PREPARATION OF GELLED BLASTING AGENTS COMPRISING NITRIC ACIDS, FUELS, AND GELLING AGENTS

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9 Claims

ABSTRACT OF THE DISCLOSURE

The storage stability of a blasting composition consisting essentially of aqueous nitric acid, a gelling agent, a cross-linking agent, ammonium nitrate and a carboxylic fuel which is miscible with the nitric acid is enhanced when the composition is formed by mixing the gelling agent with either the nitric acid or the carboxylic fuel component, or both, before bringing the gelling agent into contact with the cross-linking agent.

This invention relates to an improved method of making blasting agents containing nitric acid, ammonium nitrate and a carboxylic fuel which is at least partially nitric acid-soluble or miscible. It relates further to the preparation of non-corrosive, high strength, blasting compositions in gelled form having as essential components nitric acid, an organic carboxylic acid compound, ammonium nitrate, a gelling agent and water.

The term "carboxylic" as used herein means compounds which have at least one carboxy moiety or a moiety which is derived therefrom and has the carboxy radical covered that the combination of nitric acid and ammonium nitrate with an organic carboxylic acid derivative which is at least partially nitric acid-miscible or soluble, and a gelling agent can yield a blasting agent which is capable of detonation under field conditions, providing the components of the blasting composition are mixed in a special manner as will be outlined hereinafter. The blasting compositions produced by the process of the present invention may advantageously contain other auxiliary materials which do not materially interfere with their blasting ability. Thus, it may be desirable to add an additional fuel material or a density modifying agent.

In the process of the present invention, it is critical that the gelling agent be mixed with the aqueous nitric acid and/or carboxylic fuel prior to being brought into contact with the cross-linking agent; and also that the blasting mixture, comprising the aqueous nitric acid, ammonium nitrate, carboxylic fuel, cross-linking agent and gelling agent, be continuously agitated at an elevated temperature until the mixture has gelled.

Blending of the components of the blasting composition can be achieved by adding the components in any sequence, provided that the gelling agent is not mixed with the cross-linking agent before being mixed with nitric acid or the carboxylic fuel component. Likewise, any efficient agitator can be used to achieve the desired degree of mixing. Among these are ribbon mixers, sigma-blade mixers, flat-baster mixers and the like. Temperature during final agitation can be in the range of 70°F to 180°F, and, as stated above, it is the temperature during agitation which determines whether the explosive will be a pourable slurry or a solidified gel. It should be noted that it is the temperature of the blended mixture which determines these properties, rather than the temperatures of the components before blending. Thus, for example, if one of the individual components has a temperature below 90°F, and another has a temperature above 90°F, but the final mixture has a temperature below 90°F during agitation, the final explosive will be in slurry form.

The nitric acid which can be used herein is an aqueous solution of 30 to 98% concentration. Nitric acid of about 50 to 80% concentration is very suitable for use in the present invention and such compositions, being readily available in commerce, are preferred.

The carboxylic compounds which are useful in this invention are, as stated above, at least partially nitric acid-miscible or soluble. The degree of solubility or miscibility which is required is dependent upon the proportions of the carboxylic acid compound in the blasting composition. Solubility or miscibility should be sufficient to permit blending of the nitric acid and carboxylic acid components without a great deal of separation of these components into different phases. If the carboxylic acid compound is a solid, it is important that it is sufficiently soluble to be dissolved in the aqueous nitric acid to the extent that it is

Examples of such compounds are carboxylic acids, acid salts, anhydrides or amidates.

Blasting agents based upon nitric acid and an organic nitrofuel have been known for many years, one of the oldest known blasting compositions being of this type, i.e., the combination of nitric acid and a nitroaromatic compound. Such materials as originally conceived have the severe disadvantage of being both liquid form and corrosive in nature, and thus difficult to handle. Attempts were made to overcome the deficiencies of nitric acid-based explosives since such explosives, by reason of their low cost, are of great commercial importance. Recent attempts to prepare useful nitric acid-ammonium nitrate based explosives involved the use of a gelling agent in combination with an acid-miscible or acid-soluble carboxylic fuel. The gelling agent increased the viscosity of the explosive without affecting its detonability. However, the mere blending of the component materials often gave an explosive which, though useful as a blasting agent, was prone to separation of phases with the formation of corrosive nitric acid exudates.

