THICKENED AQUEOUS EXPLOSIVE COMPOSITION CONTAINING ENTRAPPED GAS

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No Drawing. Continuation of application Ser. No.
422,034, Dec. 29, 1964, which is a continuation-in-
part of application Ser. No. 324,193, Nov. 18,
609,270

14 Claims. (Cl. 149-39)

ABSTRACT OF THE DISCLOSURE

This invention relates to blasting agents and more par-
ticularly to slurry blasting agents containing strong
oxidizer salt, sensitizer, water, etc., which have air or other
gas introduced to reduce density. Organic liquid, e.g.,
ethylene glycol, formamide, may replace part of the water
to lower its freezing point.

This application is a continuation of application Ser.
No. 422,034, filed Dec. 29, 1964, now abandoned, which
is a continuation-in-part of application Ser. No. 324,193,
filed Nov. 18, 1963 now abandoned.

The term slurry, as employed herein refers to a liquid-
solid mixture containing sufficient liquid to render the
liquid phase continuous. Thus, the slurries of this inven-
tion have a continuous liquid phase with particulate solids
uniformly dispersed therein as distinguished from a mass of
wet or moistened solids. The liquid phase may be of
any desired viscosity, from thin low viscosity liquids,
liquids thickened with colloids, to gelled liquids. In the
latter case, the gelatinous phase must be essentially con-
tinuous in order to fall within the above definition of a
slurry.

A slurry within the above definition theoretically should
have a density determined by the densities of the indi-
vidual solid and liquid constituents and the relative pro-
portions of such constituents. In practice, however, it is
difficult if not impossible to achieve the theoretical den-
sity, particularly in slurries of high viscosity or gelled slurr-
ies, because of air entrainment. It has been found, how-
ever, that lowering of the density by air entrainment to
up to twenty-five percent of the theoretical density still
produces slurries within the above definition having es-
tentially continuous liquid phases. The density of a given
slurry, therefore, is a measure of the air entrainment there-
in and hence is a criterion for the contiuity of the liquid
phase. Thus, a composition which has a density lower
than seventy-five percent of the theoretical density is not
a slurry within the definition intended herein because the
liquid phase is not essentially continuous.

Aqueous slurry blasting agents comprising water,
oxidizer and solid sensitizer as described and claimed in
Cook and Farnam U.S. Patent 2,930,685 have enjoyed
wide commercial use. As disclosed in Patent 2,930,685,
the slurries contained from 5 to 30% water by weight. It
has been found however that it is difficult to achieve true
slurries within the definition at lower water contents, in
the range of 5 to 10%, unless the water used in the com-
position is methyl alcohol. The composition according to
Cook and Farnam patent containing as little as 5% water
at room temperature are not pumpable and are not slur-
ries under the definition.

The minimum sensitizer content of the Cook and
Farnam slurries is about 15% coarse TNT (trinitrotolu-
enone) in order to yield blasting agents of adequate sensi-
tivity to be commercially useful. With single base smoke-
less powder, on the other hand, it has been found that a
minimum of about 20% is required to yield a true slurry
which is sensitive enough to be composed of explosive
detonable by low cost boosters. Similarly such smoke-
less powder slurries required a minimum of about 11%
water to yield true slurries.

It is an object of this invention to provide slurry blast-
ing agents containing less explosive sensitizer than prior
art compositions and which are more economical than
prior art compositions.

It is a further object of this invention to provide blast-
ing agents which possess superior properties including
high density, high bulk strength, water resistance, freeze
resistance and high sensitivity.

Further objects and advantages will be apparent to
those skilled in the art.

According to this invention, true aqueous slurries are
provided which have densities of at least 1.3 grams/cc.,
when free of air or other entrapped gases, and which con-
tain less than 5% by weight of water. The slurries have
high bulk strength and are sensitive enough to be de-
tonated by inexpensive boosters. The liquid phase in such
improved slurries comprises less than 5% by weight of
water plus one or more water-soluble polar at least or-
ganic substances to form a solvent capable of dissolving
approximately its own weight of inorganic oxidizer salt
at ambient temperatures. The oxidizer salts useable in
the slurries of the invention include ammonium nitrate,
sodium nitrate, barium nitrate, or mixtures thereof,
the preferred oxidizer being ammonium nitrate. The polar or-
ganic materials include alcohols such as isopropyl alco-
hol, polyhydric alcohols such as glycerol, ethylene glycol,
ethylene glycol, glycerol; sugars such as sucrose, maltose,
dextrose; amides such as formamide, acetamide, urea; and
amines such as guanidine and dicyandiamidine.

The slurries of this invention preferably contain from
about 2 to 4.5% by weight of water and 8 to 14% by
weight of polar organic substance.

The sensitizer for the slurry explosives may comprise
crude TNT, or any of the "tols" including composition B
(RDX/TNT/wax), pentolites (PETN/TNT), Ednatols
(EDNA/TNT), etc. Composition B is a mixture of cyclo-
trimethylene-trinitramine (sometimes called cyclonite),
trinitrotoluene, and wax. Pentolite is a mixture of
taenylthol titantrate and trinitrotoluene in various pro-
portions, Ednatols are mixtures of ethylene dinitramine
and trinitrotoluene. It may also comprise smokeless
powder of the single, double and triple-base varieties. The
single base smokeless powders contain predominately ni-
trocellulose; the double-base smokeless powder propel-
lants contain also nitroglycerine, but are still pre-
dominantly nitrocellulose. The triple-base smokeless pow-
ders contain, in addition to nitroglycerine and nitrocel-
 lulose, an insoluble solid explosive. For example, the flash-
less (triple base) propellant type designated propellant
PGS military publications as M15 contains about 55% nitro-
guanidine together with nitrogupton/nitroglycerine in the
ratio of 20/19. Other triple base smokeless powders con-
tain in addition to nitrocellulose and nitroglycerine such
explosives as RDX and HMX (hexamethylentetramine).

Slurry explosives made according to this invention may
be sensitized also with aluminium or other heat producing
metals such as magnesium. The sensitizer may also be any
of the high strength, granular explosives including nitro-
starch, PETN, RDX, tetryl (ethylenediaminedinitrate),
Haleite (trinitrophenylmethylnitramine), or it may be
one of the propellants known as compound propellants
formulated into granular form, preferably in the range of
particle size from minus 4 to plus 30 mesh although other
formulations may be used, though sometimes less effec-
tive. The sensitizer may also comprise any suitable com-
bination of these substances.
The liquid phase of the slurry explosives of this invention may be regulated as to viscosity by the use of various hydrophilic colloids including the guar gums, the water-soluble carboxymethyl cellulose substances, starch, and other suitable hydrophilic colloids. The thickened liquid phase may likewise be gelatinized by the use of a suitable cross-linking agent such as borax in the case of guar gum. Such thickeners or gelling agents are present in amounts of 0.2 to 5% by weight.

In the following examples, all percentages and parts are by weight of the total slurry composition.

**EXAMPLE I**

To show the relative merits of slurry explosives made according to this invention with those of prior art, the results shown in Table I were obtained using the composition: TNT—14%, ammonium nitrate—59%, sodium nitrate—10%, sulfur—2.0%, cross-linking borated guar gum—0.5%, water—4.5% and organic liquid—10%. These were compared with a standard slurry prepared according to Patent 2,930,685 containing 16% TNT, 59% ammonium nitrate, 8% sodium nitrate, 2% sulfur, 0.5% cross-linking borated guar gum and 14.5% water. In all cases the TNT was minus 4 to plus 20 mesh particle size.

<table>
<thead>
<tr>
<th>Organic Liquid</th>
<th>Standard Isopropl Alcohol</th>
<th>Formamide</th>
<th>Ethylene Glycol</th>
<th>Glycerine</th>
</tr>
</thead>
<tbody>
<tr>
<td>Percent organic (x)</td>
<td>None</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Percent water (y)</td>
<td></td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Slurry density (g.fcc.)</td>
<td></td>
<td>1.30</td>
<td>1.30</td>
<td>1.30</td>
</tr>
<tr>
<td>Critical Dia. (unconfined) (in.)</td>
<td></td>
<td>0.26</td>
<td>0.26</td>
<td>0.26</td>
</tr>
<tr>
<td>booster (in.)</td>
<td></td>
<td>0.26</td>
<td>0.26</td>
<td>0.26</td>
</tr>
</tbody>
</table>

While the slurry made with isopropyl alcohol was no better than the standard, there was a substantial improvement in sensitivity resulting by the substitution of 10% formamide, ethylene glycol or glycerine for 10% of the 14.5% water. Furthermore, the slurries with organic additives were lower in freezing point and provided better swelling of the guar gum. They also had better water resistance than the standard water slurry. Moreover, the TNT slurry explosives of prior art were found to require about 5% more TNT to sensitize them to the same level as that of the slurries made with 10% formamide, ethylene glycol or glycerine.

