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3,333,998

AQUEOUS BLASTING COMPOSITIONS CONTAINING FLAKE ALUMINUM AND SUGAR**John D. Ferguson, Wilmington, Del., assignor to Hercules Incorporated, a corporation of Delaware****No Drawing. Filed July 20, 1965, Ser. No. 473,509****7 Claims. (Cl. 149-21)**

This invention relates to aqueous inorganic oxidizer salt type slurry blasting compositions of the nitrocarbonate type containing a combination of aluminum and a sugar as the sensitizer component.

Inorganic oxidizer salt blasting compositions of the aqueous slurry type have had wide use in the explosives industry in recent years. However, it has been necessary that these compositions, in order to be detonatable by a conventional booster charge, contain smokeless powder or a high explosive such as TNT, PETN or the like as the sensitizer except that in a number of instances, large amounts of finely divided metals such as particulate aluminum have been utilized for that purpose. The use of smokeless powder and high explosives in these slurry compositions has been disadvantageous particularly from the standpoint of manufacturing hazards involving handling of these highly sensitive materials, and the use of large amounts of finely divided metals has been economically unfeasible.

This invention is concerned with aqueous aluminum-sensitized blasting compositions of the inorganic oxidizer salt type, free from sensitizers of the high explosive and smokeless powder type, containing smaller amounts of aluminum than required heretofore, and characterized by improved detonation rates.

In accordance with the invention, aqueous inorganic oxidizer salt slurry type blasting compositions are provided which contain, on a weight basis, a combination of from 5 to 20 percent aluminum with from 1 to 25 percent of a sugar, as the sensitizer component, the said aluminum being in flaked form in an amount of at least 5 percent based on the total slurry composition. The slurry compositions generally contain from 30 to 75 percent of an inorganic oxidizer salt, from 8 to 25 percent water, the above described sensitizer component, and a thickener, usually in amount of from 0.2 to 5 percent.

In preferred practice, the oxidizer salt component is either ammonium nitrate alone or together with sodium nitrate in a weight ratio to the sodium nitrate as low as about 0.5:1, generally within the range of from about 2:1 to 4:1, and the thickener is guar gum in crosslinked (or gelled) form. The now preferred compositions of the invention contain (weight basis) from 6 to 15 percent and 3 to 10 percent of the aluminum and sugar ingredients respectively, as the sensitizer component; from 12 to 18 percent water; from 40 to 70 percent ammonium nitrate and from 5 to 30 percent sodium nitrate, as the oxidizer salt component; and from 0.2 to 2 percent guar gum.

By the term "inorganic oxidizer salt," as is well known in the explosives art, is meant one which under the conditions of the detonation, liberates oxygen for the 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. Of these supplementary salts, the alkali metal nitrates are now preferred. Often when ammonium nitrate is utilized with a supplementary salt, it comprises a major proportion of the total oxidizer salt, i.e., at least 50 percent of the total oxidizer salt. Exemplary inorganic oxidizer salts that can be used alone, or together with ammonium nitrate, are alkali metal and alkaline earth metal nitrates and perchlo-

rates (including ammonium) as for example, sodium nitrate, magnesium nitrate, calcium nitrate, potassium nitrate, barium nitrate, sodium perchlorate, ammonium perchlorate, calcium perchlorate and magnesium perchlorate.

Particle size and type of the oxidizer salt ingredient are not generally critical. For example, ammonium nitrate can consist of prills such as used in fertilizers and which are substantially all on 20 mesh, or it can be granular and in that form, vary from coarse to fine. Other oxidizer salt ingredients are generally of comparable particle size.

When referring herein to a sugar as a sensitizer ingredient, it is meant any one or a mixture of those members of the class of monosaccharide and disaccharide carbohydrates. Exemplary sugars are molasses, d-xylose, d-glucose, d-monose, d-fructose, 1-sarbose, sucrose, lactose and maltose. Sucrose, as ordinary table grade cane or beet sugar, and molasses, are now preferred.