In view of this state of the art, it is an object of the present invention to provide a blasting agent based upon nitric acid, ammonium nitrate and an organic carboxylic fuel. It is a further object of the present invention to provide a blasting agent based upon nitric acid, ammonium nitrate and an organic carboxylic fuel in the form of a water-containing slurry or solid gel which is less corrosive, of high blasting strength and extremely stable under normal field conditions. Other objects will be apparent from the ensuing description of this invention.

In accordance with this invention, it has been dis
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If the carboxacyl derivative is a liquid, it is important that it is acid-miscible to the extent of its presence in the composition since otherwise it will form a second liquid phase which might not gel and would create handling and packaging problems. A small amount of undissolved solid carboxylic fuel is tolerable within the framework of the present invention. However, it is desirable to minimize the quantity of undissolved fuel components. The monomeric carboxacyl compound should have between one and twelve carbon atoms. It may be an acid, anhydride, salt or amide. Monocarboxylic and polycarboxylic acid derivatives as above noted, whether in monomeric or polymeric form, are useful. Mixtures of different acids, or of acids with the above noted derivatives of acids, are also useful in the practice of the present invention. Acids and their derivatives may be aliphatic or aryl in structure. The organic acid derivatives which are particularly useful in the present invention are miscible with aqueous nitric acid, since such compositions are highly stable to separation and thus less corrosive. Among the mono acids which can be used in the practice of the present invention are acetic, propionic, butyric, valeric, isopantoanic, methylglutaronic and trimethylene dicarboxylic acids. Salts of such acids, e.g., ammonium, sodium, potassium, calcium, magnesium, and the like, are also useful in the present invention. Of these salts the preferred members are the alkali metal salts and others which are at least partially soluble in acid. Amides such as benzamide and propionamide can also be used in the practice of the present invention. Likewise, anhydrides such as acetic anhydride, propionic anhydride, and the like, can also be used.

Other aliphatic acids such as acrylic, butyral, hexenoic acid, as well as anhydrides, amides and salts of these acids can also be used as the carboxylic fuel component of the composition of this invention.

Aromatic acids such as benzoic acid, phthalic acid, terephthalic acid, cinnamic acid, as well as the anhydrides, salts and amides derived therefrom are also useful to supply the oxidizable component of the blasting agent of this invention.

The organic carboxylic component useful in the composition of the present invention may be substituted by halogen groups. Among such halogen-substituted acids and derivatives which can be used are chlorocarboxylic, dichlorocarboxylic, trichlorocarboxylic, bromopropionic, iodopropionic, dibromobutyric, chloroacetic, parahalobenzoic and parahalocarboxylic acids.

Polybasic aliphatic acids as well as anhydrides, partial esters and salts of such carboxylic acids may also be used to supply the oxidizable carboxylic component useful in the present invention. Among such polybasic acids are oxalic, malonic, succinic, glutaric, adipic, pimelic, suberic, azelaic, male, maleic and fumaric. Similarly, alkali metal salts and amides of such polybasic acids may also be used for the practice of the present invention. Also, substituted derivatives of such acids, e.g., halogenated derivatives, are also useful for the practice of the present invention.

Polymeric acids, represented by polyacrylic acid, polyacrylic acid copolymer and copolymers of such acids with each other or vinyl derivatives such as alkyl vinyl ethers or vinyl halides are also useful herein.

From the foregoing group of carboxylic compounds, those which are fully miscible or fully soluble in aqueous nitric acid are preferred. Examples of these are the lowest aliphatic groups, e.g., acetic acid, propionic acid, aliphatic polybasic acids such as oxalic acid and succinic acid; and polybasic acetic acids, e.g. phthalic acid.

