrate oxidizer, such as sodium nitrate, may be employed in amounts up to about 25 percent, preferably about 10–20 weight percent. The remainder of the composition is comprised of water and a gelling agent in proportions similar to those stated for the NCN composition. As has been indicated, the principle of the invention is applicable to any such explosive gel composition in which the gelling agent used is the cross-linked polyacrylamide defined herein. Thus, as has been indicated herein, the cross-linked polyacryl-

amide is an unusually advantageous gelling agent in that it provides soft, pourable gels of uniform consistency and stability. The incorporation of the urea and the metal chloride along with the polyacrylamide in accordance with the instant invention imparts a further important property to the gels, viz., resistance to hardening or freezing at temperatures in the order of −10° F. or below. Accordingly, it is seen that it is the conjoint use of the urea and the metal chloride with the cross-linked polyacrylamide which brings about the outstanding all-round properties of the compositions of this invention.

The amount of polyacrylamide employed in accordance with this invention ranges from about 0.05 to about 2 weight percent of the gel composition, about 0.5 to about 1 percent being the preferred amount. The polyvalent metal salt cross-linking agent used in conjunction with the gelling agent is employed in an amount of from about 0.01 to about 0.5 weight percent with 0.04 to 0.12 percent being preferred.

The amount of urea to be used in the compositions of the invention will range from about 1 to about 15 weight percent, the usual amount being from about 5–10 percent. Thus, while the latter amount is ordinarily used, significant improvement is obtained (in the presence of sodium chloride) with as little as 1 percent in some instances. On the other hand, amounts up to 15 percent can be used to advantage where extreme temperature conditions are encountered. Correspondingly, the amount of sodium chloride used in the present compositions may range from about 1 to about 15 weight percent, the usual amount being from about 5 to above 10 percent.

The new and improved compositions within the scope of this invention may be defined as having the following general ranges of components:

Component:	Weight percentage
Ammonium nitrate	15–80
Metal nitrate	0–25
Sensitizer	2–50
Polyacrylamide	0.05–2
Polyvalent metal salt cross-linking agent	0.01–0.5
Water	5–25
Urea	1–15
Metal chloride	1–15

While the present invention has been described and illustrated herein in terms of specific embodiments and examples thereof, it is not intended that the scope of the invention be limited in any way thereby, but only as indicated in the following claims.

I claim:

1. A stable, soft, non-separating explosive gel composition of improved anti-freeze properties comprising on a weight basis (a) from about 15 to about 80 percent of ammonium nitrate, (b) from 0 to about 25 percent of an alkali metal nitrate, (c) from about 2 to about 50 percent of a nitrated organic sensitizer, (d) from about 5 to about 25 percent of water, (e) from about 0.05 to about 2 percent of a polyacrylamide having an apparent molecular weight of from about 1 million to about 25 million and a hydrolyzed free acid content of from about 0.1 to about 8 weight percent, (f) from about 0.01 to about 0.5 percent of an inorganic polyvalent metal salt cross-linking agent, (g) from about 1 to about 15 percent of urea, and (h) from about 1 to about 15 percent of sodium chloride.

2. An explosive gel composition according to claim 1 in which the sensitizer is trinitrotoluene.

3. An explosive gel composition according to claim 1 in which the sensitizer is smokeless powder.

4. An explosive gel composition according to claim 1 in which the sensitizer is dinitrotoluene.

5. An explosive gel composition according to claim 1 in which said polyacrylamide has a hydrolyzed free acid content of from about 1 to about 2 weight percent.

6. An explosive gel composition according to claim 1 in which said polyvalent metal salt is aluminum sulfate.

7. An explosive gel composition according to claim 1 in which said polyvalent metal salt is chromic nitrate.

8. An explosive gel composition according to claim 1 in which said polyvalent metal salt is a combination of aluminum sulfate and chromic nitrate.

9. A stable, soft, non-separating explosive gel composition of improved anti-freeze properties comprising on a weight basis (a) from about 20 to about 35 percent of ammonium nitrate, (b) from about 10 to about 20 percent of sodium nitrate, (c) from about 30 to about 40 percent of a sensitizer selected from trinitrotoluene and smokeless powder, (d) from about 8 to about 15 percent of water, (e) from about 0.5 to about 1 percent of a polyacrylamide having an apparent molecular weight of from about 5 million to about 7 million and a hydrolyzed free acid content of from about 1 to about 2 weight percent, and (f) from about 0.04 to about 0.12 percent of a polyvalent metal salt cross-linking agent selected from the group consisting of aluminum sulfate and chromic nitrate, (g) from about 5 to about 10 percent of urea, and (h) from about 5 to about 10 percent of sodium chloride.

10. A stable, soft, non-separating explosive gel composition of improved anti-freeze properties comprising on a weight basis (a) from about 60 to about 75 percent of ammonium nitrate, (b) from about 5 to about 15 percent of sodium nitrate, (c) from about 6 to about 12 percent of dinitrotoluene, (d) from about 8 to about 15 percent of water, (e) from about 0.5 to about 1 percent of polyacrylamide having an apparent molecular weight of from about 5 million to about 7 million and a hydrolyzed free acid content of from about 1 to about 2 weight percent, and (f) from about 0.04 to about 0.12 percent of a polyvalent metal salt cross-linking agent selected from the group consisting of aluminum sulfate and chromic nitrate, (g) from about 5 to about 10 percent of urea, and (h) from about 5 to about 10 percent of sodium chloride.

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CARL D. QUARFORTH, *Primary Examiner.*

BENJAMIN R. PADGETT, *Examiner.*

S. J. LECHERT, JR., *Assistant Examiner.*

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,321,344 May 23, 1967

John Anthony Arbie

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 4, in TABLE I, the third and fifth columns, line 2 thereof, for "-60", each occurrence, read -- >60 --; column 5, line 32, for "above" read -- about --.

Signed and sealed this 28th day of November 1967.

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents