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CHEMICAL FOAMING OF WATER-BEARING EXPLOSIVES

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ABSTRACT OF THE DISCLOSURE

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

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., guar gum or 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. Pats. 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. 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 in 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 gas-generating chemical compounds that are simple to use; inexpensive; form 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 are 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 an alkali metal borohydride gas-generating material thereby foaming and sensitizing the blasting agent. When preparing water gels, a thickening agent, e.g., guar gum, 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 alkali metal borohydride added to the mix is about from 0.002 to 0.10% based on the weight of the total composition.

DESCRIPTION OF PREFERRED EMBODIMENTS

The gas-generating materials that are used in the process of this invention are alkali metal borohydrides. These borohydrides decompose in the system and give off gas at temperatures at which the blasting agent ingredients are formulated to produce a foamed product that is sensitized by small gas bubbles formed in the blasting agent. Any alkali metal borohydride can be used as the gas-generating material in the present process. Representative alkali metal borohydrides that are used include lithium borohydride, potassium borohydride and sodium borohydride. The exact amount of gas-generating material 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 0.002 to 0.10% by weight, preferably 0.01 to 0.06%, are incorporated into the mix. The gas-generating agents are added to the composition at ordinary mixing temperatures, usually between 90° to 170° F. However, for optimum results, the alkali metal borohydride 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 produced when the temperature of the composition during addition of alkali metal borohydride to the mix is from about 100° to 150° F. The alkali metal borohydride gas-generating material is added to water-gel type explosives after the mix has 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 small gas bubbles form 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% by weight of the composition. Preferably, a mixture of inorganic nitrate salts is used of which at least about 45% by weight of the total composition is ammonium nitrate and of the order of 15 to 25%, preferably about 15%, 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 a thickening agent to gel the composition, thus forming the well-known blasting agents known as water gels or slurry explosives. The amount of thickening agent added regulates the consistency of the blasting agent and such thickeners are used in amounts ranging from about 0.2 to 5%. Representative thickeners include galactomannans such as guar and locust bean gum; gum arabic; starches and modified starches such as dextrins, polyvinyl alcohol; polyacrylamides; high molecular weight polyethylene oxides; or mixtures of two or more of the above thickening agents. Best results are obtained when either guar gum or polyacrylamide is used as the thickener. 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 fuel, and emulsifying agent. The amount of emulsifying agent used is from about 0.5 to 10% by weight, and preferably from about 1 to 2%. Larger quantities of emulsifying agent may 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., soribtan 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 tall oil amides such as the tall oil amide of tetraethylene pentamide, "EZ-Mul," manufactured by the Baroid Division of National Lead Co.

The fuels used in thickened water gel blasting agents include self-explosive fuels, nonexplosive fuels and metallic fuels as well as mixtures 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% by weight, based on the weight of the composition. Non-explosive 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, 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 include oil alone, a wax and oil, a wax and a polymeric material, or a wax and a polymeric modified oil component. The fuels used thus include hydrocarbons such as paraffinic, olefinic and aromatic that are saturted 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 such as No. 2 fuel oil. Polymeric materials such as natural or synthetic rubber may be used as a carbonaceous fuel component. Preferably, the fuel comprises oil alone. Generally the amount of fuel used is from about 3 to 10% 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 agent will be from −25 to +10% 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 by weight, preferably, about from 10 to 25 percent by weight 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 are applicable to this invention are disclosed, for example, in U.S. Pat. 3,431,155. Preferably, the nitrogen-base salts used are monomethylammonium nitrate and ethylenediammonium dinitrate. Such salts can be added to the composition in amounts of from about 5 to 40% by weight. As is conventional in the preparation of thickened water gels, the composition can, and usually does, contain a crosslinking agent such as, for example, an alkali metal dichromate or a soluble antimony compound, e.g. potassium antimony tartrate, in amounts of from 0.001 to 1% 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 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 at temperatures usually between about 140° and 170° F. to effect maximum solubility. Then the remaining ingredients, except thickener, crosslinking agent and gas-generating material, are added. The addition of these ingredients cools the mix. Subsequently, the mixture is agitated briefly and thickener added. Mixing is continued until thickening occurs, generally about 4 minutes; the alkali metal borohydride gas-generating material is added and the temperature of the mix is preferably about from 100° 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 120° to 170° F. such that the fuel is liquified. Separately, the inorganic oxidizing salts and other water-soluble materials are dissolved in water at about 120° to 170° 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 usually about from 100° to 150° F. or can be regulated therebetween, if desired; the emulsion begins to thicken and the gas-generating agent is added to the thickened emulsion.

The following examples further illustrate the invention in detail.

