United States Patent

[11] 3,617,402

[72] Inventor **Herbert G. Knight, Jr.**
Flanders, N.J.

[21] Appl. No. **786,686**
[22] Filed **Dec. 24, 1968**
[45] Patented **Nov. 2, 1971**

[73] Assignee **Hercules Incorporated**
Wilmington, Del.

[54] AQUEOUS SLURRY BLASTING COMPOSITION CONTAINING AN ALIPHATIC AMINE SALT AND A WATER SOLUBLE INORGANIC PERCHLORATE

20 Claims, No Drawings

[52] **U.S. Cl.** **149/2,**
149/38, 149/42, 149/44, 149/75, 149/76, 149/77, 149/78, 149/83, 149/85, 149/92

[51] **Int. Cl.** **C06b 19/00**

[50] **Field of Search** 149/42, 78, 92, 83, 85, 38, 44, 75, 76, 77

[56] **References Cited**

UNITED STATES PATENTS

3,212,945	10/1965	Berthmann et al.	149/78 X
3,318,740	5/1967	Fee et al.	149/78 X

Primary Examiner—Benjamin R. Padgett
Assistant Examiner—Stephen J. Lechert, Jr.
Attorney—William F. Smith

ABSTRACT: The invention provides inorganic oxidizer salt blasting compositions of the aqueous slurry type containing a combination of an aliphatic amine salt and a water-soluble inorganic perchlorate as a sensitizer component. Preferably, each of said amine salt and perchlorate is present in the sensitizer combination in a proportion at least stoichiometrically equivalent to that required for reaction with the other to form a corresponding amine perchlorate as at lest 3 weight percent of the composition. Often, the proportion of each ingredient of the sensitizer combination is at least 2, and generally up to 25, weight percent of the composition.

AQUEOUS SLURRY BLASTING COMPOSITION CONTAINING AN ALIPHATIC AMINE SALT AND A WATER SOLUBLE INORGANIC PERCHLORATE

This invention relates to inorganic oxidizer salt blasting compositions of the aqueous slurry type, free from self-explosive ingredients and containing a combination of amine salt and inorganic salt ingredients providing for improved sensitivity.

Inorganic oxidizer salts blasting compositions of the aqueous slurry type have had extensive use in the explosive 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 any of the various ingredients.

Various sensitizer materials have been utilized in the above compositions including smokeless powder as disclosed and claimed in U.S. Pat. No. 3,235,435, and particulate metals and high explosives, such as TNT and/or aluminum as disclosed and claimed in U.S. Pat. No. 2,930,685. These compositions are insensitive to detonating action of a standard No. 8 blasting cap except that, in certain instances, as for example, when containing large amounts of a high explosive, flake aluminum of small particle size, or the like, a higher sensitivity is obtained and in some instances, the composition is cap sensitive.

Due to safety hazards involved in the use of high explosives as sensitizers in these slurry compositions, and particularly when utilizing large proportions of high explosive for high sensitivity, the industry has more generally utilized those slurry compositions free from self-explosive ingredients. However, even in utilization of this latter type slurry, there are serious hazards involved in the handling of finely divided metal ingredients during manufacture and particularly in those instances requiring the handling of finely divided flake aluminum.

This invention is concerned with slurry type composition above described, containing a combination of aliphatic amine salt and water-soluble inorganic perchlorate ingredients as a novel sensitizer component imparting improved sensitivity to the slurry and in some instances cap sensitivity.

In accordance with the invention an inorganic oxidizer salt blasting composition of the aqueous slurry type is provided which contains, as a sensitizer component, a sensitizing amount of a combination of an aliphatic amine salt and a water-soluble inorganic perchlorate. Generally, each of the aliphatic amine salt and inorganic perchlorate is present in a proportion at least stoichiometrically equivalent to that required for reaction with the other to form a corresponding amine perchlorate as at least 3 weight percent, and more often from 3 to about 50 weight percent, of said composition. However, the requisite sensitizing amount of the above-described sensitizer component combination, and the relative proportions of the ingredients thereof, depends on the particular formulation and is, therefore, in some instances, outside the range of those values specifically set forth hereinabove.

In general, based on the entire slurry composition, the sensitizer component contains at least about 2 weight percent of each of the aliphatic amine slat and inorganic perchlorate ingredient, and one or the other of those ingredients can be in excess of the described stoichiometric proportion and still function as a sensitizer component ingredient; the sensitizer combination (basis entire slurry composition) generally containing from about 2 to about 25 weight percent of each of the sensitizer ingredients.