By the term "molasses" it is meant the dark-colored syrupy residue from the extraction of crystallizable sugar from sugar cane and beets. The molasses composition varies greatly but is often in the order of about 80 percent solids, of which 50 to 60 percent are sugars, e.g., sucrose, dextrose and levulose. An exemplary molasses is cane blackstrap molasses having a total solids content of 76 percent, total sugars, 50 to 54 percent and minerals, 8 to 10 percent with a minor content of available protein, soluble gums, organic acids, and vitamins, constituting the remaining solids.

The aluminum component is in flaked form in a proportion equal at least to 5 percent of the finished composition. When the proportion of flake aluminum is below the 5 percent level, the slurry composition is so insensitive as to be nondetonatable by conventional booster systems, e.g., by a 500 gram booster charge of PETN. The flakes of the aluminum ingredient generally have a thickness less than about 0.002" and a diameter (or maximum cross-sectional dimension) in the range of from somewhat less than 0.0098 to 0.0232", chopped aluminum foil being particularly well suited.

The thickener content can be as high as 5 percent dependent upon the particular thickener and the desired consistency of the finished composition. Generally, a thickener content up to about 2 percent is sufficient. When the thickener content is within the range of 0.2 to 0.5 weight percent, there is sufficient thickening to prevent settling of the composition ingredients, although additional thickener is often required in order to impart a satisfactory degree of cohesiveness so that the composition retains its form as a unit mass, preferably plastic but deformable. Exemplary thickeners are sodium carboxymethylcellulose, mannogalactans, e.g., guar gum, methyl cellulose, water-soluble starches, and the like. When the thickener is guar gum in cross-linked form, in accordance with preferred practice, the guar content is most advantageously within the range of from 0.5 to 1.5 percent, under which conditions the finished composition is a plastic, rubbery, but deformable, mass.

The compositions of the invention are in most instances insensitive to detonating action of a No. 8 commercial blasting cap but are, in all events, detonatable by conventional "booster" charges of PETN (pentaerythritol tetranitrate), RDX (cyclotrimethylenetrinitramine), Pentolite (PETN-TNT, 50/50), tetryl, Composition B (RDX-TNT, 60/40) and the like. Temperature of the composition at the time of initiating detonation appears to effect sensitivity, the higher temperatures being often accompanied by a corresponding sensitivity increase. One booster advantageously employed is a dispersion of a crystalline high explosive, e.g., PETN or RDX in a plastic carrier such as described in U.S. 2,965,456, issued Dec. 20, 1960 to Alpheus M. Ball, and which is

detonated by either a commercial blasting cap or a detonating fuse. In general, these compositions are detonatable in response to any secondary explosive.

The explosive compositions of the invention are of the well known class of nitrocarbonitrates, by which term it is meant there are no sensitizers which in themselves are high explosives, and the mixtures will not detonate with a No. 8 blasting cap when packed for shipment.

The invention is illustrated with reference to the following formulations, all on a weight percent basis.

taining more aluminum; and by a higher detonation rate utilizing a 20 gram booster. These unexpected differences are directly attributable to the presence of the molasses in combination with the aluminum as the sensitizer component. Example 4 further demonstrates the effect of the presence of 5 percent molasses with 5 percent flake aluminum, i.e., it provides a detonation rate of 3350 m./sec. (475 gram booster) which, except for the molasses present, would be markedly lower than that detonation rate of Example 2. Example 4 also demon-

