

1

3,788,909

## AQUEOUS BLASTING COMPOSITIONS CONTAINING AN IMMISCIBLE LIQUID HYDROCARBON FUEL AND METHOD OF MAKING SAME

Lex Lynn Udy, Salt Lake City, and Harvey Alfred Jessop and Daniel Aaron Wasson, Murray, Utah, assignors to Ireco Chemicals, Salt Lake City, Utah

No Drawing. Filed Nov. 24, 1972, Ser. No. 309,178

Int. Cl. C06b 1/04

U.S. Cl. 149—60

19 Claims 10

### ABSTRACT OF THE DISCLOSURE

Aqueous blasting agents containing an immiscible liquid hydrocarbon fuel are formulated by prethickening the liquid phase of the composition by the addition of a thickening agent, preferably a biopolymer gum, thereafter adding the liquid fuel and subsequently mixing the combination so as to form a stable, fine dispersion of immiscible liquid hydrocarbon fuel droplets throughout the liquid phase.

The present invention relates to an improved method of thickening and cross-linking explosive compositions containing an immiscible hydrocarbon liquid as a fuel and to the resulting explosive composition and, more particularly, to the method of preparing water-bearing explosive compositions having good sensitivity to detonation as a result of forming and maintaining a fine dispersion of droplets of an immiscible hydrocarbon liquid fuel throughout the composition by preincorporating a thickening agent into an inorganic oxidizing salt solution thereby rendering it viscous to a predetermined degree prior to the addition of said liquid fuel.

### BACKGROUND

Blasting agents of the type known as water-bearing or slurry explosives or aqueous blasting compositions have gained considerable commercial acceptance in recent years. Fuel-sensitized ammonium nitrate (AN) explosives have become significant factors in the field of commercially successful blasting agents. ANFO (ammonium nitrate prills oxygen balanced with fuel oil) explosive compositions, even though widely used and suitable for some uses, are not suitable per se for use in water-containing boreholes. Aqueous slurry blasting agents comprising generally an inorganic oxidizing salt (predominantly ammonium nitrate), a thickening agent for the liquid phase, a fuel and sensitizer have been very successful even in water-containing boreholes. In addition, both solid and liquid hydrocarbon fuels, for example, fuel oil, have also been incorporated into aqueous blasting agents. One prior art approach to the problem of incorporating immiscible liquid fuels into aqueous blasting agents has been the use of conventional emulsifying agents.

There have been other attempts at incorporating immiscible liquid fuels into aqueous blasting agents. One such attempt has been the use of some means to break up the liquid into particles of colloidal size which would not readily coalesce in solution. This attempt has been relatively unsuccessful due to the difficulty of effecting a colloidal distribution in the highly ionic solution present in aqueous blasting compositions. Furthermore, this approach requires a mechanical means such as a colloid mill or a means for producing a high velocity liquid fuel stream which can be cumbersome, expensive, and relatively impractical—particularly for on-site mixing operations.

Another attempt at incorporating an immiscible liquid fuel into an aqueous blasting agent has been to include

2

within the blasting composition a material, preferably a fuel, that can absorb the liquid. Thus by distributing the absorbent material throughout the composition the absorbed liquid fuel is also distributed. One such material is sawdust which functions both as an absorbent and as a fuel. The basic disadvantages of this approach are that the liquid fuel is dispersed only as fine as the particulate matter itself, and thus the degree of dispersion is limited, and the very requirement of the absorbent material itself limits ingredient versatility.

In these or other prior art attempts to incorporate an immiscible liquid fuel—in order to provide more economical explosive compositions by eliminating the metal sensitizer (e.g., aluminum) or high explosive sensitizer (e.g., trinitrotoluene)—compositions in various forms including aqueous slurries comprising essentially AN (or AN/sodium nitrate (SN) combinations), immiscible liquid fuel such as fuel oil, and water have been suggested but these latter compositions have not detonated satisfactorily in dry or water-containing boreholes except by use of multiple boosters at high booster/slurry weight ratios, e.g., 1/25 or higher.

In commonly assigned U.S. application Ser. No. 148,941 the problem of forming a sensitive aqueous explosive composition containing fuel oil as the primary fuel was solved by the use of calcium nitrate (CN) in the slurry composition as a major oxidizer component. It was there found that CN had a tendency to form an emulsion-like dispersion of fuel oil throughout the slurry composition, and its use, coupled with proper thickening and density control, resulted in the formation of relatively sensitive compositions.

It has now been found in the present invention that an effective dispersion can be effected by using a method involving carefully controlled thickening and mixing of the composition and that such dispersion is possible irrespective of the oxidizer or oxidizer salts employed and without the use of emulsifiers or absorbent materials. Furthermore, compositions of this invention are relatively sensitive to detonation without requiring metal or high explosive sensitizers or the use of high booster/slurry weight ratios or multiple boosting and therefore are very economical.

Thus, in accordance with this invention, a slurry or aqueous blasting composition comprising an aqueous solution containing an oxidizing salt or salts, such as AN, CN, or SN or other oxidizers, and an immiscible hydrocarbon liquid fuel, such as fuel oil, can be efficaciously formulated in such a manner that a fine dispersion of the liquid fuel is effected and maintained throughout the composition by proper thickening and mixing procedures and, preferably, by the use of a small amount of a biopolymer or other similar functioning gum as the thickening agent or part thereof.

### THE COMPOSITIONS OF THE PRESENT INVENTION

The essential ingredients for forming the explosive compositions of the present invention are an inorganic oxidizing salt or salts present in amount from about 60% to about 90% by weight of the total composition; sufficient water at least about 10% by weight, to form a pumpable composition at the preparation or mixing temperature an immiscible liquid hydrocarbon fuel; and a thickening agent or agents.

In forming the explosive compositions of the present invention, the immiscible liquid hydrocarbon fuel is the primary fuel and is incorporated into a prethickened salt solution in the final form of a uniform and homogeneous dispersion of discrete liquid droplets. Under service conditions, the dispersed liquid particles are approximately

.025 cm. or smaller in diameter which, because of the effect of the thickening agent, do not rapidly separate out of or coalesce in the medium in which such particles are suspended.

The immiscible hydrocarbon fuels can be aliphatic, alicyclic, and/or aromatic. Suitable fuels can be either saturated and/or unsaturated. For example, benzene, toluene, and the xylenes can be employed. Preferred fuels include mixtures of normally liquid hydrocarbons generally referred to as petroleum distillates such as gasoline, kerosene, and diesel fuels. A particularly preferred liquid fuel is No. 2 fuel oil. Tall oil and paraffin oil can also be used. The liquid fuel is preferably present in amount of about 4% to about 12% by weight.

It is essential that the immiscible liquid fuel be introduced into an aqueous solution of the oxidizing salt(s), which has been prethickened to a predetermined viscosity in order to effect the fine dispersion. Additionally, the proper choice of a thickening agent or agents or prethickening the solution can have important effects on the ease of forming and maintaining this dispersion. A preferred type of thickening agent for this purpose is a biopolymer gum produced by a process comprising the microbial transformation of carbohydrate material; for example, such as by transforming a carbohydrate with a microorganism to obtain a polymeric material differing in form and substance from the parent material. Suitable carbohydrates include sugars, such as pentoses or hexoses (for example, glucose, sucrose, fructose, maltose, lactose, galactose), and starches, such as soluble starch, corn starch, and the like. Unrefined carbohydrates may be used. Microorganisms suitable for effecting the microbial transformation of carbohydrates may be, for example, plant pathogenic bacteria such as plant pathogens which produce exudates at the site of lesions on infected plants. Typical of such microorganisms are the species of the genus *Xanthomonas*. For example, the exellular bacterial polysaccharides produced biochemically with *Xanthomonas campestris* from simple sugar nutrients such as glucose are composed of D-glucose, D-mannose, and D-glucuronic acid in a ratio of 2.8/3.0/2.0. Acetic and pyruvic acid substitutes are present in amounts of about 4.7% and 3.0% to 3.5%, respectively. Although the structure of these polysaccharides is somewhat obscure, apparently acetic acid exists as the O-acetyl ester, whereas pyruvic acid is attached through a ketal linkage. Biopolymers may also be produced from similar organisms other than those of the genus *Xanthomonas*.