It is also within the scope of the invention to include larger amounts of one or both of the aliphatic amine salt and inorganic perchlorate, above described, in proportions outside the range of those which function as ingredients of the sensitizer component, and which respectively function primarily as a fuel and as a supplemental inorganic oxidizer salt component of the resulting slurry composition; or, when desired, a sufficiently large additional proportion of the inorganic perchlorate can be included to enable the use of the perchlorate as the sole inorganic oxidizer salt component. Accordingly, the compositions of the invention, in some embodiments, contain independently of the perchlorate and amine salt sensitizer component ingredients, from 0 to as high as 40 percent, often from 5 to 20 percent, of the amine salt as a fuel, and say from 5 to 30 percent of the inorganic perchlorate as a supplemental inorganic oxidizer salt ingredient, or, as the sole inorganic oxidizer salt component in an amount in the order of about from 40 to 75 percent.

The compositions of the invention generally comprise on a weight basis, from 8 to 30 percent water, from 40 to 75 percent inorganic oxidizer salt, the above-described sensitizer combination of inorganic perchlorate and amine salt, and from 0.2 to 5 percent of a suitable thickener. It is to be understood that in accordance with conventional practice, the slurry compositions of the invention, in selected embodiments, contain one or more of various particulate metal energizers and/or supplemental sensitizers such as aluminum, magnesium, silicon and iron-silicon, generally in a total amount of from about 1 to about 30 percent, and supplemental carbonaceous fuels and/or sensitizers such as ethylene glycol, fuel oil, coal and the like, generally in a total amount of from about 1 to about 20 percent.

Sensitivity of the compositions of the invention varies with specific gravity, which is not only determined by the particular ingredients and relative proportions thereof, but also by the extent to which gas bubbles are present in the ingredient mixture. As set forth in U.S. Pat. Nos. 3,390,031, 3,390,032, 3,288,658, 3,288,661 and others, specific gravity of slurry type compositions of the kind with which this invention is concerned, can be regulated by direct aeration, i.e. by the incorporation of air or other gas bubbles into the slurry, by direct air injection or in-situ gas generation by an aeration agent present as an ingredient of the slurry composition mixture, to provide a predetermined specific gravity for the degree of sensitivity desired. Often, the desired specific gravity is that resulting from the presence of air bubbles, or particles, entrapped in the ingredient mixture during the mixing step. In preferred practice providing the desired sensitivity, the specific gravity of the slurry compositions of the invention at the time of blasting, is from 30 to 90 percent, preferably from 50 to 85 percent, of the maximum, imposed on the composition by the presence of gas particles whether they be present as result of inherent entrapment during mixing or as result of direct aeration.

By the term "inorganic oxidizer salt," as is well known in explosives art, is meant one which under the conditions of the detonation liberates oxygen for the degree of oxygen balance required. Ammonium nitrate is in many instances the only inorganic oxidizer salt component. However, other inorganic oxidizer salts can be used alone, or with ammonium nitrate as a supplementary oxidizer salt. Exemplary inorganic oxidizer salts that can be used alone or together with ammonium nitrate as supplementary oxidizer salts are alkali metal and alkali earth metal nitrates and perchlorates, as for example sodium nitrate, magnesium nitrate, calcium nitrate, potassium nitrate, barium nitrate, sodium perchlorate, ammonium perchlorate, calcium perchlorate and magnesium perchlorate. Often when ammonium nitrate is utilized with a supplementary salt, it comprises at least a major proportion, i.e. at least 50 percent of the total oxidizer salt component. However, weight ratio of ammonium nitrate to supplementary oxidizer salt can advantageously be in the range of from about 10:1 to 0.3:1, **sodium nitrate and sodium perchlorate or both together being now-preferred supplemental oxidizer salts.**

Particle size of the oxidizer salt ingredients is not critical. For example, ammonium nitrate can consist of prills, such as used in the fertilizer industry, or it can be granular or in that form vary from coarse to fine. Other oxidizer salt ingredients are generally of comparable particle size.

Suitable thickener components of the compositions of the invention include carboxymethylcellulose, methyl cellulose, water-soluble starches, cereal flour and plant gums such as guar gum. Guar gum in cross-linked form is now preferred. Various suitable cross-linking agents for guar gum are well

known of which the pyroantimonate type cross-linker is now preferred, and particularly potassium pyroantimonate.

The amount of thickener is dependent of the particular thickener and the desired consistency of the finished composition. Generally, a thickener content up to about 5 percent, and more often in the range of from 0.2 to about 2 weight percent is sufficient. Cross-linked guar gum present in an amount of from about 0.5 to 1.8 percent is advantageously utilized.