	Example No.									
	1	2	3	4	5	6	7	8	9	10
Water.....	16.0	16.0	16.0	16.0	16.0	10.0	5.0	16.0	16.0	16.0
Ammonium Nitrate ¹	55.8	58.3	52.5	54.0	55.0	55.0	61.9	54.0	54.0	54.0
Sodium Nitrate ²	15.0	15.0	18.0	19.0	23.0	19.0	7.0	14.0	14.0	14.0
Sugar ³			5.0	5.0	5.0	15.0	25.0	5.0	5.0	5.0
Aluminum:										
Flake.....	12.5	10.0	7.5	5.0				10.0		
Granular ⁴									10.0	10.0
Do ⁵										
Do ⁶										
Guar Gum ⁷	0.6	0.6	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Detonation Rate, m./sec.: ⁸										
Detonator, Grams: ⁹										
475.....	3,750	3,050	3,750	3,350	Failed	Failed	Failed	4,350	Failed	Failed
160.....		2,650		2,800				3,400		
80.....		Failed		Failed						
40.....			3,500					3,450		
20.....	2,200		Failed							
10.....								Failed		
5.....								1.26		
Density, gm./cc.....	1.39	1.40	1.23	1.24	1.36	1.33	1.36	1.26		1.36
Flowability, seconds ¹⁰			3.0	2.5	2.0					

	Example No.										
	11	12	13	14	15	16	17	18	19	20	21
Water.....	18.0	18.0	18.0	18.0	18.0	18.0	18.0	18.0	18.0	18.0	18.0
Ammonium Nitrate ¹	56.0	54.5	53.5	53.0	51.0	50.5	46.0	50.5	50.0	50.0	47.6
Sodium Nitrate ²	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	
Sodium Perchlorate ²											17.4
Sugar ³		1.5	2.5	3.0	5.0	5.5	10.0	10.0	5.5	5.5	5.5
Aluminum:											
Flake.....	10.0	10.0	10.0	10.0	10.0	10.0	10.0	5.0	5.0	7.0	10.0
Granular ⁴											
Do ⁵									5.0	3.0	
Do ⁶									1.5	1.5	1.5
Guar Gum ⁷	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.5	1.5	1.5	1.5
Detonation Rate, m./sec.: ⁸											
Detonator, Grams: ⁹											
475.....	2,200	2,380	2,500	2,850	3,750	2,850	2,750	2,800	Shot..	2,650	4,750
160.....											
80.....											
40.....											
20.....											
10.....											
5.....											
Density, gms./cc.....	1.47	1.47	1.47	1.43	1.47	1.43	1.46				

¹ Substantially all through 40-mesh screen and substantially all on 100-mesh screen.
² Granular, varying from "Fine" to "Coarse".
³ Molasses, Runs 3-10; sucrose (ordinary table grade cane sugar), Runs 12-17.
⁴ Substantially all through 200 mesh.
⁵ Substantially all through 12 mesh, on 40 mesh.
⁶ 75 percent on 60 mesh, all on 200 mesh.
⁷ Hydrated only, Runs 1-3, 5-10; crosslinked, Runs 4, 11-17.
⁸ Measured as average detonation velocity over a 20 cm. length, at the end of a 28" long column of explosive. The explosive is confined in a 5" x 28" black iron pipe (Schedule 40). The time for detonation to proceed

across the 20 cm. length of explosive is measured electronically by means of a counter-chronograph.
⁹ Pentolite, TNT/PETN (1:1); Temperature at which the detonation was initiated: Runs 1-15, 50° F.; Runs 16, 17, 60° F.; Runs 18, 19, 76° F.; Run 20, 45° F.; Run 21, 74° F.
¹⁰ Flow time determined by funnel test in accordance with which approximately 5,000 grams of slurry is poured into an aluminum funnel having a 1½" diameter by 1" orifice. When the orifice is opened to permit flow, the timing is begun. When light is visible through the orifice (looking down into the funnel), timing is stopped. The time difference is designated as the flow time.

The foregoing examples demonstrate aluminum and a sugar as a sensitizer combination in accordance with the invention. Thus, the compositions of Examples 1 and 2, each devoid of a sugar and containing 12.5 and 10.0 percent flaked aluminum, respectively, having respective detonating rates of 3750 and 3050 m./sec. The composition of Example 3, containing still a smaller amount of aluminum, i.e., 75 percent, would be expected to have a correspondingly lowered detonation rate except that it also contains 5 percent molasses and is concomitantly characterized by a detonation rate (475 gram booster) the same as that of the composition of Example 1, con-

strates a marked improvement in sensitivity over Example 2, as shown by the detonation in response to an 80 gram booster whereas under the same firing conditions, Example 2 shows a failure.
Examples 5-7 demonstrate inoperability of molasses alone, thereby demonstrating in conjunction with Examples 1-4, the uniqueness of a sugar, when in combination with aluminum, as the sensitizer component.
Examples 8-10 demonstrate flaked aluminum to be operable. It is often advantageous, however, to include a portion of granular aluminum in the aluminum ingredient of the sensitizer component, as for example, when

it is desired to maintain the energy level for a given composition while at the same time, it is desired to decrease sensitivity by reduction of the flake aluminum content.

Examples 11-17 demonstrate the role of sucrose in form of ordinary "table grade" cane sugar as a sensitizer ingredient in the practice of the invention. As shown, at constant aluminum content in the absence of the sugar ingredient, a detonation rate of 2200 m./sec. was obtained whereas at progressively increased sugar content levels up to 5 percent, there was a corresponding increase in detonation rate. These examples also demonstrate that there are optimum proportions of sugar ingredient dependent upon the particular formulation, about 5 percent in those shown.

Examples 18-20 demonstrate granular aluminum as an ingredient of the aluminum component.

Example 21 demonstrates a combination of ammonium nitrate and sodium perchlorate as the oxidizer salt component.

In accordance with a now preferred process for the manufacture of slurry compositions of the invention, the sugar and water components are admixed, and a small proportion of each of the total oxidizer salt and guar gum components is added to the resulting admixture, the guar gum being in natural form in an amount often in the order of about 0.2 percent based on the finished composition. Under these conditions, hydration of the natural guar gum is immediately initiated. The resulting admixture is maintained, under agitation, at a temperature in the order of say, 80-100° F. for a period of from 5-10 minutes, and then, due to completion of hydration, has a sufficiently high viscosity to prevent settling of all ingredients. The aluminum, together with the remaining proportion of oxidizer salt is then added over a several minute period, with continued agitation, followed by addition of the remaining portion of the guar gum, the latter being in "inhibited" form, i.e., containing an agent causing a delay in hydration that would otherwise take place immediately. The delay, or inhibition, postpones hydration of the last added guar gum so as to permit time for packaging final product mixture while still easily flowable, with final hydration and subsequent gelation (crosslinking) taking place during storage of the packaged composition.

In carrying out the process embodiment above described, and utilizing only a minor proportion of the guar gum ingredient in natural form, all guar gum is ultimately crosslinked to provide a rubbery, plastic but deformable mass. Somewhat less than complete crosslinking of the guar gum can be obtained when the natural guar gum is added in a proportion greater than that in inhibited form. Hydration with substantially no gelation can be obtained when only natural guar gum is added, and particularly at a pH below about 7. In all instances,

there is a thickening action whether it be the result of hydration alone or with some gelation, or substantially complete gelation.

When referring herein to hydration, it is meant the reaction that takes place between the guar gum and water components to form a sol, and when referring to gelation, or crosslinking, it is meant the crosslinking reaction that takes place between the guar gum and the particular crosslinking agent therein to form a gel.

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 explosive of the aqueous slurry type, the improvement comprising from 5 to 20 weight percent aluminum of which at least 5 percent, based on said slurry, is in flake form, in combination with from 1 to 25 weight percent of a sugar as the sensitizer component.

2. A slurry type explosive of claim 1 containing, on a weight basis, from 8 to 25 percent water, 30 to 75 percent of an inorganic oxidizer salt, and from 0.2 to 5 percent of a thickener.

3. A slurry type composition of claim 2 containing from 12 to 18 percent water, from 40 to 70 percent ammonium nitrate, from 5 to 30 percent sodium nitrate, from 0.2 to 2 percent guar gum, from 6 to 15 percent aluminum and from 3 to 10 percent sugar.

4. A composition of claim 3 wherein at least a portion of said guar gum is in crosslinked form.

5. A composition of claim 4 wherein said sugar is molasses.

6. A composition of claim 4 wherein said sugar is sucrose.

7. A composition of claim 1 wherein all of said aluminum is in flaked form.

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