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[54] **CHEMICAL FOAMING AND SENSITIZING OF WATER-BEARING EXPLOSIVES WITH HYDROGEN PEROXIDE**

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[58] **Field of Search** 149/2, 44, 60

[56] **References Cited**

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[57] **ABSTRACT**

Making foamed semisolid colloidal dispersions of water-bearing blasting agents containing an inorganic oxidizing salt, e.g., ammonium nitrate, fuel, water and adding thereto the gas-generating material hydrogen peroxide that foams and sensitizes the blasting agent.

8 Claims, No Drawings

CHEMICAL FOAMING AND SENSITIZING OF WATER-BEARING EXPLOSIVES WITH HYDROGEN PEROXIDE

BACKGROUND OF THE INVENTION

Semisolid colloidal dispersions of water-bearing blasting agents are well known. These products typically comprise an oxidizing component, usually predominantly ammonium nitrate, a fuel component and water. More particularly, these blasting agents are referred to in the art as water gels or slurry explosives, and emulsion type blasting agents. The blasting agents commonly referred to as water gels contain, in addition to the above ingredients, a thickening agent that gels the composition, e.g., polyacrylamides. In addition, the water gels may contain high explosives such as TNT or metallic fuels such as aluminum that function not only as part of the fuel component of the blasting agent but also increase explosive strength. Representative water gels of the type disclosed hereinabove are more fully described in U.S. Pat. Nos. 3,153,606, 3,431,155 and 3,288,658. As indicated above, other water-bearing explosive compositions that are semisolid colloidal dispersions are known as emulsion type blasting agents. Emulsion type blasting agents contain at least one oxidizing agent, water, an emulsifying agent and a fuel component that is a carbonaceous compound insoluble in water. The carbonaceous fuel used in the process for preparing these products is liquid during formation of the emulsion. The emulsifying agent generally forms a water-in-oil emulsion wherein oil is the continuous phase and water is the discontinuous phase of the emulsion. Representative water-bearing semisolid colloidal dispersions of emulsion type blasting agents are described in U.S. Pat. No. 3,447,978. Furthermore, these semisolid colloidal dispersions of water-bearing blasting agents, both the thickened water gel and emulsion type, have been prepared in such a manner that small gas bubbles are entrapped therein or they contain gas-entrapping material, e.g., microballoons. The inclusion of gas in the form of bubbles or as gas-entrapping material is known to regulate the strength of the blasting agent. Methods for preparing gas-containing water-bearing blasting agents include the mechanical incorporation of-gas and in situ chemical generation of gas by the decomposition of certain compounds. Although these procedures have produced satisfactory products, there is a need for making foamed semisolid colloidal dispersions of water-bearing blasting agents by employing a gas-generating chemical compound that is simple to use; inexpensive; forms gas bubbles in the blasting agent within a short period of time which bubbles remain formed therein for extended periods of time; form gas bubbles in the composition that are small, generally the majority of bubbles are not greater than about 100 micron diameter, preferably between 10 to 70 microns, for the most effective sensitivity; provide an effective control over the amount of gas introduced into the composition; and is applicable to water-bearing blasting agents, e.g., water gels, and emulsion type blasting agents.

SUMMARY OF THE INVENTION

This invention provides a process for preparing foamed semisolid colloidal dispersions of water-bearing blasting agents, especially water gels or thickened water-bearing explosives, and emulsion type blasting agents, which comprises mixing inorganic oxidizing salt, fuel and water, the improvement which comprises incorporating into the mix the gas-generating material hydrogen peroxide thereby foaming and sensitizing the blasting agent with the proviso that when thickener is added to the mix said thickener is nonoxidizable in the mix during preparation of the foamed blasting agent. When water gel blasting agents are prepared a nonoxidizable thickening agent, e.g., polyacrylamide, is added to the water-bearing explosive composition in order to thicken or gel the aqueous phase. When emulsion type blasting agents are prepared, an emulsifying agent and a liquid carbonaceous fuel are added to the water-bearing explosive during preparation in order to form an emulsion between the water and fuel. The amount of hydrogen peroxide added to the mix is about from 0.05 to 5 percent by weight of the entire composition.

