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3,397,097

**THICKENED AQUEOUS INORGANIC OXIDIZER
SALT BLASTING COMPOSITIONS CONTAIN-
ING GAS BUBBLES AND A CRYSTAL HABIT
MODIFIER AND METHOD OF PREPARATION**
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ABSTRACT OF THE DISCLOSURE

Water-bearing explosive compositions based on inorganic oxidizing salt and nonexplosive fuel containing the combination of soluble carbonaceous fuel, surfactant and small gas-filled cavities.

In recent years, blasting agents particularly those of the types known as water-gels or slurries have gained considerable commercial acceptance. These water gels generally comprise an inorganic oxidizing salt, predominantly ammonium nitrate, a thickening or gelling agent for the liquid, and a fuel.

For large-scale blasting operations, e.g., for blasting taconite ore, blasting agents must be sensitive enough to propagate detonation throughout the mass in confined columns of usually about 6 to 9 inches diameter, during both hot and cold conditions. In general, the blasting agent should be sufficiently sensitive for propagation of detonation in a continuous unconfined column of about 6 to 10 inches in diameter, at the borehole temperature.

Although water-bearing compositions which comprise a carbonaceous material as the sole fuel have been proposed for such blasting compositions, their use in commercial blasting has been restricted since at lower temperatures detonation is not reliably propagated through the mass. When water-bearing blasting compositions are to be used at low temperatures, e.g., 32 to 40° F. (0 to 5° C.), it is usually necessary to incorporate a relatively high proportion of a self-explosive, e.g., TNT or smokeless powder, and/or a particulate metal, e.g., aluminum, in the formulation.

The use of either the self-explosive or the metal fuel in water-bearing blasting agents requires handling of solids, a feature which is undesirable particularly when the compositions are to be prepared at the site in pump or slurry trucks. Further, the need for self-explosive can present a hazard in storage and handling of the compositions since such compositions are more sensitive than compositions which do not contain such self-explosives or metals. Still further, both self-explosive and metal fuels materially add to the cost of the blasting agent. Accordingly, there is a distinct need for a water-bearing blasting composition which will detonate reliably at low temperatures without the presence of self explosive and/or metallic fuels, and which can be easily compounded, at relatively low cost, either in a plant or at the blasting site.

This invention provides an improvement in water-bearing blasting agents which permit formulation of compositions detonatable in columns as small as 6 inches or less at temperatures as low as 40° F. (ca. 5° C.) without high explosive or metallic sensitizers. Thus, more specifically, this invention provides an improvement in thickened blasting agents consisting essentially of water, inorganic oxidizing salt at least partly dissolved in said water and non-explosive fuel, said improvement comprising providing throughout said mass about from 5 to 60% by volume of small gas-filled cavities a crystal habit modifier for said salt, and a fuel component consisting essentially of

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at least 3% by weight, based on the total weight of composition, of dissolved carbonaceous fuel. Usually the compositions have a specific gravity of about 1.0 to 1.4, and preferably 1.1 to 1.3, and an oxygen balance of -25% to +10%, and preferably -15% to about 0%.

The compositions of this invention are prepared by incorporating the crystal habit modifier, aforesaid fuel, gas filled cavities and other additives such as gelling and crosslinking agents in a hot solution of the inorganic oxidizing salt component, then cooling the resulting product. As prepared, the oxidizing salt is usually substantially all in solution in the hot product. When the product cools, part of the salt crystallizes therein so that at ambient temperature 10 to 20% of the salt component may be undissolved, while at 40° F., as much as 50% or more of the salt may be crystallized.

The inorganic oxidizing salts employed in this invention can be any of the soluble salts conventionally used in water-bearing explosives including alkali metal, alkaline earth metal and ammonium nitrates, perchlorates and dichromates. In general, for economic reasons, ease of handling and overall sensitivity and other explosive properties compositions containing a salt component consisting essentially of at least 65% by weight of ammonium nitrate are preferred. Examples of other inorganic salts are sodium nitrate, calcium nitrate, potassium nitrate, magnesium nitrate, sodium perchlorate, potassium perchlorate, ammonium perchlorate and magnesium perchlorate. Of these, sodium nitrate is a preferred auxiliary salt used with ammonium nitrate, preferably in amounts up to 25% of the salt component.

In preparing the compositions of this invention the inorganic oxidizing salt is preferably incorporated directly as hot "neutral liquor" or solution, preferably, e.g., one such as that obtained from the manufacturing of ammonium nitrate prior to graining or prilling. The inorganic salts are chosen to be soluble in the hot liquor so that substantially all oxidizing agent is in solution at the time of manufacture. This is a boon in the preparation of blasting compositions at the blasting site, since, with the provision and use of heated storage tanks, the inorganic oxidants can be handled as a liquid minimizing the need for handling solids.

As stated above, the solution of inorganic oxidant is preferably based on hot, concentrated aqueous solution of ammonium nitrate, which usually contains about from 70 to 85% ammonium nitrate by weight. Such a solution is obtained from the neutralization step in the preparation of ammonium nitrate by the reaction of ammonia and with 40-60% nitric acid in a continuous process. Crystallization of the ammonium nitrate is prevented by keeping the temperature above the "crystallization point" of the liquor. This does not present particular problems since, for example, storage of hot, neutralized liquid in 10,000 gallon tanks normally is possible for 2 to 3 days without crystallization taking place and without the need for large amounts of additional heat. The crystallizing temperature of 70% liquor is 84° F. (29° C.), 80% solution will not crystallize out above 136° F. (58° C.) and 85% solution will not crystallize out if maintained at temperatures above about 165° F. (74° C.). Since the liquor from commercial processes is well above 215° F. when it leaves the neutralizer, and in normal storage volumes it cools slowly, stored liquor of even 85% strength normally will not begin to crystallize out for several days. However, during cold winter months, it usually is necessary to insulate the tanks and frequently is desirable to apply heat occasionally to prevent crystallization from the solutions of 70 to 85% concentration commonly employed. Means for supplying this heat are commonly provided on pump or slurry trucks. The neutral liquor desirably will maintain alkalinity of 0.01 to 0.05% NH₃.

It is desired that the liquor retain this alkalinity in handling and storage so as to preclude corrosion of equipment, and prevent the contamination of blasting agent particularly with regard to ions such as of iron, copper, zinc, and aluminum, which would inhibit or destroy a gelling system.

Although auxiliary oxidizing agents, in preferred systems salts other than ammonium nitrate, can be added as finely divided solids, preferably they are added in aqueous solution. When added in solution, the water content of the solution naturally will be included in determining the total water content of the composition. Usually, gelling or thickening agents as described in more detail hereinafter will be added with the preferred sodium nitrate auxiliary oxidizing agent to facilitate dispersion of ingredients.

The soluble fuel added to the hot inorganic oxidizing salt solution is an organic, i.e., carbonaceous, fuel soluble in the salt solution. "Soluble" as used herein means the fuel dissolves in the subject compositions to the extent of at least about 2 grams of fuel per 100 grams of product at ambient temperature. "Dissolved" and the like terms used herein with reference to the fuel mean the fuel is dispersed in a colloidal or smaller, e.g., molecular, state. Examples of fuels used in this invention are carbohydrates such as disaccharides and starches, aliphatic mono- and polyhydric alcohols, aldehydes, ketones, aliphatic acids, nitriles, amides, lignin sulfonates, and mixtures of these fuels. Specific examples of such soluble fuels include: monosaccharides such as dl-lyxose, d-glucose (dextrose), d-mannose, d-galactose, d-fructose, and l-sorbose; disaccharides such as maltose, lactose, and sucrose; aliphatic polyhydric alcohols such as ethylene glycol, propylene glycol, polypropylene glycol, and glycerine; aliphatic monohydric alcohols such as methanol, ethanol, isopropanol, propanol, and n-butanol; aldehyde such as formaldehyde, acetaldehyde, and propionaldehyde; ketones such as acetone; aliphatic carboxylic acids such as acetic acid, propionic acid, acrylic acid, and lactic acid; amides such as formamide, acetamide, acrylamide, and propionamide; and aliphatic nitriles such as acetonitrile.

Of these fuels, the mono- and disaccharide carbohydrates are preferred. Sucrose (common table sugar) and dextrose are particularly preferred from the viewpoint of availability at low cost. Some fuels such as the alcohols may act as solvents for cavity-contributing fuels, thus reducing cavity volume. Thus it is usually preferred to use such solvent-type fuels in small proportions or in combination with other fuels such as sucrose or dextrose. Particularly with fuels other than the soluble carbohydrates, solubility may vary with the composition; especially when large amounts of the fuel are to be used the particular soluble fuel should be added to a sample of the remainder of the composition to test for gross phase separation, which should be avoided. In addition to allowing fuel to become completely dispersed in the blasting agents, thus promoting homogeneity of the composition and leading to intimate contact of fuel with oxidizing agent, soluble fuels tend to increase the fluidity of the compositions particularly at low temperatures. Although at least 3%, based on the total composition, of fuel is of the aforementioned soluble type, the fuel component which can total up to 25%, of the product can also contain solid fuels such as finely divided coal or other common insoluble fuels. Preferably, however, at least 50% of the fuel component is of the soluble type.