There are other gums that are not of the biopolymer type which are also preferred over more conventional gums since they are functionally similar to the biopolymer gums. These gums are generally alkyl substituted guar gums such as General Mills "GenGel E2," Stein Hall "4763," and General Mills "XG-498."

Biopolymer or these other specific alkyl substituted gums are more effective on a concentration basis in forming and maintaining a fine dispersion of an immiscible liquid hydrocarbon fuel throughout an aqueous blasting composition than other conventional types of thickening agents, such as regular guar gums and starches. This effectiveness is probably due to a unique droplet entrapping network that is formed upon hydration of these gums in an aqueous solution.

A preferred biopolymer gum for use as a thickening agent in explosive compositions of the present invention is General Mills "XB-23" which is available commercially and produced from a carbohydrate which has been exposed to *Xanthomonas campestris*. This particular biopolymer has been used heretofore in other slurry explosive compositions as a thickening agent and was found to be a highly effective and stable thickener, particularly at high temperatures and over extended periods of time and wide pH ranges (see for example commonly assigned U.S. Pat. 3,658,607). "XB-23" and other thickening agents of a similar nature have certain key physical prop-

erties which enables them to be used effectively with an immiscible hydrocarbon liquid fuel, particularly in forming a fine dispersion of fuel droplets.

The biopolymer "XB-23" functions as a thickener of an aqueous solution of an explosive composition in the ordinary sense; i.e., it is similar to commonly used guar gum which swells upon hydration to thicken or increase the viscosity of the solution. However, its chemical nature is such that it, unlike guar gum, can be considered to be noncross-linking in the presence of conventional cross-linkers such as chromate ion. Aside from being an efficient thickener in terms of viscosity versus concentration as well as being very stable over a wide pH and temperature range, "XB-23" or similar biopolymers as described above exhibit two additional properties that make them exceptional for use in slurry explosive compositions containing an immiscible liquid hydrocarbon fuel:

(1) The polymeric gum molecules interact with one another to form a unique entrapping network. Thus the liquid fuel is formed and maintained in a finely dispersed state.

(2) The gums impart a thixotropic nature to the thickened salt solution. Thus the gums, by exhibiting decreased viscosity with increased shear, allow relatively easy dispersion of the liquid fuel when the solution and liquid fuel are subjected to the action of a mixing blade. When mixing concludes, the viscosity of the solution rises sharply thereby apparently entrapping or encapsulating the liquid droplets in their dispersed state.

Although the important concept of this invention is the preincorporation of sufficient thickening agent prior to the addition of the immiscible liquid fuel—and thus most guar gums and/or starches and the like can be effectively used in this manner to form a dispersion of the liquid fuel since they too form a network that can entrap liquid droplets, though generally requiring fairly rapid cross-linking for permanency and continuity—biopolymer gums are preferable because of their thixotropic nature and effective and peculiar entrapping network and because of their effectiveness without requiring the use of a cross-linker. The thixotropic nature reduces the energy required for initial dispersion. When non-thixotropic thickening agents are used, the viscosity of the solution at the time of mixing and pumping must be higher in order to assure permanency of the final dispersion and composition and good initial water resistance. Therefore, ease of handling the compositions is decreased somewhat when non-thixotropic thickening agents are used. Furthermore, biopolymer gums do not require rapid cross-linking for permanency and effectiveness. Rapid cross-linking is necessary for maintaining a permanent, stable dispersion when most conventional non-thixotropic thickening agents are used, and use of these latter agents makes the time coordination of mixing and pumping or delivery more critical.

The total thickening agent is generally present in amounts of from about 0.05% to about 0.50% of which preferably about 0.1% is a biopolymer gum.