DESCRIPTION OF PREFERRED EMBODIMENTS

The gas-generating material used in this process, i.e., hydrogen peroxide, decomposes and gives off oxygen gas at temperatures at which the blasting agent ingredients are formulated to produce a foamed product that is sensitized by small gas bubbles. The exact amount of hydrogen peroxide used in the process varies and the specific amount employed depends upon the desired final density of the resulting product and the temperature of the formulation when the gas-generating agent is added thereto. Generally, amounts ranging from about 0.05 to 5 percent by weight, preferably 0.2 to 2 percent, are incorporated into the mix. The hydrogen peroxide can be added to the composition at ordinary mixing temperatures, usually between 90° to 170°F. However, for optimum results, the gas-generating agent is added to the mix when the temperature of the mix is most favorable for decomposition of the foaming agent. Best results are obtained when the temperature of the mix during addition of hydrogen peroxide to the mix is about from 130° to 150°F. Preferably, the hydrogen peroxide is added to water-gel type blasting agents after the mix is thickened, and to emulsion type blasting agents after the emulsion has formed, so that in each case the mix is sufficiently viscous to retain gas bubbles when the composition foams and forms small gas bubbles therein.

The inorganic oxidizing salts used in this invention are those conventionally used in water-bearing blasting agents and include ammonium, alkali metal and alkaline earth metal nitrates and perchlorates as well as mixtures of two or more such salts. Representative inorganic oxidizing salts are ammonium nitrate, sodium nitrate, potassium nitrate, magnesium nitrate, calcium nitrate, ammonium perchlorate, sodium perchlorate, potassium perchlorate and magnesium perchlorate. The amount of inorganic oxidizing salt used in the water-bearing blasting agents is from about 20 to about 75 percent by weight of the composition. Preferably, a mixture of inorganic nitrate salts is used of which at least about 45 percent by weight of the total composition is ammonium nitrate and of the order of 15 to 25 percent, preferably about 15 percent, based on the weight of the total composition, is sodium nitrate.

As mentioned above, the foamed semisolid colloidal dispersion of water-bearing blasting agents can contain certain thickening agents that gel the composition, thus

forming the well-known blasting agents known as water gels or slurry explosives. However, the thickening agent used in the process of this invention must be nonoxidizable in the mix during preparation of the foamed blasting agent. By nonoxidizable thickening agent is meant one that is not oxidized by the hydrogen peroxide, or other ingredients used in formulating the water gel. Guar gum or other thickening agents that are oxidized by the hydrogen peroxide during preparation of the mix cannot be used in the process of this invention.

Representative thickening agents that are not oxidized during manufacture of the blasting agents that can be used in the process of this invention include polyvinyl alcohol, polyacrylamides, high molecular weight polyethylene oxides, silica gels, starches and modified starches such as dextrins and hydroxyethyl starch, water-dispersible derivatives of cellulose such as methyl cellulose, sodium carboxymethyl cellulose, as well as mixtures of two or more of-the above nonoxidizable thickening agents. Preferably, the thickening agent used is a polyacrylamide. The amount of nonoxidizable thickening agent added regulates the consistency of the blasting agent and such thickeners are used in amounts ranging from about 0.2 to 5 percent.

In addition, as mentioned above, this invention is applicable to the production of water and oil emulsion type water-bearing blasting agents. These compositions contain, in addition to inorganic oxidizing salt, water and carbonaceous fuel, an emulsifying agent. The amount of emulsifying agent used is from about 0.5 to 10 percent by weight, and preferably from about 1 to 2 percent. Larger quantities of emulsifying agent can be added since excess emulsifying agent merely serves as a supplemental fuel for the blasting agent. Generally, the emulsifying agents used are those that form water-in-oil emulsions such as sorbitan fatty acid esters, e.g., sorbitan monolaurate, palmitate or oleate; polyoxyethylene sorbitol esters and long-chain fatty acids and esters thereof, so that a water-in-oil emulsion of the blasting agent is formed. Especially good results are obtained when the emulsifying agent is a stearate salt, e.g., sodium stearate, alone or in combination with stearic acid. Other emulsifying agents include sodium oleate, with or without oleic acid, dodecylbenzene sulfonic acid and the tall oil amide of tetraethylene pentamide "EZ-Mul" manufactured by the Baroid Division of National Lead Co.