The choice of a gelling agent is not critical, so long as the agent is stable and effective in aqueous nitric acid. Among the commercially available materials are water-soluble interpolymeris of methyl vinyl ether and maleic anhydride, available under the tradename "Gantrez AN" resins, polyvinylpyrrolidones of various grades, polyacrylic acids and ammonium polyacrylates, copolymers of ethylene and maleic anhydride, copolymers of acrylamide and N,N'-methylene bisacrylamide monomers and polyacrylamide. The preferred gelling agent for use in the present invention is derived by the copolymization of methyl vinyl ether and maleic anhydride. Gantrez AN resins, polyacrylic acids and ammonium polyacrylates, copolymers of ethylene and maleic anhydride, copolymers of acrylamide and N,N'-methylene bisacrylamide monomers and polyacrylamide. The preferred gelling agent for use in the present invention is derived by the copolymization of methyl vinyl ether and maleic anhydride.

Cross-linking agents capable of functioning with the particular gelling agent are used in this invention. In many cases, these are metal salts. Thus, preferably, chlorides or sulfates, but also acetates, hydroxides and nitrates of such metals as tin, chromium, lead, zirconium, iron, copper, zinc, nickel, manganese, cobalt, titanium and aluminum may be used. Most preferred are trivalent chromium compounds such as chromium nitrate.

While the present invention provides blasting compositions which use ammonium nitrate as an oxidant, it may be desirable for specific uses to also include other oxidants in the blasting composition. Ammonium nitrate can be present either as a finely ground material or in the form of fertilizer grade prills. Other oxidants which can be used are sodium nitrate and sodium percarbonate.

While it is not necessary for the practice of the present invention to use oxidizable fuel materials, it is commercially advantageous and desirable to use oxidizable fuel materials or liquid fuel materials which supply the oxidizable component of the blasting composition. Suitable oxidizable fuel materials are nitroaromatics such as nitrotoluene, nitromethane, trinitromethane, tetranitromethane, nitroethane, dinitroethane, nitropropane, dinitropropene, nitrobutane, dinitrobutane, nitrosobutane, and the like. Examples of oxidizable fuels are nitroglycerine, dinitrotoluene, dinitrostilbene, and dinitrotoluene.

The nitro fuels which may be optionally used in the present invention may contain halogen groups in addition to hydroxy or alkoxy groups. Among the halogenated nitro fuels are nitrochloromethane and nitrochlorobenzene. Nitro compounds which contain carboxy groups or their anhydrides, salts or amides are useful in the present invention, but such compounds are classified for present purposes as carboxylic fuels.

It is often advantageous to include a density modifying agent in the formulations of the present invention, especially when such formulations are prepared from nitric acid solutions of less than 80% by weight nitric acid. Such density modifying agents are acid-resistant materials containing entrapped air bubbles or spheres or verniculite. Other useful materials are foaming agents of the non-ionic surfactant type, for example, esters of sorbitan with fatty acids, e.g., sorbitan monopalmitate, sorbitan monostearate and sorbitan monolaureate.

Blasting compositions of the present invention should contain between about 3 and 65% by weight of nitric acid on an anhydrous basis. Additionally, they must have a minimum of about one percent by weight of the carboxylic fuel and a gelling agent in a weight proportion of about 0.1 to about 10%, based on the weight of the entire composition. Though not entirely necessary, it is desirable to have up to about 5% by weight of a cross-linking agent to enhance the action of the gelling agent. Density modifying agents can be present in a concentration of up to about 10%. When ammonium nitrate is used as an auxiliary oxidant, as much as 70 to 80% may be present in the explosive composition. In addition to the foregoing components, the blasting composition of the present invention may have up to about 35% of an additional and different oxidizable fuel such as a liquid or solid nitro fuel. It is preferred to use for each 100 parts of anhydrous nitric acid 70 to 150 parts of the carboxylic acid component, 0 to 60 parts of the oxidizable fuel, 0 to 800 parts of
ammonium nitrate, 5 to 40 parts of the acid-stable gelling agent, 2 to 20 parts of the cross-linking agent and 10 to 240 parts of water.