Gas-filled cavities or bubbles are necessary in providing compositions which at low (40° F.) temperatures are sensitive to initiation by a standard source and which propagate detonation in six-inch diameter charges. As used herein, the term "gas filled cavities" refers to minute bubbles of a gas, e.g., mono- or diatomic molecules or a mixture thereof such as in air, uniformly and homogeneously dispersed through the composition of this invention. Gas-filled cavities can be physically or mechani-

cally entrapped in the composition during its preparation or can be provided by the incorporation of a closed cell rigid foam or cellular, low-density fuel in the composition as described more completely hereinafter. The dimensions of the gas-filled cavities within the composition will be small, i.e., their largest dimension will, in general, not exceed about $\frac{1}{16}$ inch, and will, as indicated, be uniformly distributed throughout the composition, thereby precluding discontinuities in the composition such as would be provided by large cavities or agglomerates of cavities and would preclude detonation of the entire column of the composition.

Physical or mechanical entrapment of gas, e.g., air or an inert gas such as nitrogen or carbon dioxide, can be affected in a number of ways, e.g., by (1) incorporating air during the preparation of the composition employing a mixer which imparts turbulence to and aerates the ingredients being combined. Typical of such mixers are turbine mixers and aerating mixers such as a "Waring Blender" which forms a vortex into which air is drawn during mixing; (2) injecting gas under pressure into the composition as it is fed from the mixing tanks, turbulence in pumping being sufficient to disperse the gas throughout the composition; (3) turbulently admixing the composition with gas (air), e.g., in a Venturi eductor, e.g., of the type described in U.S. Pat. 2,694,404 for forming aqueous emulsions of nitroglycerin. In such an eductor, the composition serves as the motive fluid and the gas is drawn into the throat (mixing chamber) of the eductor and turbulently intermixed with the gelled composition.

Such methods of incorporating gas into the composition naturally will best be employed when the blasting composition is prepared at the blasting site and delivered directly into the borehole, e.g., when the composition is prepared in a pump or slurry truck. These methods of entrapping air are particularly well suited for incorporating gas since with such all ingredients of the composition can be handled in a fluid form minimizing the handling of solids.

However, when the blasting compositions are to be prepared at a site away from the blasting location, stored, and transferred to the blasting location in packages, e.g., flexible bags of a polymeric material (polyethylene), from which they are to be loaded into the boreholes, or when the compositions are to be prepared at the blasting site in a mixer not conducive to incorporation of air in the composition, it is generally preferred to provide the gas-filled cavities both by physical entrapment of gas and by incorporating in the composition a low-density fuel. Materials used to incorporate gas cavities into the composition of the invention are those which, when added to the product of this invention in amounts of 1 to 20% by weight, lower the density thereof at least 5%, preferably 20 to 30%. Typical porous fuels include closed cell foams of polymeric materials such as polystyrene, poly(vinyl chloride), poly(vinylidene chloride), phenol- and urea-formaldehyde resins, polyethylene, polyurethane, poly(vinyl alcohol), and polypropylene; cellular carbonaceous materials such as piths, particularly bagasse piths, and expanded cereal products, e.g., puffed wheats or rice; and expanded, cellular mineral or silaceous materials such as pumice, perlite and vermiculite, gas-filled glass balloons, and mixtures of such fuels. The addition of low density ammonium nitrate prills to the composition can also contribute to the incorporation of gas-filled cavities in the composition. The membranes comprising the cell walls of cellular fuels preferably will be relatively rigid, water-impermeable, and insoluble in the solution of inorganic oxidant in order that the gas content thereof will be preserved during formulation and storage of the blasting compositions. Materials preferred from the viewpoint of availability at low cost and ease of incorporation include bagasse pith, vermiculite, perlite, and closed-cell rigid foams such as those of polystyrene, polyethylene, and polyurethane. About from 5 to 60%, and prefer-

ably 10 to 40%, by volume, of gas is provided in the composition with the density of the blasting composition being about from 1.0 to 1.4 g./cc., and preferably about from 1.1 to 1.3 g./cc. The solid, non-gaseous portion of these foams or cellular fuels naturally will be considered in calculating the oxygen balance of the blasting agent. In general, the porous or foamed fuel will constitute, on a weight basis, about from 1 to 10% and preferably about from 2 to 5% of the composition. When the density of the composition is about 1.4 or above, corresponding to the incorporation of less than about 5% of gas by volume, the compositions cannot reliably be initiated at temperatures of 40° F. in diameters of 6 inches; when more than about 60% by volume of gas is present explosive strength of the composition is reduced. The gas-filled cavities also can be provided by chemically generating gas in situ, for example, by the action of alkali, alkaline earth, or ammonium carbonates or bicarbonates on acid ammonium nitrate solutions.

As stated, the crystal habit modifier, employed in combination with gas-filled cavities and soluble fuel to greatly enhance the sensitivity of the blasting compositions at low temperatures, must be added to the solution of inorganic oxidizing salts while the solution is at a temperature above the crystallization point of the oxidizing salt(s) in solution. Addition of the crystal habit modifier after crystallization of the salts has occurred does not materially enhance the sensitivity of the blasting compositions and such modifiers cannot be dispersed readily in compositions containing a gelling agent. The crystal habit modifier, particularly an anionic surfactant such as sodium methyl-naphthalene sulfonate ("Petro-AG Special") induces the formation of crystals of smaller particle size and larger specific surface than those formed in the absence of the crystal modifier. Further, the crystals of ammonium nitrate which are formed from solutions containing the crystal habit modifier are dendritic and generally exhibit evidence of cracks and strains and are more sensitive to an initiation stimulus than those which do not have such cracks and strains. Preferably the crystal habit modifiers are anionic surfactants, although amphoteric surfactants such as alkyl betaines can also be used. Representative anionic surfactants are higher (C_8 - C_{18}) alcohol sulfonic esters, e.g., sodium lauryl sulfate and sodium stearyl sulfate; aliphatic alcohol phosphates, e.g., sodium alkyl phosphates and alkyl phosphate triethanol amine; aliphatic amide sulfonates, e.g., sodium stearyl amide methylethyl-sulfonate, and sodium aliphatic amide alkylethyl sulfonate; alkyl-aryl sulfonates, e.g., sodium dodecylbenzene sulfonate, butyl-naphthyl-sulfonate, alkylbenzenesulfonates and alkyl-naphthalenesulfonate; and sodium dinaphthyl-methane disulfonates. Preferred surfactants are alkali metal salts of the higher (C_8 - C_{18}) alkanol sulfonic esters, e.g., sodium lauryl sulfate, and the alkyl aryl sulfonates, employed as water soluble alkali metal salts of alkyl aryl sulfonic acids, which acids have a total of 7 to 30 and preferably 10 to 20 carbon atoms per molecule, the aryl portion of the compound being either a benzene or naphthalene nucleus. The sodium salts of methyl-naphthalene sulfonic acid ("Petro-AG Special") and of dimethyl-naphthalene sulfonic acid, sodium dodecylbenzene sulfonate and sodium lauryl sulfate, which are commercially available, are particularly preferred anionic surfactants. Of these, the sodium salt of methyl-naphthalene sulfonic acid ("Petro-AG Special") is particularly preferred since it also contributes to frothing (foaming) and the entrapment of gas in the composition. It is preferred to add "Petro-AG" to hot ammonium nitrate liquor prior to the incorporation of other ingredients. The amount of modifier varies with the particular composition and modifier, and, in general, decreases as the amount of gas-filled cavities and soluble fuel increases. Usually it falls within the range of about 0.1 to 3% or more. Generally at least about 0.5% of anionic surfactant is used to sensitize the compositions to detonation at 40° F.; the use of more than

about 2% anionic surfactant increases the cost without materially increasing the sensitivity.

The compositions of this invention, which usually contain 5 to 30% and preferably about 10 to 20% of water, are thickened. "Thickened" as used herein refers to compositions in which the viscosity of the aqueous phase has been materially increased, e.g., to 20,000 cps. or more, as well as gelled products including those gels which are crosslinked. The compositions can vary in consistency from pourable, pumpable semifluid solutions, slurries and dispersions to moldable, tough, plastic masses. Examples of thickening agents are those conventionally used in water-bearing explosives and generally are used in amounts ranging from, by weight of the compositions, 0.1 to 10%, and preferably from 0.2 to 5%. Examples thereof include tree exudates such as gum arabic, ghatti, karaya, and tragacanth; seaweed colloids such as agar-agar, Irish moss, carrageenin and the alginates; seed extracts such as locust bean, locust kernel, guar and quince seed gums; starches and modified starches such as dextrans, hydroxyethyl starch and British gums; water-dispersible derivatives of cellulose such as methylcellulose, sodium carboxymethyl cellulose and sodium sulfoethylcellulose; gelatin; casein; polyvinyl alcohol; polyacrylamides and modified polyacrylamides; high molecular weight polyethylene oxides; exocellular heteropoly saccharides made by fermenting starch-derived sugars, silica gels, as well as mixtures of two or more of the above thickening agents. Of these, galactomannans such as guar and locust bean gum, and particularly guar gum, are preferred. When the gelling agent is a galactomannan, particularly guar gum, about from 0.25 to 2% of the galactomannan is usually employed. The galactomannan can be a self-complexing guar gum, e.g., EX-FC-50 and EX-FC-DP supplied by Stein-Hall Co., or a noncomplexing guar gum such as Stein-Hall's Jaguar 100 or Jaguar 10 in which no cross-linking agent is incorporated. When a non-complexing guar gum is used, small portions, e.g., about 0.001 to 1% by weight of the total composition, of cross-linking agents, e.g., borax or potassium dichromate, for the gelling agent can be employed. Other suitable cross-linking agents are those discussed more completely in U.S. 3,202,556 or co-pending, coassigned U.S. patent application Ser. No. 343,140, filed Feb. 6, 1964, the teachings of which are included herein by reference. When, as is preferred, the product is gelled in situ by the crosslinking of a gum such as guar gum which can be self complexing or can be cross-linked by the addition of a crosslinking agent, it is desirable to continue mixing with aeration of other incorporation of gas for at least about three minutes after addition of the last ingredient, usually the crosslinker for the gum. The crosslinking (complexing) of the gum markedly strengthens the gel and precludes migration of gas within the composition during storage. As with the crystal habit modifiers, carbonaceous thickening agents serve the dual functions of fuel and thickener, may comprise all or part of the soluble fuel and are included in the calculation of the requisite fuel values.

To impart fluidity to the water-bearing thickened or gelled explosive compositions, particularly at temperatures below -10° F., the composition can contain about from 0.25 to 10% and preferably about 1 to 5%, by weight, based on the total composition, of those materials which function as winter-fluidizing (antifreezing) agents as described in U.S. Patent 3,190,777. Of the compositions enumerated in this patent, methanol, formamide, dimethyl sulfoxide and methyl Cellosolve yield compositions with particularly desirable low-temperature properties. These fluidizing agents can be considered as a portion of the soluble fuel contained in the composition.

Small proportions, e.g., preferably less than 50%, of the total fuel value, of solid fuels can be included in the compositions of this invention without reducing the sensitivity of these compositions at low (40° F., 5° C.) temperatures including, for example, finely divided coals, sulfur and

sulfur-containing compounds such as iron pyrites, ferro-phosphorus and ferrosilicon. In incorporating such fuels the total weight of fuel should be adjusted so that the oxygen-balance of the composition is within the range of -25 to +10%, preferably -15 to 0% and the density of the composition is less than about 1.4 g./cc.

In the following examples, parts and percentages are by weight unless indicated otherwise.

EXAMPLES 1-6

Blasting agents of the compositions shown in Table 1 below, are prepared in a rotary mixer in the following sequence of steps.

(1) Ammonium nitrate "neutral liquor" (normally 80% ammonium nitrate) at >150° F. is placed in the mixer and agitation is begun.

(2) Crystal habit modifier (sodium methylnaphthalene sulfonate ("Petro-AG")), then soluble fuel (granulated sugar), sodium nitrate and guar gum are dissolved in the hot neutral liquor.

(3) Other fuels (if specified) and cellular or foam fuel is added.

(4) Crosslinking agent for the guar gum is added; the blend is mixed for at least 3 minutes.

The compositions formed are loaded into 6-inch diameter containers and samples of each composition initiated at 40° and at 90° F. by conventional cast primers. In the table, F indicates that the composition fails to propagate a detonation, when the composition detonate measurements of detonation velocity are given in meters/second.

TABLE I

Example	1	2	3	4	5	6
80% AN liquor (Ammonium Nitrate)	70.0	70.0	71.0	72.0	73.0	74.0
(Water)	(56.0)	(56.0)	(57.0)	(57.6)	(48.4)	(49.2)
Sodium Nitrate	(14.0)	(14.0)	(14.0)	(14.4)	(14.6)	(14.8)
Sugar (granulated)	15.0	15.0	15.0	15.0	15.0	15.0
Bagasse Pith	8.0	8.0	8.0	8.0	8.0	8.0
Vermiculite	3.0				3.0	3.0
Expanded Corn Flakes (Brewer's grit)		3.0				
Polyethylene foam ¹				0.5		
"Petro-AG Special" ²	1.0	1.0	1.0	1.0	1.0	1.0
Stearic Acid	3.0	3.0	3.0			
Guar gum	1.0	1.0	1.0	1.0	1.0	1.0
Fine coal				4.0		2.0
Velocity, m./sec.:						
90° F.	4,500	3,650	4,250	3,900	4,500	3,820
40° F.	4,150	2,125	3,550	2,250	4,250	3,550
Density, g./cc.	1.2	1.2	1.2	1.08	1.2	1.2
Volume percent gas-filled cavities	20-30	20-30	20-30	30-40	20-30	20-30

¹ Serap, closed cell foamed polyethylene pellets (0.2" diam. x 0.2" length) from Douray Products Co. as "Ethafom."

² Sodium methylnaphthalene sulfonate.

³ Tested at 78° F.

All products are crosslinked with about 450 cc./cwt. of 5% aqueous potassium dichromate. All products have gas-filled cavities of less than about 1/16 inch in major dimension and, at ambient temperature, about 10 to 20% of the inorganic oxidizing salt therein is crystallized out.

Similar results are obtained when about 2% of sodium lauryl sulfate is employed as the surfactant in place of "Petro-AG Special" in the above compositions.

For comparison, compositions are prepared as in Example 1 above except that insoluble fuels, sulfur and coal are substituted for the sugar in one composition (equal parts by weight of each of sugar and coal). This composition detonates at 2850 m./sec. at 90° F. but fails to detonate at 40° F. When a light-bodied paraffin oil ("Corvus" oil available from Texaco) is substituted for the sugar, the composition fails to detonate both at 90° F. and at 40° F.

EXAMPLE 7

Blasting agents of the formulation shown below are prepared by adding to 72 parts 80% ammonium nitrate liquor at 150° F in a turbine-type slurry mixer 1 part sodium methylnaphthalene sulfonate, 15 parts sodium

nitrate, 8 parts sugar, 4 parts coal, and 1 part guar gum. Potassium dichromate as crosslinker is added during pumping. Agitation and aeration of the mixture is begun and continued as the composition is pumped into boreholes. In six diameter charges the composition detonates at 3550 m./sec. at 90° F. and at 2900 m./sec. at 40° F. The content of gas-filled cavities is about 20 to 30%, by volume, the density is 1.2 g./cc., and the overall composition is:

10	Ammonium nitrate	57.6
	Water	14.4
	Sodium nitrate	15.0
	Sugar	8.0
	Coal	4.0
15	Sodium methylnaphthalene sulfonate	1.0
	Guar gum	1.0
		100.0

When compositions of identical formulation but without gas-filled cavities are prepared, the compositions have a density of about 1.42 and detonate at about 2950 m./sec. at 90° F. but fail at 40° F.

EXAMPLE 8

Blasting compositions of the formulation shown below are prepared in a bench-type agitating mixer by Procedures A and B also set forth below:

Composition	Parts
76% ammonium nitrate liquor	66
Sodium nitrate	15
Sugar	10
Formamide	8
Sodium methylnaphthalene sulfonate	8
Guar gum ¹	1

¹ Cross-linked by 10 cc. of 5% aqueous K₂Cr₂O₇.

Mixing procedures

(A)

- (1) Ammonium nitrate added to mixer.
- (2) Sodium methylnaphthalene sulfonate, sugar, and formamide added and mixing continued 30 seconds.
- (3) A preblended mixture of guar gum and sodium nitrate is added and the composition mixed 2 minutes.
- (4) K₂Cr₂O₇ is added, and mixing is continued and the composition aerated mechanically 1 minute before the composition is discharged and tested.

The resulting product has a density of 1.02 g./cc., contains about 40% of gas-filled cavities 1/16 inch in diameter, and detonates in 3 1/2 inch diameters with a 35 g. booster at 40° F.

(B)

- (1) Ammonium nitrate added to mixer.
- (2) Sodium methyl naphthalene sulfonate, sodium nitrate and guar gum, sugar and formamide are added simultaneously and the composition mixed with agitation for 2 1/2 minutes.

(3) K₂CrO₇ is added and the composition mixed with agitation 1 minute before it is discharged and tested.

The composition prepared by Procedure B has a density of 1.13 g./cc., contains about 20 to 30% by volume of gas-filled cavities, and detonates in 3 1/2-inch diameters with a 35 g. booster at 40° F.

EXAMPLES 9 TO 12

The following compositions of this invention are prepared by the general procedures shown in the preceding examples by first adding the sodium methylnaphthalene sulfonate crystal habit modifier thereto, then the fuels, sodium nitrate, guar gum and finally crosslinking agent. Air-filled cavities less than about 1/16-inch in major dimension are incorporated in the product mechanically with a high-speed agitator; the product of Example 9 also contains a low density fuel, bagasse pith.

TABLE II

Example.....	9	10	11	12
80% AN liquor.....	74	70	56	72
(Ammonium Nitrate).....	(59.2)	(56.0)	(44.8)	(57.6)
(Water).....	(14.8)	(14.0)	(11.2)	(14.4)
Sodium Nitrate.....	15.0	15.0	25.0	15.0
Stearic Acid.....	3.0			
Dextrose.....		5.0		
Sucrose.....			5.0	5.0
Ethylene Glycol.....	3.0			
Bagasse Pith.....	4.0			
Sulfur.....				5.0
FeS ₂			10.0	
Coal.....			3.0	2.0
Formamide.....		8.0		
Sodium Methyl-naphthalene Sulfonate.....	1.0	1.0	1.0	1.0
Guar Gum.....	1.0	1.0	1.0	1.0
5% Aq. K ₂ Cr ₂ O ₇ , cc./cwt.....	450	450	450	450
Density, g./cc.....	1.2	1.1	1.36	1.35
Percent Gas-filled cavities, by volume.....	20-30	20-30	10-15	5-15

The products of Examples 9 and 10 detonate at about 40° F. in 3½-inch diameters while the products of Examples 11 and 12 detonate at about 40° F. in 6-inch diameters at velocities of 3500 and 2950 meters per second, respectively.

We claim:

1. In thickened blasting agents consisting essentially of water, inorganic oxidizing salt at least partly dissolved in said water and nonexplosive fuel, the improvement which comprises providing throughout said mass about from 5 to 60% by volume of small gas-filled cavities and crystal habit modifier, said crystal habit modifier being a surfactant, and using as said fuel, a fuel component consisting essentially of at least 3% by weight, based on the total composition, of dissolved carbonaceous fuel.

2. A composition of claim 1 wherein said fuel is a carbohydrate.

3. A composition of claim 2 wherein said crystal habit modifier is an anionic surfactant.

4. A composition of claim 3 wherein said composition contains at least a portion of said inorganic oxidizing salt crystallized in situ in the presence of said modifier.

5. A composition of claim 4 wherein said fuel is a soluble carbohydrate and said crystal habit modifier is selected from the group consisting of alkaryl sulfonates and C₈-C₁₈ alcohol sulfonic esters and said inorganic oxidizing salt consists essentially of ammonium nitrate.

6. A composition of claim 5 wherein said carbohydrate is a mono- or disaccharide, said modifier is sodium lauryl sulfate and said inorganic oxidizing salt component includes a minor proportion of sodium nitrate.

7. A composition of claim 5 wherein said carbohydrate is a mono- or disaccharide, said modifier is sodium methyl-naphthalene sulfonate and said inorganic oxidizing salt component includes a minor proportion of sodium nitrate.

8. A composition of claim 7 wherein said gas-filled cavities are contained in a low-density cellular carbonaceous material.

9. A composition of claim 7 wherein said cavities are gas bubbles entrapped in the aqueous phase of said thickened composition.

10. A process which comprises introducing into a hot aqueous solution of inorganic oxidizing salt, crystal habit modifier, about 3 to 25% by weight based on the total composition of soluble carbonaceous fuel, small gas-filled cavities, and thickener, said crystal habit modifier being a surfactant, then cooling the resulting product.

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