In preferred practice, the slurry compositions contain an aeration agent, as above described, for generation of gas bubbles generally at the time of blasting, to regulate the specific gravity of the composition at that time. However, the aeration can be initiated at any time as desired, as for example at the time of packaging (when bagging the composition); or, when the composition is pumpable and cross-linking is effected after pumping into final emplacement, aeration is thereafter carried out in accordance with known practice. Although air particles can be directly injected into the composition for regulation of specific gravity, it is often more advantageous to use an aeration agent incorporated into the composition for generation of the gas particles as required.

The slurry compositions of the invention can be prepared in accordance with any suitable procedure. Thus, by way of illustration, to a mixer, and in the sequence shown (all conditions made with mixing),

1. add ammonium nitrate in water as an 80 percent solution at about 180° F., together with total sodium perchlorate and aliphatic amine, ingredients,
2. when utilizing guar gum as the thickener and ethylene glycol as a fuel, add about one-half of the contemplated amount of guar gum, in natural form, dispersed in about one-half of the contemplated amount of ethylene glycol and mix until the slurry begins to thicken,
3. when utilizing sodium nitrate as a supplementary salt, add the sodium nitrate,
4. all remaining guar gum in the remaining ethylene glycol portion,
5. add fumaric acid dispersed in a small portion of water for the aeration pH, viz, at about 40 to 50,
6. utilizing a sodium nitrite-ammonium sulfamate aeration system, add the sodium nitrite and the ammonium sulfamate, each dispersed in a separate, and small, portion of water retained above from the formula weight of water, and
7. add the guar gum cross-linking agent, preferably potassium pyroantimonate dispersed in a small portion of retained water from the formula weight.

The above-preferred procedure can be varied as desired, it being required only that addition of the ingredients be timely to provide for generation of gas particles prior to the time the packaged slurry is to be loaded into the borehole or the charge delivered to the borehole, as the case may be.

As above illustrated, the incorporation of sodium nitrite with sulfamic acid and/or ammonium sulfamate, as an aeration system is now preferred. This system is described in detail in the copending application of Armantrout and Person, Ser. 694,387, filed Dec. 29, 1967. As described more fully in that copending application, the aeration system comprises at least one nitrite of the group of sodium nitrite, potassium nitrite, calcium nitrite, barium nitrite and silver nitrite in combination with a sufficient amount of an additive component to increase the rate of aeration to above that of the inorganic nitrite alone and the additive component being at least one of the group consisting of sulfamic acid, ammonium sulfamate, potassium sulfamate and sodium sulfamate. The mole ratio of additive component to total nitrite is generally within the range of from 0.1:1 to 20:1. Sodium nitrite-ammonium sulfamate is a now-preferred combination, and when using both sulfamic acid and a sulfamate. The total proportion of nitrite-sulfamate and/or sulfamic acid aeration mixture added to the formulation is within the range of from about 0.002 to 2 weight percent.

The term "maximum specific gravity" as used herein means the specific gravity of the aqueous blasting agent exclusive of the presence of gas particles. Generally, a specific gravity of from about 0.90 to 1.35 at time of blasting is desired.

The invention is illustrated with reference to formulations, and of properties thereof, set forth in the following tabulation:

TABLE 1

Formulation No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
Water	16.0	16.0	16.0	16.0	16.0	16.0	16.0	16.0	16.0	16.0	16.0	16.0	17.6	16.0	17.69	16.0	16.0
Ammonium nitrate	44.0	44.0	44.0	44.0	44.0	52.3	52.3	52.3	52.3	49.0	49.1	44.1	27.1	37.9	49.1	43.0	39.1
Sodium nitrate	5.0	5.0	5.0	20.0	20.0					5.0	5.0	15.6	6.7	20.0	11.7	5.0	10.6
Sodium perchlorate	15.0	15.0	15.0			15.0	15.0	15.0	15.0	15.0	15.0	5.0	15.0	8.5	2.0	15.0	15.0
Hexamethylene tetramine mononitrate	5.5	5.5	5.5	5.5	5.5	7.25	7.25			10.7		5.5	5.5	14.0	4.0		5.5
Triethanolamine mononitrate																6.4	
Silicon-iron alloy [1]												10.0	25.0				10.0
Aluminum [2]	10.0	10.0	10.0	10.0	10.0	5.0	5.0	5.0	5.0						12.5	10.0	
Ethylene glycol	2.8	2.8	2.8	2.8	2.8	2.75	2.75	10.0	10.0	2.6	13.3	2.2	2.0	2.0	2.0	3.0	2.2
Guar gum [3]	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25	0.84	1.25	0.84	1.25	1.32
Aerating agent	None			None													None
$NaNO_2$		0.01	0.06		0.09	0.09	0.09	0.06	0.12	0.04	0.04	0.06	0.075	0.02	0.055	0.05	
Ammonium sulfamate	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20
Fumaric acid	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.04	0.07	0.04		
Zinc oxide	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06		0.06			0.06
Pine oil													0.05		0.05	0.10	
Specific gravity, 60/60° F.	1.33	1.29	1.00	1.22	0.93	0.92	0.88	0.99	0.85	1.20	1.18	1.07	1.27	1.34	1.15	1.28	1.49
Sensitivity [4]:																	
Minimum strength [5] detonator	([6])	([7])	([8])			([6])	([7])			([9])		([9])				([6])	
Grams PETN				10	5			2	5		2						500
Detonation rate, [4] meter/sec.	4,750	4,650	4,000	3,750	2,950	3,900	3,550	3,840	3,450				4,250	5,250	4,000		2,200