One or more conventional cross-linkable thickening agents are preferably employed in the course of preparing the explosive compositions of the present invention to supplement the thickening function of the preferred biopolymer gums in regulating the viscosity of the composition so as to permit pumping of compositions containing finely divided sensitizing gas bubbles, to prevent any substantial segregation and/or coalescence of the ingredients, and to improve the water resistance of the composition. Conventional cross-linkable thickening agents which are known in the art include guar gums, starches, and synthetic polymeric products. It is also economically desirable to replace some of the biopolymer gums with these cross-linkable thickening agents since the biopolymer gums are relatively more expensive.

Other preferred ingredients are a density-lowering or gassing agent such as sodium nitrite to lower the density

of the composition to a predetermined degree and a cross-linking agent to effect the gelation of any cross-linkable thickening agent.

As is well known in the art, gassing agents such as sodium nitrite and hydrogen peroxide have been employed heretofore to lower the density and thereby, in part, control the sensitivity of explosive slurry compositions. The compositions of the present invention preferably employ a small amount, e.g., about 0.01% to about 0.2% or more (most preferably about 0.05%), of such gassing agent in order to obtain a density under service conditions of less than about 1.5 gm./cc.

Cross-linking agents in combination with suitable cross-linkable thickening agents are also preferably employed in order to further stabilize the fine dispersion or distribution of the droplets or particles of liquid hydrocarbon fuel, as well as to prevent the undesired escape of gas bubbles, and thus maintain the sensitivity to detonation resulting from the fine dispersion. Cross-linking agents are also especially useful where the stability or integrity of the composition must be maintained in the presence of water-containing boreholes. Excellent cross-linking of guar gum can be obtained by using a small amount, e.g., about 0.05% to about 0.2%, of an aqueous solution of sodium dichromate. Other cross-linking systems will also be apparent to those skilled in the art.

Various optional ingredients can also be included in the compositions of the present invention. For example, supplemental solid fuels such as particulate aluminum, magnesium alloys, sulfur, and normally solid hydrocarbons such as wheat and other vegetable grain, starch, etc., and the like may be added to increase the strength and/or sensitivity of the compositions. Starches and vegetable grains can be added in amounts up to about 15% by weight and can function as fuel, sensitizer, and thickener combined, as disclosed in commonly assigned U.S. application Ser. No. 309,177. If starches or grains are added they can function either primarily or secondarily as sensitizer and thickener in compositions of the present invention and as a secondary fuel, being supplemental to the primary immiscible liquid hydrocarbon fuel. If used as the primary thickener, at least a portion must be preincorporated into the oxidizer solution prior to addition of the immiscible fuel. Thiourea may also be employed in very small amounts, e.g., about 0.05%, to control the rate at which sodium nitrite gassing agent functions ethylene glycol, formamide, and other mutually water-soluble ingredients may also be included in varying amounts.

#### THE METHOD OF THE PRESENT INVENTION

Briefly, the method of preparation of the explosive compositions of the present invention comprises finely dispersing or distributing a liquid hydrocarbon fuel in an aqueous oxidizer salt solution to which a thickening agent has been previously added.

It is essential to preincorporate the thickening agent into the aqueous solution thereby increasing its viscosity prior to the addition of the immiscible liquid fuel in order to make the solution viscous enough that the fuel oil droplets which are dispersed during mixing will not coalesce. Preincorporation of a thickening agent into the salt solution of an explosive composition has been used before in the prior art to entrap tiny air bubbles formed during the addition and subsequent mixing of solid particulate ingredients or formed by agitation or formed by the use of chemical gassing agents added to the prethickened solution. (See, e.g., U.S. Pat. 3,453,158.)

It has now been discovered that an immiscible liquid fuel can be added to such a prethickened salt solution and subsequently mixed such that a fine dispersion of fuel droplets throughout the composition can readily be formed. This dispersion thus formed is essentially dynamically stable and coalescence of the droplets is prevented. It is critical that the dispersion of liquid fuel is perma-

nently maintained to insure intimate contact of the fuel with the oxidizer since intimacy of fuel and oxidizer directly affects the sensitivity of the explosive composition. The more intimate the mixture, the more sensitive the explosive. The resultant dynamically stable dispersion is either loaded into suitable containers for use as packaged explosives or pumped by means of pump trucks similar to those described in U.S. Pat. 3,303,738 in an on-site mixing and pumping operation used for direct loading of boreholes.