EXAMPLE 1

Formulation:	Percent by weight
Water	15.4
Ammonium nitrate	48.4265
Sodium nitrate	15.0
Monomethylammonium nitrate	10.3
Sugar	2.0
Sulfur	5.0
Coal	3.0
Thickener (guar gum)	0.8
Sodium borohydride	0.036
Crosslinking agent:	
Sodium dichromate	0.03
Potassium antimony tartrate	0.0075

The monomethylammonium nitrate fuel, 13/15 of the sodium nitrate and all of the ammonium nitrate were dissolved in water at 140° F. The thickener was premixed with sugar and the balance of the sodium nitrate was added to the ammonium nitrate solution together with the sulfur and coal. The mixture, cooled to 100° F. as a result of the addition of the sodium nitrate as well as the result of heat loss by radiation, thickened, and sodium borohydride was added, followed by addition of the crosslinking agents.

The specific gravity of the resulting foamed water gel blasting agent stabilized at 1.25 at ambient temperature and remained at that level for at least 30 days. The foamed explosive composition detonated at 40° F. in 6-inch-diameter (unconfined) at a velocity of 3810 meters/sec. Gas bubbles in the foamed composition were 20 to 100 microns in diameter.

EXAMPLE 2

The procedure described above in Example 1 was repeated except that 0.5 gram per kilogram (0.05% by weight) of lithium borohydride was added to the composition in place of the sodium borohydride. Small gas bubbles formed within the composition thus sensitizing said composition. The foamed blasting agent detonated under the conditions described above in Example 1 with substantially the same results.

EXAMPLE 3

Formulation:	Percent by weight
Ammonium nitrate	60.97
Water	17
Sodium nitrate	15
Fuel oil #2	5
EZ-Mul (tall oil amide of tetraethylene pentamine)	2
Sodium borohydride	0.03

Ammonium nitrate, sodium nitrate and the tall oil amide of tetraethylene pentamine were mixed with the water at about 160° F. The fuel oil was added thereto when the mix was at 130–140° F. and agitated to form a water-in-oil emulsion. The mixture started to thicken in about 2 minutes after agitation at which time the sodium borohydride was added to the thickened mix. Mixing was continued for about 1 minute to incorporate the foaming agent in the mix. The resulting water-in-oil emulsion blasting agent foamed and contained small gas bubbles of from about 20 to 100 microns in diameter. The blasting agent at 40° F. had a detonation velocity of about 5400 meters per second.

EXAMPLE 4

The procedure described above in Example 3 was repeated except that potassium borohydride was substituted in place of sodium borohydride, and the emulsifying agent used was 2% sodium stearate. The resulting foamed emulsion blasting agent contained small gas bubbles. The blasting agent detonated at 40° F. with a detonation velocity comparable to that obtained in Example 3.

I claim:

1. In a process for preparing foamed semisolid colloidal dispersions of water-bearing blasting agents comprising mixing inorganic oxidizing salt, fuel and water, the improvement which comprises incorporating into the mix an alkali metal borohydride gas-generating material that foams and sensitizes the blasting agent.

2. 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 incorporating into the mix an alkali metal borohydride gas-generating material that foams and sensitizes the thickened blasting agent.

3. The process of claim 2 wherein the gas-generating material is sodium borohydride.

4. The process of claim 2 wherein the amount of sodium borohydride added is about from 0.002 to 0.10% by weight.

5. The process of claim 2 wherein the amount of sodium borohydride added is about from 0.01 to 0.06% by weight.

6. The process of claim 3 wherein the thickener is polyacrylamide.

7. The process of claim 3 wherein the thickener is guar gum.

8. The process of claim 3 wherein the inorganic oxidizing salt is ammonium nitrate.

9. The process of claim 3 wherein the mix is at a temperature of about from 100° to 150° F. when the gas-generating material is added thereto.

10. The process of claim 3 wherein a nitrogen-base salt is added to the mix.

11. The process of claim 10 wherein the nitrogen-base salt is monomethylammonium nitrate.

12. In a process for preparing foamed semisolid colloidal dispersions of water-bearing blasting agents comprising mixing inorganic oxidizing salt, liquid carbonaceous fuel, emulsifying agent and water, the improvement which comprises incorporating into the mix an alkali metal borohydride gas-generating material that foams and sensitizes the emulsified blasting agent.

13. The process of claim 12 wherein the emulsifying agent is one that form a water-in-oil emulsion.

14. The process of claim 13 wherein the gas-generating material is sodium borohydride.

15. The process of claim 14 wherein the amount of sodium borohydride added is about from 0.002 to 0.10% by weight.

16. The process of claim 14 wherein the amount of sodium borohydride added is about from 0.01 to 0.06% by weight.

17. The process of claim 14 wherein the fuel is fuel oil.

18. The process of claim 14 wherein the inorganic oxidizing salt contains ammonium nitrate.

19. The process of claim 14 wherein the mix is at a temperature of about from 100° to 150° F. when the gas-generating material is added thereto.

20. The process of claim 18 wherein the inorganic oxidizing salt contains sodium nitrate.

21. The process of claim 14 wherein the emulsifying agent is a stearate salt.

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