The fuel-oxidizer components in the composition of the presented invention should preferably be present in such quantities as to give an "oxygen balanced" composition. By "oxygen balance" is meant the availability of sufficient oxygen in the composition to oxidize the fuel components to their maximum state of oxidation, i.e., sufficient oxygen is present so combined carbon can be converted to carbon dioxide.

The blasting composition produced by this invention is stable against separation of components when stored at temperatures as high as 75–85°F over extended periods. This invention thus provides a practical and economical way of obtaining blasting compositions which are excellent for conventional blasting needs. They can be used for wet bore holes, tough rock conditions and difficult toes. The high detonation pressure which is generated, produces good fragmentation in direct hole blasting. These compositions are thus contemplated for applications such as open pit mining, construction, quarrying, sewer blasting, coal stripping and river crossings.

The following examples are presented to illustrate the present invention. In the examples, parts and percentages are on a weight basis unless otherwise noted.

Example 1.—Preparation of a blasting composition in slurry form
To a dispersion of 10 parts of Gantrez AN–169 resin in 130 parts of acetic acid is added 140 parts of aqueous nitric acid. The mixture is thoroughly agitated until all the resin is dissolved and then heated to a temperature of 150–155°F. While at this temperature, 15 parts of sorbitan monopalmitate is added followed by 5 parts of chromium nitrate. The resulting mixture is agitated while maintaining the mixture at 150–155°F until gelation is achieved. With continued agitation, 700 parts of ammonium nitrate at a temperature of about 80°F is added and agitation is continued 5 minutes after the ammonium nitrate has been homogeneously blended in. The resulting explosive composition has a density of 1.20–1.40 g./cc.

Example 2.—Preparation of a solid gel blasting composition
To a solution of 140 parts of ammonium nitrate in 140 parts of aqueous nitric acid solution, heated to 130°F, is added 15 parts of sorbitan monopalmitate with continued heating to 160°F. A dispersion of 10 parts of Gantrez AN–169 resin in 130 parts of acetic acid is added to the heated nitric acid mixture. The mixture is agitated until all the resin is dissolved and then 5 parts of chromium nitrate is added with continued agitation at 155°–160°F until gelation is complete. To the gelled mixture is then added 560 parts of ammonium nitrate with continued agitation for five minutes after addition to form a homogeneous mixture at a final temperature above 90°F. The product is cooled to give a solid gel having a density of 1.20–1.40 g./cc.

Example 3.—Preparation of a slurry blasting composition
To a solution of 118 parts of ammonium nitrate and 118 parts of aqueous nitric acid heated to 130°F is added 2 parts of chromium nitrate. The temperature is maintained while 15 parts of melted sorbitan monopalmitate is added and then 65 parts of acetic acid is added to the acid solution. A dispersion of 10 parts of Gantrez AN–169 resin in 60 parts of acetic acid is added to the acid solution and the mixture is agitated until the resin dissolves and the desired gelation has occurred. With agitation, 612 parts of ammonium nitrate is added to the gelled mixture and agitation is continued five minutes after the addition is completed, thereafter the mixture during agitation being 75°F. The density of the final composition is 1.20–1.40 g./cc.

Example 4.—Preparation of a slurry blasting composition
To 123 parts of aqueous nitric acid is added 15 parts of melted sorbitan monopalmitate at 130°F, followed by 5 parts of chromium nitrate. A dispersion of 10 parts of Gantrez AN–169 resin in 132 parts of acetic acid is added to the mixture, followed by agitation at a temperature of 130°F until gelation is completed. With continued agitation of the gelled mixture at 130°F is added 715 parts of ammonium nitrate at 75°F and agitation is continued for 5 minutes after the addition is completed. The temperature of the mixture during agitation is 80°F. The final blasting composition has a density of 1.20–1.40 g./cc.