In a typical preparation (which accommodated the preparation of all the examples presented below) the oxidizer salt (or salts) is dissolved in water to form a solution of fudge point around 50° C. The solution is heated to about 60° C. or 70° C. prior to mixing. Further temperature control is not necessary during mixing. Water soluble liquid fuels, if any, may also be added at this juncture. A small amount of a thickening agent or agents is next added, thereby thickening the solution to the desired degree. It is preferred that the composition be cross-linked for extended storage stability and increased water resistance and therefore at least part of the thickening agent is preferably cross-linkable.

The predetermined solution viscosity of the thickened solution should preferably be above about 600 centipoise since at lower viscosities the liquid fuel will tend to coalesce, and initial water resistance of the delivered composition will be impaired. A common viscosity would be about 800 centipoises. There is no corresponding specific upper limit of prethickened solution viscosity. A practical upper limit is determined mainly by the type of mixing and pumping apparatus employed.

To this heated and thickened solution is added the immiscible liquid hydrocarbon fuel in a conventional manner such as by metering through a positive displacement pump, dribbling, or squirting the liquid hydrocarbon into the thickened solution or by injecting it under pressure through a nozzle which helps to initially break up the liquid into small droplets. Simultaneously, the cross-linking agent such as sodium dichromate is added (if used) as well as the gassing agent such as sodium nitrite. If thiourea is employed it is generally added to the heated solution prior to the addition of the cross-linking and gassing agents. A typical solution thus formed can be represented by the following ratio, parts by weight: AN 50/H<sub>2</sub>O 15/biopolymer gum 0.1/guar gum 0.2/thiourea 0.1. All other above described, preferred, desirable, and/or optional ingredients can now be simultaneously added. Additionally, dry particulate oxidizer salt may now be added for proper oxygen balance. The resulting solution with added ingredients is simply mixed to a desired degree of relative homogeneity and then placed into a container or borehole by appropriate means. It is important that mixing is present and continuous as the liquid hydrocarbon is initially introduced in order that as much mechanical dispersion as possible takes place. The prethickened solution assures that the dispersion will remain fixed and stable after such mixing. Mixing can be accomplished by any conventional equipment known in the art.

For the entire preparation procedure, conventional equipment such as mixing funnels, pumps, solids educators and the like can be employed—provided that the resulting composition consists essentially of a substantially homogeneous fine dispersion which is gasified to the desired bulk density by stirring in air, for example, or by incorporating a gassing agent.

As the composition cools some of the oxidizer salt or salts may crystallize out depending upon the temperature reached. If crystallization occurs, the composition will then become firm but pliable. However, with proper thickening (and/or cross-linking) the compositions will be stable and the liquid fuel will remain properly and uniformly dispersed at temperatures both above and below the crystallization temperature of the salt solution.

The present invention will be further understood by reference to the following illustrative examples. In the examples, unless otherwise indicated, all references to amounts are on a parts-by-weight basis.

### Example I

In this example compositions of the present invention having the ingredients and characteristics set forth in Table I were prepared in the manner described above and successfully detonated as indicated in Table I. As shown, tall oil, paraffin, and fuel oil can readily be used for the immiscible liquid hydrocarbon fuel. Composition C shows the use of fine aluminum particles as a supplementary fuel, as a sensitizer, and for added explosive strength. Compositions B through E contain dry particulate AN which was added to the prethickened solution. Composition A had an initial solution viscosity of 920 centipoise at 55° C.

TABLE I

Composition	A	B	C	D	E
Ingredients (parts by weight):					
Solution containing:					
AN	52.50	49.84	49.84	49.84	49.84
H <sub>2</sub> O	15.50	41.80	14.80	14.80	14.80
Biopolymer gum <sup>1</sup>	0.10	0.09	0.09	0.09	0.09
Thickening agent <sup>2</sup>	0.18	0.17	0.17	0.17	0.17
Thiourea	0.10	0.10	0.10	0.10	0.10
Tall oil				5.70	
Paraffin					5.0
Fuel oil, No. 2	2.85	5.0	3.0		
Aluminum (atomized)			6.0		
Dry solid AN		30.0		28.85	29.55
Gassing agent <sup>3</sup>	0.35	0.30	0.25	0.30	0.30
Cross-linking agent <sup>4,5</sup>	0.15	0.15	0.15	0.15	0.15
Properties:					
Solution pH	4.50	4.50	4.50	5.30	5.30
Density (gm./cc.)	1.00	1.05	1.06	1.02	0.97
Detonation results (in cardboard tubes, length=6X diameter): <sup>6</sup>					
At 20° C.:					
4"		D	D	F	F
5"				D	D
At 5° C.:					
5"			D		
6"		F			

<sup>1</sup> Biopolymer gum=XB-23.

<sup>2</sup> Thickening agent=Stein-Hall "J-100" guar gum.

<sup>3</sup> Gassing agent=1 part NaNO<sub>2</sub>/4 parts H<sub>2</sub>O.

<sup>4</sup> Cross-linking agent=1 part Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>·2H<sub>2</sub>O/1 part H<sub>2</sub>O.

<sup>5</sup> Cross-linking agent=15 parts H<sub>2</sub>O/5 parts HNO<sub>3</sub>/5 parts SN/7 parts NaCr<sub>2</sub>O<sub>7</sub>·2H<sub>2</sub>O.

<sup>6</sup> Composition A detonated in 4" dia. at 20° C. after 3 days storage, in 5" dia. at 10° C. at velocity of 3,850 m./sec., and in 5" dia. at 20° C. at velocity of 3,950 m./sec., all with one pound cast primmer.

NOTE.—D=Detonated; F=Failed.

### Example II

In this example the following composition was prepared:

SN	17.0
AN	52.0
H <sub>2</sub> O	15.0
XB-23	0.10
Thickening agent <sup>1</sup>	0.18
Thiourea	0.10
Fuel oil, No. 2	5.50
Dry solid AN	10.0
Cross-linking agent <sup>2</sup>	0.15
Gassing agent <sup>3</sup>	0.30

<sup>1</sup> Stein-Hall "J-100" guar gum.

<sup>2</sup> 1 part Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>·2H<sub>2</sub>O/1 part H<sub>2</sub>O.

<sup>3</sup> 1 part NaNO<sub>2</sub>/4 parts H<sub>2</sub>O.

This composition had a density of 1.10 gm./cc. at 22° C. It detonated in a 4" diameter at 22° C. with a 3645 m./sec. velocity and in a 5" diameter at 15° C.

### Example III

In this example the following composition was prepared:

5	AN	49.80
	H <sub>2</sub> O	14.82
	XB-23	0.10
	Thiourea	0.10
	Fuel oil, No. 2	4.0
10	Dry solid AN	28.0
	Starch <sup>1</sup>	3.0
	Gassing agent <sup>2</sup>	0.10
	"J-100" guar gum	0.18
	Cross-linking agent <sup>3</sup>	0.15

<sup>1</sup> Potato starch.

<sup>2</sup> 1 part NaNO<sub>2</sub>/4 parts H<sub>2</sub>O.

<sup>3</sup> 1 part Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>·2H<sub>2</sub>O/1 part H<sub>2</sub>O.

This composition had a density of 0.95 gm./cc. and detonated in a 4" diameter at 20° C. The solution viscosity was about 800 centipoise at 65° C. prior to the addition of the fuel oil and dry solid AN.

### Example IV

In this example the following solution was prepared:

25	AN	60.0
	H <sub>2</sub> O	15.0
	Thiourea	0.1
	NaHSO <sub>3</sub>	0.015
30	"J-100" guar gum	0.2
	Wheat <sup>1</sup>	1.0

<sup>1</sup> Ground whole grain wheat has a particle size distribution of essentially minus 48 Tyler screen.

To 70 parts by weight of this solution, which was prethickened by the guar gum and wheat, was added 5 parts No. 2 fuel oil, 25 parts dry solid AN, 0.2 part of a gassing agent (1 part NaNO<sub>2</sub>/4 parts H<sub>2</sub>O), and 0.25 part of a cross-linking agent (15 parts H<sub>2</sub>O/5 parts HNO<sub>3</sub>/5 parts SN/7 parts NaCr<sub>2</sub>O<sub>7</sub>·2H<sub>2</sub>O). The resulting composition successfully detonated in a 6" charge diameter at a density of 1.13 gm./cc.

While the present invention has been described with reference to certain illustrative examples and preferred embodiments, various modifications are intended to be within the scope of the invention as set forth in the appended claims.

What is claimed is:

1. A method for forming a stable, explosive blasting composition having an aqueous liquid phase and containing a stable, fine dispersion of a water-immiscible liquid hydrocarbon fuel throughout said aqueous liquid phase without using an oil-in-water emulsifying agent which comprises in combination the following steps:

- (a) forming said aqueous liquid phase of at least one inorganic oxidizer salt in an aqueous solution at a temperature above the salt crystallization temperature;
- (b) incorporating a thickening agent into said liquid phase to prethicken said liquid phase to a predetermined viscosity prior to the addition of other ingredients;
- (c) adding said water-immiscible liquid hydrocarbon fuel to said prethickened liquid phase; and,
- (d) mixing said liquid fuel into said prethickened liquid phase.

2. A method as recited in claim 1 wherein at least a portion of said thickening agent is cross-linkable and which comprises the additional step of adding a cross-linking agent simultaneously with said liquid fuel to cross-link cross-linkable portion of said thickened agent.

3. A method as recited in claim 1 which comprises the additional step of adding a gassing agent simultaneously with said liquid fuel to gasify said composition to a predetermined density.

4. A method as recited in claim 2 which comprises the additional step of adding a gassing agent simultaneously with said liquid fuel to gasify said composition to a predetermined density.

5. A method as recited in claim 4 wherein said thickening agent includes an alkyl substituted guar gum.

6. A method as recited in claim 4 wherein said thickening agent includes a biopolymer material produced by a process comprising the microbial transformation of carbohydrate material.

7. A method as recited in claim 6 wherein said biopolymer material is produced from *Xanthomonas campestris*.

8. A method as recited in claim 4 wherein said inorganic oxidizer salt is ammonium nitrate.

9. A method as recited in claim 4 wherein said inorganic oxidizer salt comprises ammonium nitrate and sodium nitrate.

10. A method as recited in claim 4 wherein said immiscible liquid hydrocarbon fuel comprises an aromatic hydrocarbon.

11. A method as recited in claim 4 wherein said immiscible liquid hydrocarbon fuel comprises a petroleum distillate.

12. A method as recited in claim 4 wherein said immiscible liquid hydrocarbon fuel comprises No. 2 fuel oil.

13. An aqueous explosive blasting composition free of an oil-in-water emulsifying agent comprising a liquid phase of an aqueous inorganic oxidizer salt solution, a thickening agent for thickening said liquid phase to a predetermined viscosity, and an immiscible liquid hydrocarbon fuel stably and finely dispersed throughout said liquid phase which has been added to said thickened liquid phase.

14. An explosive blasting composition free of an oil-in-water emulsifying agent gasified to a predetermined density and comprising an aqueous solution of at least one inorganic oxidizer salt, a finely dispersed immiscible liquid hydrocarbon fuel, and a thickening agent at least part of which comprises a biopolymer gum.

15. A composition as defined by claim 14 wherein at least part of said thickening is cross-linkable and which includes a cross-linking agent for cross-linking said thickening agent.

16. A composition as defined by claim 14 wherein said biopolymer gum is produced from *Xanthomonas campestris*.

17. A composition as defined by claim 14 wherein said immiscible liquid hydrocarbon fuel is No. 2 fuel oil.

18. A substantially oxygen balanced, gasified explosive composition free of an oil-in-water emulsifying agent having a bulk density of about 0.90 gm./cc. to about 1.3 gm./cc. comprising about 60% to about 90% by weight of an inorganic nitrate oxidizer salt comprising aluminum nitrate or aluminum nitrate combined with sodium nitrate, at least about 10% total water, about 4% to about 12% of an immiscible liquid hydrocarbon fuel in finely dispersed form, a thickening agent comprising about 0.1% of a biopolymer material produced from *Xanthomonas campestris* and about 0.2% of a crosslinkable gum or starch, and about 0.15% of a cross-linking agent.

19. A method for forming a stable, explosive blasting composition having an aqueous liquid phase and containing a stable, fine dispersion of a water-immiscible liquid hydrocarbon fuel throughout said aqueous liquid phase which consists essentially of a combination of the following steps:

- (a) forming said aqueous liquid phase of at least one inorganic oxidizer salt in an aqueous solution at a temperature above the salt crystallization temperature;
- (b) incorporating a thickening agent into said liquid phase to prethicken said liquid phase to a predetermined viscosity prior to the addition of other ingredients;
- (c) adding said water-immiscible liquid hydrocarbon fuel to said prethickened phase; and
- (d) mixing said liquid fuel into said prethickened phase.

#### References Cited

##### UNITED STATES PATENTS

3,330,706	7/1967	Griffith	149—43 X
3,361,604	1/1968	Griffith	149—44
3,378,415	4/1968	Griffith	149—60 X
3,395,056	7/1968	Bronstein	149—44
3,449,181	6/1969	Armantrout et al.	149—60 X
3,617,406	11/1971	Young	149—60 X
3,653,996	4/1972	Edwards	149—41 X
3,282,753	11/1966	Cook et al.	149—46
3,658,607	4/1972	Cook et al.	149—44 X
3,711,345	1/1973	Tomic	149—60 X

STEPHEN J. LECHERT, JR., Primary Examiner

U.S. Cl. X.R.

149—44, 60, 61, 87, 115

UNITED STATES PATENT OFFICE  
CERTIFICATE OF CORRECTION

Patent No. 3,788,909 Dated January 29, 1972

Inventor(s) LEX LYNN UDY, HARVEY ALLRED JESSOP and DANIEL AARON

WASSON

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, Line 47, "oxidinzing" should be --oxidizing--.

Column 1, Line 47-48 "predeminantly" should be --predominantly--.

Column 2, Line 60, "oxidiing" should be --oxidizing--.

Column 2, line 64, after "temperature" add --;--.

Column 3, line 7, after "unsaturated" the period should be a comma --,--.

Column 3, line 19, after "agents" delete "or" should be --for--.

Column 7, Table I, Footnote 5, "linjing" should be --linking--.

Column 7, Table I, Footnote 6, last word, "primre" should be --primer--.

Column 7, Table I, Under B, for H<sub>2</sub>O "41.80" should be --14.80--.

Column 8, Example IV, Footnote 1, "has" should be --had--.

Column 8, line 37, "part" should be --parts--.

Column 8, line 38, "part" should be --parts--.

Column 10, line 30, add Claim 20 as follows:

--20. An aqueous explosive blasting composition consisting essentially of a liquid phase of an aqueous inorganic oxidizer salt solution, a thickening agent for thickening salt liquid phase to a predetermined viscosity, and an immiscible liquid hydrocarbon fuel stably and finely dispersed throughout said liquid phase which has been added to said thickened liquid phase.--

UNITED STATES PATENT OFFICE Page 2  
CERTIFICATE OF CORRECTION

Patent No. 3,788,909 Dated January 29, 1972

Inventor(s) Lex Lynn Udy, et al.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 10, "19 Claims" should read -- 20 Claims --.

Signed and sealed this 9th day of April 1974.

(SEAL)

Attest:

EDWARD M. FLETCHER, JR.  
Attesting Officer

C. MARSHALL DANN  
Commissioner of Patents