[1] 85 percent Si.
[2] Particle size, <15 microns (nonflake).
[3] Natural guar gum from 0.04 to 0.05 percent antimonate type cross-linking agent based on the finished compositions.
[4] Minimum sensitivity, and detonation rate: each measured at 40° F. and 3° diameter, Formulations 1-9 and 17 incl.; sensitivity measured at 85° F., 3" diameter, Formulations 10 and 11; detonation rate measured at 40° F., 4" diameter, conventional PETN booster; Formulations 13-15 incl.; sensitivity measured at 85° F., Formulation 12; sensitivity measured at 40° F., 4" diameter, Formulation 16.
[5] Detonating strength of Army cap about 1.87 times that of a No. 8 blasting cap; F-cap, detonating strength of about No. 4 blasting cap.
[6] Army cap. [7] No. 8 cap. [8] F-cap. [9] No. 6 cap.

Formulations 1–3, 6, 7, 20, 23, 13, 14 and 15 illustrate compositions of the invention containing sodium perchlorate with hexamethylenetetramine mononitrate as the sensitizer combination. Example 16 illustrates compositions of the invention in which the amine salt is triethanolamine mononitrate in combination with sodium perchlorate. The remaining examples illustrate similar formulations except that they are devoid of either the amine salt or the sodium perchlorate and the lower sensitizing activity that accrues in the absence of the aliphatic amine salt-perchlorate sensitizer system in accordance with the invention.

Thus Examples 1, 2 and 3, the same except for specific gravity differences illustrate sensitivity—specific gravity rela-

tionship of the compositions of the invention. In example 1, the formulation has a specific gravity of 1.33 as result of the presence of gas bubbles incorporated therein by entrainment during mixing, i.e. there being no aeration agent present. As shown, the formulation of example 1 required an "Army Cap," i.e. of detonating strength of about 1.87 times that of a No. 8 blasting cap, for detonation. The formulation of Example 2 had a specific gravity of 1.29 resulting from the presence of air entrainment during mixing plus the presence of .01 percent sodium nitrite as aeration agent component, and was more sensitive than that of Example 1 due to the lower specific gravity level, i.e. it detonated in response to action of a No. 8 cap. Similarly, Formulation No. 3 at a specific gravity of 1.00 detonated in response to action of an "F-cap," i.e. of about No. 4 strength.

Formulations 4 and 5 are the same as those of Formulations 1 and 3 except for the absence of perchlorate and show a definite loss in sensitivity attributable to the absence of the perchlorate, even at lower specific gravities.

Similarly, examples 6 and 7 illustrate compositions of the invention which have specific gravities respectively of 0.92 and 0.88 and detonate in response to action of an army cap and a No. 8 cap, whereas examples 8 and 9 illustrate similar formulations except for the absence of the aliphatic amine slat and are detonable only by larger charges.

Examples 10 and 11 illustrate compositions at substantially the same specific gravity level except that no aliphatic amine salt is present in the formulation of No. 11, the latter requiring a two-gram booster charge (PETN) whereas in the presence of the aliphatic amine salt, detonation was accomplished by a No. 6 cap.

Examples 12–15 illustrate compositions of the invention of varying proportions of ammonium nitrate, sodium nitrate, and sodium perchlorate ingredients and of these, Formulation 15 illustrates the presence of a amount of aliphatic amine salt in excess of the stoichiometric equivalent, described hereinabove, of the sodium perchlorate. Example 16 illustrates triethanolamine mononitrate as the aliphatic amine salt together with sodium perchlorate to form the sensitizer combination. Example 17 illustrates sensitivity of a slurry composition of the invention at a specific gravity of 1.49 which is higher than generally preferred and contains substantially a minimum of gas bubbles.