**EXAMPLE II**

As another example the composition: 75 mm, M-1 smokeless powder—25 parts, ammonium nitrate—43 parts, sodium nitrate—10 parts, sulfur—2 parts, water—y parts, cross-linking borated guar gum—0.7 part and x parts organic liquid was studied with the following results:

<table>
<thead>
<tr>
<th>Organic Additive</th>
<th>Formamide</th>
<th>Formamide/ Ethylene Glycol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parts (x)</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Parts water (y)</td>
<td>4.5</td>
<td>4.5</td>
</tr>
<tr>
<td>Density (g.fcc.)</td>
<td>1.40</td>
<td>1.40</td>
</tr>
<tr>
<td>Critical Dia. (unconfined) (in.)</td>
<td>5</td>
<td>5</td>
</tr>
</tbody>
</table>

**TABLE III**

<table>
<thead>
<tr>
<th>Organic Additive</th>
<th>Formamide</th>
<th>Glycerine</th>
<th>Ethylene Glycol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parts (x)</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Parts water (y)</td>
<td>4.5</td>
<td>4.5</td>
<td>4.5</td>
</tr>
<tr>
<td>Density (g.fcc.)</td>
<td>1.40</td>
<td>1.40</td>
<td>1.40</td>
</tr>
<tr>
<td>Critical Dia. (unconfined) (in.)</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
</tbody>
</table>

In most cases these improved slurry explosives appeared to be better in sensitivity, plasticity, swelling of the gum and freezing point than the corresponding slurries using all water as the solvent.

Realizing from these examples that a solvent comprising less than 5% water together with a certain amount of organic material soluble in water may be used to act to produce slurry explosives of equal or better sensitivity and gelation properties than the original all water-solvent slurries, it becomes important to determine the x and y values (organic solvent=x percent and water=y percent) necessary to obtain suitable slurries. Some observations of the approximate minimum values of x for a given y are summarized in Table III.

**TABLE III**

(1) Organic solvent required, x and water requirement, y for high density slurry explosive formulation

<table>
<thead>
<tr>
<th>Solvent</th>
<th>x</th>
<th>y</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formamide</td>
<td>8.0</td>
<td>4.5</td>
</tr>
<tr>
<td>Ethylene Glycol</td>
<td>9.0</td>
<td>4.5</td>
</tr>
<tr>
<td>Glycerine</td>
<td>10.0</td>
<td>4.5</td>
</tr>
</tbody>
</table>

In order to determine the minimum water requirement, several slurries were made using the general composition shown in Example II except that the x and y values were varied. Using either formamide or ethylene glycol it was found that slurries were inferior and required excessive organic liquid when no water at all was used; the best results were obtained in both cases by the use of about 2 to 3 parts water in conjunction with these solvents. Thus, at y=2 and x=9.5 for formamide the critical diameter was 5" at a density of 1.36 g./cc. The density was increased to 1.45 g./cc. by increasing the formamide by only 1%. Two or three parts more ethylene glycol were required to obtain a good high density slurry than when formamide was used in mixtures with 2 to 3% water.

Various combinations of formamide with glycerine, ethylene glycol and sugar, and ethylene glycol and molasses were studied with essentially the same results. For example, a 5/5/4.5 mixture of formamide/glycerine/water gave a slurry explosive of 4" critical diameter at 1.3 g./cc., slightly more liquid phase being needed to obtain a density in the range 1.45 to 1.5 g./cc. A mixture of 10 parts of 7/3/4.5 formamide/sugar/water yielded a slurry having a density of 1.46 and having a sensitivity comparable to those of the prior art slurries.

The slurries of the invention thus comprise compositions in which the water content is from 2 to 4.5%, polar organic material 8 to 14%, sensitizer 8 to 30% and the remainder oxidizer and thickeners, all by weight. Preferred amounts of sensitizer are 10 to 25%; of TNT, 15 to 30% for smokeless powder, and 1/2 to 20% for particular aluminum.

Thus, the slurries of this invention possess sensitivities equal to or greater than those of the prior art while utilizing smaller amounts of the sensitizer, which is the most expensive ingredient employed in the composition. Because they are true slurries having densities of 1.3 g./cc. and higher when free of air or other entrapped gases, they possess high bulk strength. Additionally, the water resistance and antifreeze properties of the slurries are greater than those of the prior art.

While the minimum density of the slurries of this invention when free of entrapped gases is 1.3 g./cc., air entrapment produced in the mixing of thickened slurries may reduce the density up to 25% of this value. Thus, such thickened, air-containing slurries having densities of
1.0 g./cc. or slightly lower have been found to be operable and are within the scope of this invention. It is to be understood that the definition of slurries as used herein applies to the state of the material as it is mixed. Thus, slurry blasting agents may be prepared at elevated temperatures which facilitate the mixing operation. Upon introduction into the bore hole, such hot slurries will cool and the resulting product may not be a true slurry, because of crystallization of ammonium nitrate, etc. However, it is intended to cover slurries within the definition as mixed.

While the invention has been described in terms of certain examples, they are to be considered illustrative rather than limiting and it is intended to cover all further modifications and embodiments that fall within the spirit and scope of the appended claims.

What is claimed is:

1. A pumpable aqueous explosive slurry blasting composition, which comprises a major proportion of inorganic oxidizer salt, ½ to 30 percent of a sensitizer selected from the group which consists of particulate trinitrotoluene, smokeless powder, mixtures of cyclonite-trinitrotoluene-wax, mixtures of trinitrotoluene-pentaerythritoltrinitrate, trinitrotoluene-ethylendinitramine mixtures, nitrostarch, pentaerythritoltrinitrate, cyclonite, trinitrophenylmethylnitramine, ethylenediaminedinitrate, aluminum and magnesium, and mixtures thereof, a liquid in proportions sufficient to form a substantially continuous phase and consisting of water and a water soluble polar substance selected from the group which consists of alcohols, polyhydric alcohols, sugars, amides and amines, the composite liquid being capable of dissolving at least approximately its own weight of the inorganic oxidizer salt at ambient temperatures, and a thickener for said slurry to inhibit segregation of said particulate matter from the suspending liquid, said blasting composition having a density of at least 1.3 grams per cubic centimeter when free of entrapped gases.

2. Composition according to claim 1 wherein there is included sufficient entrapped gas to lower the density up to 25 percent.

3. Composition according to claim 1 wherein the sensitizer comprises TNT.

4. Composition according to claim 1 wherein the sensitizer comprises aluminum particles.

5. Composition according to claim 1 wherein the sensitizer comprises smokeless powder.

6. Composition according to claim 1 wherein the oxidizer salt consists essentially of ammonium nitrate and sodium nitrate, wherein the sensitizer comprises aluminum, and wherein the overall density of the composition is reduced up to 25 percent by inclusion of the entrapped gases.

7. Composition according to claim 1 wherein the polar organic compound comprises ethylene glycol and wherein a guar gum is included as a thickener.

8. Composition according to claim 7 wherein a cross-linking agent is included.

9. Composition according to claim 1 wherein formamide is included in the liquid.

10. Composition according to claim 1 wherein the oxidizer salt comprises 53 to 69 percent, by weight of the total composition, of a combination of a major amount of ammonium nitrate and a minor amount of sodium nitrate.

11. Composition according to claim 10 which also includes sulfur.

12. Composition according to claim 1 which contains less than 5 percent water.

13. An inorganic oxidizer salt type blasting composition formed by admixing water, an inorganic oxidizer salt, a sensitizer, a thickener, and a gas to form a blasting composition of aqueous slurry type, said resulting slurry containing said gas in an amount sufficient to cause a predetermined lowering of the density of said slurry.

14. A blasting composition according to claim 13 wherein the gas is air incorporated in proportions such as to lower the density of said composition up to 25 percent.

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