Example 5.—Preparation of a slurry blasting composition
To a solution of 10 parts of Gantrez AN–169 resin in 140 parts of aqueous nitric acid heated with agitation to 150°–155°F is dissolved 5 parts of chromium nitrate, followed by 15 parts of sorbitan monopalmitate and 130 parts of acetic acid. Agitation is continued while maintaining the temperature at 150°–155°F until gelation has been completed. To the gelled mixture maintained at 150–155°F is added 700 parts of ammonium nitrate at 75°F. The resulting mixture is agitated at a temperature of 85°F for 5 minutes to form a homogeneous product with a density of 1.20–1.40 g./cc.

The foregoing examples show the preparation of slurry blasting compositions and solid gel blasting compositions in accordance with the present invention. Other gelling agents that specifically used in the examples could have been used with equivalent effects. Similarly, compositions can be obtained in accordance with the present invention by the substitution of other acids for the acetic acid use in the examples. Among such equivalent acids are propionic acid, trichloroacetic acid, nitropropanic acid and the like. Similarly, other cross-linking agents such as stannous chloride, can be substituted for chromium nitrate used in the examples.

1. In the process for the preparation of aqueous gelled blasting compositions which are stable against phase separation during storage, by forming a mixture consisting essentially of aqueous nitric acid, a gelling agent, a cross-linking agent, ammonium nitrate and a carboxylic acid which is miscible with the nitric acid to the extent said fuel is present in said composition, and agitating the mixture until a homogeneous blend is formed, the improvement which comprises:

(1) mixing the gelling agent with either the nitric acid or the carboxylic fuel component, or both, before bringing the gelling agent into contact with the cross-linking agent; and

(2) continuing to agitate the blended components until gelation is complete whereby the desired physiologically stable blasting composition is obtained.

2. The process of claim 1 wherein the gelling agent is a synthetic organic polymer.

3. The process of claim 2 wherein the gelling agent is derived by copolymerization of methyl vinyl ether and maleic anhydride.

4. The process of claim 3 wherein the cross-linking agent is a chromic salt.

5. The process of claim 1 wherein at least a part of the ammonium nitrate component is added after gelation is complete and the final agitation is conducted at a temperature below about 90°F, whereby the blasting composition is obtained in a soft gel.

6. The process of claim 1 wherein at least a part of the ammonium nitrate component is added after gelation is complete and the final agitation is conducted at a temperature above about 90°F, whereby the blasting composition is obtained in a solid gel.

7. The process of claim 1 wherein the mixture which is agitated contains a density modifying agent.
8. The process of claim 7 wherein the density modifying agent is sorbitan monopalmitate.
9. The process of claim 1 wherein said carboxylic fuel is an aliphatic monocarboxylic acid having from 2 to 6 carbon atoms.

References Cited

UNITED STATES PATENTS

<table>
<thead>
<tr>
<th>Patent Number</th>
<th>Date</th>
<th>Inventor(s)</th>
<th>Class</th>
</tr>
</thead>
<tbody>
<tr>
<td>3,216,872</td>
<td>11/1965</td>
<td>Wells</td>
<td>149—57 X</td>
</tr>
<tr>
<td>3,242,019</td>
<td>3/1966</td>
<td>Gehrig</td>
<td>149—74 X</td>
</tr>
<tr>
<td>3,288,658</td>
<td>11/1966</td>
<td>Ferguson et al.</td>
<td>86—20</td>
</tr>
<tr>
<td>3,296,044</td>
<td>1/1967</td>
<td>Gehrig</td>
<td>149—74 X</td>
</tr>
<tr>
<td>3,361,601</td>
<td>1/1968</td>
<td>Chrisp</td>
<td>149—19</td>
</tr>
</tbody>
</table>

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