The emulsion type blasting agents with the hydrogen peroxide foaming agent generally contain a catalyst that aids in the decomposition of the hydrogen peroxide. This catalyst reduces the activation energy of hydrogen peroxide decomposition. Such catalysts are well-known in the art and are generally used in amounts of from 0.5 to 1 percent by weight. Representative hydrogen peroxide decomposition catalysts include manganese dioxide, ferric nitrate, potassium iodide, ferrous sulfate and manganese sulfate. However, if sharp particles of, for example, aluminum or coarse sand, are used in the explosive composition, there is no need to employ a particular catalyst since it is known that such particles have a catalytic effect on the decomposition of hydrogen peroxide.

The fuels used in thickened water gel blasting agents containing nonoxidizable thickener include self-explosive fuels, nonexplosive fuels and metallic fuels as well as mixture of the aforementioned types of fuels. Representative self-explosive fuels that can be used in the composition are organic nitrates, nitro compounds and nitramines such as trinitrotoluene, pentaerythritol tetranitrate, tetranitro-N-methylaniline, nitrostarch, explosive grade nitrocellulose, smokeless powder and mixtures thereof. Generally, the amount of self-explosive fuel used is from 10 to 40 percent by weight, based on the weight of the composition. Nonexplosive fuels such as certain nitro aromatic hydrocarbons, for example, mono- and dinitrobenzenes can be used, and sulfurous fuels including sulfur itself. Carbonaceous fuels such as finely-divided coal and hydrocarbons such as fuel oil and paraffin wax can be added to the composition. Metallic fuels can also be used and these include light elements such as aluminum, magnesium, boron and silicon, both singly and in combination. Heavier metallic compounds and alloys including ferrophosphorus and ferrosilicon can be added to the mix. Blasting agents of the emulsion type wherein a water and oil emulsion is formed must contain carbonaceous fuel that is liquid during formation of the emulsion. The carbonaceous fuel is not soluble in water and generally forms the continuous phase of the emulsion so that the blasting agent is in the form of a water-in-oil emulsion. The carbonaceous fuel that is emulsified when used in the emulsion type blasting agents can comprise oil alone, a wax and oil, a wax and a polymeric material, or a wax and a polymeric modified oil component. The fuel used thus includes hydrocarbons such as paraffins, olefins and aromatics that are saturated or unsaturated. Waxes that can be used include paraffin wax and mineral waxes. Petroleum oil of varying viscosities can be used as the fuel, especially fuel oil. Polymeric materials such as natural or synthetic rubber may be used as a carbonaceous fuel component. Preferably, the fuel comprises oil alone, especially No. 2 fuel oil. Generally the amount of fuel used is from about 3 to 10 percent by weight. Optionally, the emulsion type blasting agents can contain supplementary fuels, as disclosed hereinabove, especially particulate metals, e.g., aluminum and finely-divided coal. In general, the amount of fuel used in the blasting agents of the present invention is such that the oxygen balance of the blasting agents will be from −25 to +10 percent and preferably from −10 to +5.

The amount of water used in the blasting agents of the thickened water gel and emulsion type is from 5 to 30 percent, preferably about from 10 to 25 percent water is used in preparing thickened water gels and emulsion type blasting agents.

Optionally, other ingredients can be incorporated in the blasting agents. For example, nitrogen-base salts can be added to the water-bearing blasting agents to increase their effectiveness. The nitrogen-base salt functions, among other things, as a fuel component and such salts that can be used in this invention are disclosed, for example, in U.S. Pat. No. 3,431,155. Preferably, the nitrogen-base salts used are monomethylammonium nitrate and ethylenediammonium dinitrate. Such salts are added in amounts of from about 5 to 40 percent by weight. As is conventional in the preparation of thickened water gels, the composition can also contain a crosslinking agent such as an alkali metal dichromate or a soluble antimony compound, e.g., potassium antimony tartrate, in amounts of from 0.001 to 1 percent by weight. Likewise, a crystal habit modifier for the inorganic oxidizing salt such as Petro AG, which is a derivative of naphthalene sulfonic acid salts, can

also be added to the water gel compositions, if desired. Generally, the procedure for making thickened water gels is as follows. The oxidizer salts and other water-soluble materials are mixed with water usually at temperatures between about 140° to 170°F to effect maximum solubility. Then the remaining ingredients (except the thickener that is not oxidizable in the mix during preparation of the blasting agent), crosslinking agent, and hydrogen peroxide are added. The addition of these ingredients cools the mix. Subsequently, the mixture is agitated briefly and nonoxidizable thickener added. Mixing is continued until thickening occurs and the gas-generating material hydrogen peroxide is added preferably when the mix is 130° to 150°F. The composition is mixed for about 30 seconds and then the crosslinking agent is added and a thickened foamed blasting agent sensitized with gas bubbles is obtained.