Further exemplary of aliphatic amine salt ingredients of the sensitizer component of the invention are nitrates, chlorides and sulfates of primary amines, secondary amines, tertiary amines, heterocyclic amines, and branched chain alkyl amines such as methyl ammonium nitrate, dimethyl ammonium nitrate, trimethyl ammonium nitrate, isopropyl ammonium nitrate, and ethylenediamine diperchlorate.

Exemplary water-soluble inorganic perchlorate ingredients of the sensitizer system of the invention are the alkali metal perchlorates, and alkaline earth metal perchlorates such as sodium perchlorate, calcium perchlorate, strontium perchlorate, barium perchlorate, magnesium perchlorate, and lithium perchlorate.

As illustrated, the compositions of the invention exhibit improved sensitivity due to the presence of the aliphatic amine salt-inorganic perchlorate sensitizer system. They are often cap-sensitive, and in all events are detonable by unexpectedly small amounts of conventional booster type explosives such as PETN, tetryl, Composition B, pentolite, and the like.

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 blasting composition of the aqueous slurry type, the improvement comprising as a sensitizer component, a sensitizing amount of a combination of stoichiometric proportions of an aliphatic amine salt and a water-soluble inorganic perchlorate for the formation of a corresponding amine perchlorate.

2. A blasting composition of claim 1 containing at least about 2 weight percent of each of said amine salt and perchlorate ingredients of said sensitizer combination.

3. In a blasting composition of claim 1, gas bubbles incorporated within said composition to maintain the specific gravity thereof within the range of from about 30 to 90 percent of the maximum.

4. A blasting composition of claim 3 containing an aeration agent in sufficient amount to generate said gas bubbles within said composition.

5. A blasting composition of claim 3 wherein each of said aliphatic amine salt and inorganic perchlorate is present in said sensitizer combination in a proportion at least stoichiometrically equivalent to that required for reaction with the other to form a corresponding amine perchlorate as at least 3 weight percent of said composition.

6. A blasting composition of claim 5 wherein each said proportion is stoichiometrically equivalent to that required for said reaction to form up to 50 percent of said corresponding amine perchlorate.

7. A blasting composition of claim 5 wherein said aliphatic amine salt is an amine nitrate and said perchlorate is an alkali metal perchlorate.

8. A blasting composition of clam 7 wherein said amine salt is hexamethylenetetramine mononitrate and said perchlorate is sodium perchlorate.

9. A blasting composition of claim 7 wherein said amine salt is triethanolamine mononitrate and said perchlorate is sodium perchlorate.

10. A blasting composition of claim 5 containing on a weight basis from 40 to 75 percent of an inorganic oxidizer salt component, from 8 to 30 weight percent water and from 0.2 to 5 percent of a thickener.

11. A blasting composition of claim 10 containing from 1 to 30 percent of a particulate metal energizer.

12. A blasting composition of claim 11 containing particulate aluminum as metal energizer.

13. A blasting composition of clam 11 containing a ferrosilicon alloy as a metal energizer.

14. A blasting composition of claim 10 containing from 1 to 20 percent of a carbonaceous fuel ingredient.

15. A blasting composition of claim 14 containing ethylene glycol as a carbonaceous fuel ingredient.

16. A blasting composition of claim 10 containing a water-soluble inorganic perchlorate as a supplemental ingredient of the inorganic oxidizer salt component.

17. A blasting composition of claim 10 containing sodium perchlorate and at least one of the group of triethanolamine mononitrate and hexamethylenetetramine mononitrate as said sensitizer ingredients.

18. A blasting composition of claim 17 containing ammonium nitrate as at least one ingredient of said inorganic oxidizer salt component.

19. A composition of claim 18 containing at least one of the group of sodium perchlorate an sodium nitrate as a supplemental ingredient of said inorganic oxidizer salt component.

20. A blasting composition of claim 17 containing sodium perchlorate as the sole oxidizer salt of said inorganic oxidizer salt component.

* * * * *

70

75

PO-1050
(5/69)

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,617,402 Dated November 2, 1971

Inventor(s) Herbert G. Knight, Jr. (Case 5)

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

In the abstract, line 8, "lest" should read --least--

Column 1, line 17, "3,235,435" should read --3,235,425--

Column 1, line 58, "slat" should read --salt--

Table 1, Column 15, line 1, "17.69" should read --17.6--

Column 4, line 63, "20,23," should read --10,12,--

Column 5, line 24, "slat" should read --salt--

Column 6, Claim 8, line 31, "Clam" should read --Claim--

Column 6, Claim 13, line 45, "clam" should read --Claim--

Signed and sealed this 16th day of May 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents