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AQUEOUS SLURRY BLASTING COMPOSITION OF NON-EXPLOSIVE INGREDIENTS CONTAINING SILICON AND AN AERATION AGENT

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ABSTRACT OF THE DISCLOSURE

An aqueous slurry blasting composition of ingredients which per se are non-explosive containing silicon and an aeration agent. The aeration agent lowers the maximum specific gravity of the composition at the time of blasting.

This invention relates to aqueous slurry blasting agents and more particularly to an improved aqueous slurry blasting agent utilizing a metal fuel.

The use of metals as fuels to increase the energy of explosive compositions has for years been known throughout the art. Of the metals utilized, aluminum has been one of the metals most widely used due to its ability to enter the explosive reaction. However, the use of aluminum in aqueous slurry blasting agents has certain undesirable characteristics including that of high cost as compared to the present invention. This will be more readily appreciated from the following.

As previously pointed out, the prior art in the preparation of aqueous slurry blasting agents or explosives containing metals is well known. The use of fine, or mixtures of coarse and fine aluminum in combination with explosive ingredients has been demonstrated. The use of fine aluminum in connection with ammonium nitrate and water to the exclusion of explosive ingredients has also been demonstrated. In these cases the fineness of the aluminum was important to the operability of the compositions. In the presence of fine aluminum other metallic ingredients were also claimed to be useful. The use of fine aluminum introduced distinct disadvantages in that fine aluminum contributed to the hazard of dust explosions. In addition, the reaction between ammonium nitrate solutions and fine aluminum with evolution of hydrogen was encountered and special buffering and stabilizers were often necessary.

In other teachings in the addition of fine ingredients (200 microns or less), the absence of dissolved fuels was usually required. Inherent in the use of all fine ingredients is the cap sensitivity of such compositions, which in some instances is desirable depending on conditions of use while in other instances is undesirable, such as, where large quantities of slurry explosive are being bulk delivered to blasting sites. In addition, excluding dissolved fuels eliminates many of the most convenient fuels such as the glycols and the carbohydrates, some of which may be handled as liquids. The use of soluble fuels is also desirable in bulk delivered slurries because they do not add to the solids-to-liquid ratio. Additional advantages

in using a soluble fuel will become evident in the examples to follow.

Furthermore, in order to avoid the problems inherent in using fine aluminum, other forms were tried. It was observed that flaked and balled aluminum would contribute a measure of sensitivity to the compositions (as contrasted with ordinary aluminum filings, for instance), and it has become common practice to use this form. Resorting to flaked aluminum has introduced a different set of problems. The sensitizing effect, i.e., the ability to change an insensitive composition to an explosive composition, of the flaked aluminum apparently results from the entrapment of air and the resulting inclusion of the air in the form of tiny bubbles in the slurry. It has been conjectured that the inclusion of such bubbles in an explosive serves to provide "hot spots" which help initiate the compositions (Moder, C. L., The Physics of Fluids, vol. 6, No. 3, page 375, 1963). One problem, therefore, is to maintain the air bubbles in the aqueous environment. Attempts have been made to solve this problem by coating the aluminum with hydrophobic material in a separate operation. The use of boron and magnesium has also been claimed to be effective after treatment which, of course, entails additional expense to the already expensive metal ingredient. A further disadvantage to flaked aluminum is the excessive thickening imparted when high energy compositions are required and the aluminum content is increased or the water content is lowered.

The primary object of the present invention is, therefore, to provide aqueous slurry blasting agents which while being at least as energetic as conventional metallized slurries, eliminate the shortcomings and disadvantages outlined above.

Other objects of the invention will appear hereinafter the novel features and combinations being set forth in the appended claims.

Generally described, the present invention contemplates an aqueous slurry blasting agent of ingredients which per se are non-explosive comprising inorganic oxidizing salt, particulate silicon, carbonaceous fuel, thickener, and an aeration agent present in an amount to lower the maximum specific gravity of the aqueous slurry blasting agent to between about 30 and 90% of the maximum at the time of blasting.

Examples for operation of the invention are given as well as an example for preparing an aluminized aqueous slurry for comparison of the end products. In these examples parts are by weight unless otherwise indicated. Example 1 contained no silicon, Examples 2, 3 and 4 contained silicon, and Example 5 contained aluminum. These examples are given in Table I and were prepared as follows:

1. Make a solution by combining the AN, SN and water. Heat to dissolve.

2. Adjust the pH to between 5.4 and 6.0 with ammonium hydroxide or acetic acid as is required.

3. Blend the sodium bicarbonate, the sodium nitrite, the coal, the guar gums together in that order and then blend with the silicon or with the aluminum.

4. With the solution at a temperature of 140° F. mix the dry ingredients into the solution.

TABLE I

Example No.	1	2	3	4	5
Components:					
Silicon type I		8.5			
Silicon type II			8.5		
Silicon III				8.5	
Aluminum Flakes					8.5
Water	16.9	16.5	16.5	16.5	16.5
Ammonium Nitrate, prills	53.5	52.0	52.0	52.0	52.0
Sodium Nitrate, prills	16.1	15.6	15.6	15.6	15.6
Ethylene Glycol	11.1	5.0	5.0	5.0	5.0
Ground Coal	1.2	1.2	1.2	1.2	1.2
Guar Gum [1]	0.4	0.4	0.4	0.4	0.4
Guar Gum [2]	0.8	0.8	0.8	0.8	0.8
Sodium Nitrite	0.025	0.046	0.046	0.046	0.046
Sodium Bicarbonate	0.025	0.046	0.046	0.046	0.046
Oxygen Balance, percent	−0.8	−3.4	−3.4	−3.4	−4.1
Final-24 Hour Specific Gravity [3]	1.24	1.14	1.15	1.14	1.13
pH	5.0	4.8	5.2	4.7	5.0
Detonation Rate, M/S	5,550	4,650	5,250	5,000	4,750
Pipe Diameter, in	5	5	5	5	5
Booster	XC-49	XC-49	XC-49	XC-49	XC-49
Slurry Temperature, ° F	89	86	88	87	90
Underwater Measured Energy Weight Basis, Relative to Confined 60% HP Gel:					
Shock Energy	0.52	1.83	0.84	0.78	0.73
Thrust Energy	0.74	0.91	0.93	0.95	0.96

[1] Natural guar gum.
[2] Crosslinkable.
[3] Maximum specific gravities 1.4–1.5.

All of the examples shown in Table I were tested for explosive energy and/or detonation rate while confined underwater. Detonation rates were measured over a length of 20 cm. and were recorded on a counter chronograph. The underwater thrust (bubble) and shock energies were determined in the manner indicated by Cole (Cole, H. C., Underwater Explosions, Princeton University Press, Princeton, New Jersey (1948), pages 228 to 285) and as reported by Sadwin (Sadwin, L. D., Cooley, C. M., Porter, S. J., Stresau, R. H., Underwater Evaluation of the Performance of Explosives, International Symposium on Mining Research, Missouri, February 1961, vol. 1) and his collaborators with some minor modifications.

The data are reported relative to confined 60% HP gel. The charges, 20 lb. to 30 lb. in weight, are confined in 5-inch diameter by 28-inch long black iron pipe. The pipes were suspended vertically, 12 feet below the surface of the water to the charge center, and 28 feet from the bottom of the pond. The charges were initiated from the bottom with pentolite boosters (50/50 PETN/TNT), 3-inch diameter by 1-inch high and 190 grams in weight. The pressures generated by the detonations were sensed by piezoelectric hydrophone transducers and were recorded on an oscilloscope. The bubble times were also sensed by the transducers and were recorded on the oscilloscope.

With reference to the examples and Table I, it will be seen as graphically presented in the attached drawing in linear form, that the shock energy for the silicon compositions was somewhat higher than that for the aluminum flake and that the thrust energy for Si III and aluminum were about equivalent, while that for Si I and Si II slightly less. This was most surprising since heretofore, silicon and ferrosilicon have always required either the addition of a more reactive metal such as aluminum or required the use of a high explosive sensitizer such as TNT in preparing a detonable aqueous slurry explosive. Although silicon is shown in the examples in an amount of 8½% which represents a practical amount, the amount of silicon used depends primarily upon the explosive energy required but as a practical limit would start at about 3 and not ordinarily exceed 30%, with about 3 to about 15% being preferred. Typical particle size distribution and purity are shown in Table II. In the operation of this invention, particle size and purity are not critical as seen by comparing Examples 2, 3 and 4. This permits the use of economical technical grades of alloys and blends thereof. It will be appreciated, however, that finely divided silicon can be used in accordance with this invention free from the hazard of flammability as compared to that of finely divided aluminum, as shown in Table III.

TABLE II.—SILICON PARTICLE SIZES AND PURITY

Silicon Type	I	II	III [1]
U.S. Standard Sieve Sizes:			
On 30	Trace		
On 40			
On 50	16.2		
On 60	15.5	Trace	
On 80			
On 100	31.5	6.0	
Through 100			
On 200	26.7	29.0	
Through 200		65.0	82% smaller than 74 microns.
On 325	8.1		
Through 325	2.0		39% smaller than 44 microns.

TYPICAL ASSAY OF SILICON

	Types I and III	Type II
Percent Silicon	95-97	85

[1] Sharples "Micromerograph" particle size distribution analysis.

Silicon type II is a preferred material due to its ability to enter the explosive reaction and its economy. Type II is a silicon alloy blend averaging about 85% silicon, with a nominal silicon range of 82 to 88%. The range analysis of major residual elements bound in the alloy is as follows:

	Percent
Aluminum	.70–1.25
Calcium	.35–.60
Carbon	.10–.15
Chromium	.20–.30
Copper	.03–.08
Magnesium	.02–.05
Molybdenum	.01–.04
Nickel	.04–.08
Phosphorous	.01–.03
Titanium	.08–.12
Manganese	.05–.15
Iron	Balance

Silicon types I and III are silicon alloys containing 95 to 97% silicon and having a range analysis of major residual elements bound in the alloy as follows:

	Percent
Aluminum	0.20–0.65
Calcium	0.02–0.05
Carbon	0.04–0.09
Chromium	0.01–0.03
Copper	0.01–0.03
Nickel	0.035–0.06
Titanium	0.03–0.07
Phosphorous	0.002–0.006
Sulfur	0.06–0.10
Vanadium	0.06–0.10
Manganese	0.01–0.03
Iron	0.5–1.5

TABLE III.—DUST FLAMMABILITY TESTS [1]

Paint grade aluminum (97%<74 microns) (6%<44 microns)	Flash—6 to 8 feet high.
Aluminum (<400 mesh)	Flash—1 foot.
Aluminum (<200 mesh)	Flash—4 feet.
Silicon fines (type III)	No flash.
Silicon fines (type II)	No flash.

[1] Tests were conducted by dropping approximately 100 grams of sample, about 16 inches down an 8-inch diameter tube, ventilated at the bottom and open at the top and simultaneously initiating an electric squib.

The inorganic oxidizing salts are shown in the examples pertaining to silicon as being present in amount of 67.6% of the compositions. If requirements so dictate, these salts could comprise between 30 and 75% of the compositions. The physical form of the salts is not critical, coarse or fine, or mixtures of coarse and fine prilled and/or granular to powdery material all being suitable. In fact, in some preferred applications of this invention, the oxidizing salts are introduced into the compositions as an aqueous solution. Ammonium nitrate (A.N.), because of its availability, is the preferred oxidizing salt but sodium nitrate (S.N.) in practice almost always makes up a portion of the oxidizing salts, preferably to the extent of about 5% to 25% of the composition, but 0% to about 30% may be used. Although the examples given are all formulated with inorganic nitrates, the use of other inorganic oxidizing salts are within the scope of this invention. For instance, various of the alkali or alkaline earth nitrates may be used for all or a portion of the A.N., but in practice, not more than 80% of the A.N would be so substituted. A preferred range for the presence of A.N. is from about 30% to about 75%. In addition, salts selected from the perchlorates and less desirably, the chlorates in the absence of ammonium nitrate may be used. Examples of these are the ammonium, sodium and potassium salts with ammonium and sodium perchlorates being especially advantageous.

The nonexplosive carbonaceous fuels appear in the examples as being present in amount of 6.2% of the compositions. Depending upon the conditions, 3% to 15% of the compositions may be made up of one or more carbonaceous fuels, but 3% to 7% is more commonly used. The nature of the carbonaceous material is not ordinarily critical but at lower levels, soluble fuels, amine nitrates, glycols, such as ethylene glycol and saccharides, such as ordinary granulated sugar, are preferred. Where insoluble particulate carbonaceous fuel or immiscible carbonaceous liquids are used, they must, of course, be suspended in or dispersed throughout the aqueous phase.

Water is shown as 16.5% by weight of the compositions in the examples. Between 10 and 30% of the compositions may be composed of water but in conventional practice 14 to 24% is more commonly employed.

It will be appreciated that the compositions of this invention are composed of a blend of liquid and solid components. It is essential that the solid phase or nonhomogeneous liquid phase, when such is utilized, be uniformly dispersed throughout the liquid phase. Solid materials, such as DNT, coal, sulfur, gilsonite and the like, and liquid materials such as, DNT, nitroparaffins, fuel oil and the like may be so utilized. This is accomplished by employing thickening agents which retard or arrest the separation of the solid and liquid materials. Suitable thickeners include carboxymethylcellulose, methyl cellulose, water soluble starches, cereal flour and the like. Preferred practice is to employ guar gum and to cross-link (gel) the gum with a suitable cross-linking agent. The cross-linking agent may be combined with the gum and is commercially available in such form or may be added as a separate ingredient in very small amounts, usually less than 0.1% of the total composition. The gum may be used in as low amount as 0.4% or thereabouts and up to about 4%, but more generally 0.7% to 1.8% is used.

Furthermore, it will be appreciated that the specific gravity of the compositions of this invention at the time of blasting is important. A specific gravity of between about 30 and 90% of the maximum specific gravity of the aqueous slurry blasting agent and preferably between about 50 and 85% at the time of blasting has been found necessary for successful performance. A specific gravity at the time of blasting from about 1.0 to about 1.3 has been found particularly effective. The adjustment and maintenance of the compositions to the specific gravities given above are accomplished by incorporation of an aeration agent into the composition. The term an "aeration agent" as used herein means an agent which causes the composition to be combined with or charged with gas. The term "maximum specific gravity" as used herein means the specific gravity of the aqueous slurry blasting agent exclusive of gas.

As is discussed in the reference previously given, the presence of small evenly dispersed air or gas bubbles throughout an explosive can be beneficial to initiation and propagation. The operation of this embodiment is in accord with the aforementioned hot spot theory and encompasses the inclusion of small amounts of tiny gas bubbles throughout the liquid phase. Examples of this type of composition are given in Table I. Also, gas bubbles may be generated as disclosed by Ferguson et al. (U.S. 3,288,658) and Swisstack (U.S. 3,288,661). However, a preferred aeration agent for the present invention is that shown in the examples wherein the reactions involved are visualized as proceeding as follows:

(I) $2H^+ + NaHCO_3 \rightarrow Na^+ + H_2O + CO_2$

(II) $NaNO_2 + NH_4NO_3 \rightarrow NaNO_3 + 2H_2O + N_2$

Reaction I is considered to be the simple acidic decomposition of sodium bicarbonate while Reaction II is conceived as the oxidation reduction reaction between sodium nitrite and ammonium nitrate. The properties of the individual gases employed have to be considered in designing the proper composition and mixing procedure. For instance, since carbon dioxide is somewhat soluble in aqueous solutions, the gas is used where quick initial aeration is desired. In these cases the slower acting sodium nitrite is also employed to replace the carbon dioxide with nitrogen as the former dissolves. Specific gravities as low as 0.3 have been obtained with analogous compositions having a maximum specific gravity of about 1.4 but in practice 0.5 would constitute the normal lower limit. A specific gravity of about 1.3 is a practical upper limit for this type of composition although since temperature directly affects sensitivity at a temperature of about 40° F., a specific gravity of about 1.1 is preferred.

Thus, a particularly efficacious aeration agent for use in lowering and maintaining specific gravities in accordance with this invention is a substantially equal mixture of sodium nitrite and sodium bicarbonate in an amount of from about 0.04 to about 0.4% by weight of the blasting composition. As demonstrated in the examples, this aeration agent present in the small amount of 0.09% gave 24 hour specific gravities of about 1.14–1.15 at a

pH of 4.7–5.2 and gave extremely good performance of the silicon containing compositions in respect to detonation rate, shock energy, and thrust energy. It will be appreciated, however, that in some instances, the sodium nitrite may be used alone when rapid initial aeration is not required. When so used, an amount of from about 0.01 to about 0.2% has been found to give satisfactory results.

It is evident that the inclusion of various minor ingredients is within the scope of this invention. Adjustments are routinely made with appropriate acids and bases to obtain desired pH ranges. Other variations and modifications are apparent to those versed in the art and the examples given are not intended to nor do they represent limits on the scope of this invention.

The advantages of the invention are multifold. Unlike some conventional compositions the use of the fine easily flammable and overly reactive metallic sensitizers is not required. Where it is convenient or desirable to use the energetic metal fuel component partially in the fine particulate form, the compositions of the invention represent a great improvement through a decreased susceptibility to dust explosions. No special buffering is required for the compositions of this invention other than the normal pH adjustments. The form of the metallic energizer whether chemically pure or technical grade is not critical in these compositions and no special treatment of the energizer component is necessary, thus providing improved economy. Through the availability of these compositions it will be possible to obtain the explosive energy of conventional compositions while avoiding their shortcomings and disadvantages.

It will be seen, therefore, that this invention may be carried out by the use of various modifications and changes without departing from its spirit and scope with only such limitations placed thereon as are imposed by the appended claims.

What we claim and desire to protect by Letters Patent are:

1. An aqueous slurry blasting agent of ingredients which per se are non-explosive comprising inorganic oxidizing salt, particulate silicon, carbonaceous fuel, water, thickener, and an aeration agent present in an amount to provide sufficient air or gas bubbles to lower the maximum specific gravity of the aqueous slurry blasting agent to between about 30 and 90% of the maximum.

2. The aqueous slurry blasting agent of claim **1** wherein the silicon is present in an amount of from about 3 to about 30% by weight.

3. The aqueous slurry blasting agent of claim **2** wherein the silicon is present as a silicon alloy containing from about 80 to about 97% silicon by weight of said alloy.

4. The aqueous blasting agent of claim **2** wherein the silicon is present as a mixture of silicon alloys containing from about 80 to about 97% silicon by weight of said mixture.

5. An aqueous slurry blasting agent of ingredients which per se are non-explosive comprising from about 30 to about 75% ammonium nitrate, from 0 to about 30% of sodium nitrate, from about 3 to about 15% of particulate silicon, from about 3 to about 15% of carbonaceous fuel, from about 0.4 to about 4% of thickening agent, from about 10 to about 30% of water, all percentages by weight, and an aeration agent present in an amount to provide sufficient air or gas bubbles to lower the maximum specific gravity of the aqueous slurry blasting agent to between about 50 and 85% of the maximum.

6. The aqueous slurry blasting agent of claim **5** wherein the specific gravity of said blasting agent is from about 1.0 to about 1.3.

7. The aqueous slurry blasting agent of claim **5** wherein the silicon is present as a silicon alloy containing from about 80 to about 97% silicon by weight of said alloy.

8. The aqueous slurry blasting agent of claim **5** wherein the silicon is present as a mixture of silicon alloys containing from about 80 to about 97% silicon by weight of said mixture.

9. An aqueous slurry blasting agent of ingredients which per se are non-explosive comprising by weight from about 30 to about 75% ammonium nitrate, from 5 to about 25% of sodium nitrate, from about 3 to about 15% of particulate silicon, from about 3 to about 15% of carbonaceous fuel, from about 0.4 to about 4% of thickening agent, from about 10 to about 30% of water, and from about 0.04 to about 0.4% of a substantially equal mixture of sodium nitrite and sodium bicarbonate as an aeration agent to provide sufficient gas bubbles to lower and maintain the maximum specific gravity of the aqueous slurry blasting agent to between about 50 and 85% of the maximum.

10. The aqueous slurry blasting agent of claim **9** wherein the silicon is present as a silicon alloy containing from about 80 to about 97% silicon by weight of said alloy.

11. The aqueous slurry blasting agent of claim **9** wherein the silicon is present as a mixture of silicon alloys containing from about 80 to about 97% silicon by weight of said mixture.

12. An aqueous slurry blasting agent of ingredients which per se are non-explosive comprising by weight from about 30 to about 75% ammonium nitrate, from about 5 to about 25% of sodium nitrate, from about 3 to about 15% of particulate silicon, from about 3 to about 15% of carbonaceous fuel, from about 0.4 to about 4% of thickening agent, from about 10 to about 30% of water, and from about 0.01 to about 0.2% of sodium nitrite as an aeration agent to provide sufficient gas bubbles to lower and maintain the maximum specific gravity of the aqueous slurry blasting agent to between about 50 and 85% of the maximum.

13. The aqueous slurry blasting agent of claim **12** wherein the silicon is present as a silicon alloy containing from about 80 to about 97% silicon by weight to said alloy.

14. The aqueous slurry blasting agent of claim **12** wherein the silicon is present as a mixture of silicon alloys containing from about 80 to about 97% silicon by weight of said mixture.

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