A procedure for making emulsion type blasting agents involves mixing the emulsifiable carbonaceous fuel and emulsifier at a temperature of about 100° to 160°F such that the fuel is liquified. Separately, the inorganic oxidizing salts and other water-soluble materials are dissolved in water at about 100° to 160°F, and the other materials (except for the liquid fuel/emulsifier mix) admixed therein. To this aqueous mixture is added the liquid fuel/emulsifier mix to form a water and oil emulsion. Preferably at this point in the procedure the temperature of the emulsion is between about 130° to 150°F or can be regulated therebetween. The emulsion begins to thicken and the gas-generating agent hydrogen peroxide is added to the thickened emulsion thus forming small gas bubbles.

The following examples further illustrate the invention in detail.

EXAMPLE 1

Formulation	Percent by Weight
Water	21.9
Ammonium nitrate	46.5
Sodium nitrate	14.5
Monomethylammonium nitrate	2.4
Sugar	1.9
Sulfur	4.8
Carbon	2.9
Thickener (polyacrylamide)	2.5
Crosslinking agent	
Sodium Dichromate solution (5%)	0.6
Hydrogen peroxide solution (3%)	2.0

Monomethylammonium nitrate, the ammonium nitrate, and 70 percent of the sodium nitrate were dissolved in the water at 165°F and the sugar was admixed. The sulfur, balance of the sodium nitrate, carbon, and nonoxidizable thickener were premixed and subsequently incorporated in the mix at 160°F. Hydrogen peroxide was added thereto when the mix was cooled to about 130°F, followed by the addition of the crosslinking agent.

The specific gravity of the resulting foamed water gel blasting agent containing small gas bubbles having diameters between about 10 to 100 microns, was 1.1. The material gave a lead block compression test of 2⅛ inches and detonated at 3,800 meters/sec in a 6-inch-diameter package at 40°F in air. Comparable material without the hydrogen peroxide had a specific gravity of 1.4 and did not detonate under the same conditions.

EXAMPLE 2

Formulation	Percent by Weight
Ammonium nitrate (75%)	76.3
Ferric nitrate	0.5
Sodium nitrate	15.0
*Tuffin wax	2.0
Fuel oil	4.0
Tall oil amide of tetraethylene pentamide (EZ Mul)	2.0
Hydrogen peroxide solution (30%)	0.2

*A wax fortified by the inclusion of an ethylene vinyl acetate copolymer. Product of the Atlantic Refining Co.

The sodium nitrate and ferric nitrate were dissolved in the ammonium nitrate solution such that the resultant composition had a temperature of 140°–150°F. Separately, the fuel oil, wax and EZ Mul were mixed with each other and then admixed with the aqueous solution until the mix began to thicken. The temperature of the mix was about 140°F. Hydrogen peroxide was then added and mixing continued for another minute. The resulting foamed emulsion type blasting agent had a specific gravity of 1.26 and contained small gas bubbles having diameters of between about 10 to 100 microns. The aerated material at 40°F compressed a lead block 2⅝ inches and detonated at 4,800 meters/sec in a 6-inch-diameter at 40°F in air.

I claim:

1. In a process for preparing foamed semisolid colloidal dispersions of water-bearing blasting agents comprising mixing inorganic oxidizing salt, fuel, thickener and water, the improvement which comprises foaming and sensitizing the mix by incorporating into the mix the gas-generating material hydrogen peroxide, and wherein said thickener is nonoxidizable in the mix during preparation of the foamed blasting agent.

2. The process of claim **1** wherein the amount of hydrogen peroxide added is about from 0.05 to 5 percent by weight.

3. The process of claim **1** wherein the amount of hydrogen peroxide added is about from 0.2 to 2 percent by weight.

4. The process of claim **2** wherein the thickener is polyacrylamide.

5. The process of claim **2** wherein inorganic oxidizing salt is ammonium nitrate.

6. The process of claim **2** wherein the mix is at a temperature of about from 130° to 150°F when the gas-generating material is added thereto.

7. The process of claim **2** wherein a nitrogen-base salt is added to the mix.

8. The process of claim **7** wherein the nitrogen-base salt is monomethylammonium nitrate.

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