# **United States Patent**

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[54]	METHOD OF FORMING IN PLACE A GELLED				
	AQUEOUS SLURRY EXPLOSIVE				

4 Claims, No Drawings

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## [56] **References Cited** UNITED STATES PATENTS

3,097,120	7/1963	Hoffman et al	149/60 X
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## [11] 3,619,308

3,097,121	7/1963	Bowkley	149/60
3,301,723	1/1967	Chrisp	149/60 X
3,321,344	9/1967	Arbie	149/60 X
3,341,383	9/1967	Bergwerk	149/60
3,442,729	5/1969	Knight	149/60 X
3,445,305	5/1969	Lyerly	149/44 X
3,446,681	5/1969	Slykhouse et al	149/60 X
3,451,868	6/1969	Peterson	149/44 X
3,523,048	8/1970	Hopler	149/44 X

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**ABSTRACT:** The extrudability of an aqueous slurry explosive stabilized with a gelled polysaccharide gum is improved by incorporating an effective amount of water-soluble polyacrylamide in the composition. Preferably this is accomplished by injecting into the exit stream of the pump a solution of borax as gelling agent and polyacrylamide to reduce resistance of the gel to extrusion through a tubular conduit into the desired location.

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### METHOD OF FORMING IN PLACE A GELLED AQUEOUS SLURRY EXPLOSIVE

## DESCRIPTION OF THE INVENTION

There is now in use a class of blasting explosives based on ammonium nitrate, finely divided solid fuel, at least 10 percent water and a hydroxylated polymer stabilizer which is gelled with a cross-linking agent to prevent settling of solids and penetration by ground water in wet boreholes. These blasting compositions appear to consist of of about one-third undissolved solids, suspended in a relatively weak aqueous gel. They are very difficult to pump, particularly since they are inclined to extrude through tubular conduits with a high degree of frictional resistance, rather than to flow in the manner of conventional viscous fluids. The poor pumping behavior of the gelled slurry explosives has prompted the development of unusual pumping and extrusion apparatus for placement of the material in blasting holes.

gums, locust bean gums, and guar gum in particular are employed as stabilizers, being gelled with borax or a dichromate. Gelling is substantially instantaneous. In U.S. Pat. application Ser. No. 691,949 there is disclosed the formation of a stable exit stream from the pump, as the composition is pumped into the hole. By this means efficient pumping is obtained, the output pressure of the pump being used to extrude the gel a relatively short distance through a tubular conduit into a blasting hole.

It has been proposed to break up gelled explosive into small lumps so that the composition becomes pourable although not readily extrudable. This technique is not very successful with gelled hydroxylated polymers because the gels which are stiff enough to resist water in the bore hole do not pack firmly into 35 position in the desired manner.

In U.S. Pat. No. 3,097,121 there is disclosed the use of a dry mixture of solids, including partially hydrolyzed polyacrylamide and alum as gelling agent for the polymer. The dry mixture is poured in place and water is then pumped in to form 40the gelled suspension in situ. In this way the pumping or extrusion of a gel is avoided.

Partially hydrolyzed polyacrylamide has been employed alone as a gel-forming stabilizer in aqueous slurry explosives, gelling being accomplished by cross linking free carboxy groups with polyvalent ions or chelate complexes. The combination of both cross-linked polyacrylamide and gelled hydroxylated polymer in an explosive composition is disclosed in U.S. Pat. No. 3,355,336. Such a dual gel system is unusually stable to pH shift in storage because one of the gels becomes firmer at a lower pH whereas the other becomes stiffer at a higher pH, each compensating for the other's softening as pH changes. However, if a firm enough gel is desired so as to keep the explosive in place in a borehole, the problem of resistance 55 to pumping and extrusion still exists.

We have discovered that water-soluble polyacrylamide which is not cross-linked may be used to reduce the resistance to pumping and extrusion of a slurry stabilized with a gelled hydroxylated polymer. For want of a better description of the 60effect produced, it may be characterized as lubrication of the external surface of a gel. Judging by the appearance of the finished explosive composition, the lubricating polymer is not completely compatible with the gel. However, this appearance may be mainly the result of differences of index of refraction 65 pumping. rather than incompatibility. Since cross-linking of the polyacrylamide interferes with the desired result, free carboxy groups in the polymer are useful only insofar as they contribute to water solubility. The polyacrylamide used is a polymer having a molecular weight between 1 and 25 million 70 as calculated from intrinsic viscosity determined at 30° C. in an Ostwald Fenske viscosimeter, in dilute aqueous solution, using the relation:  $V=3.73\times10^{14}(m.w.)^{0.66}$ . The polymers which are useful dissolve readily to yield dilute solutions of

by borax. Polymers of this type are articles of commerce, or may be made by polymerization in aqueous solution using a potassium persulfate catalyst, according to published procedures. The practice of the invention is illustrated in the following examples.

Two explosive slurries were prepared for use in comparative experiments carried out with and without polyacrylamide lubricant. Composition A was prepared by thoroughly mixing together the following ingredients, given in weight percent: 51 10 percent ammonium nitrate, 5 percent sodium nitrate, 4 percent hexamethylenetetramine, 10 percent coarse granular aluminum, 2 percent pigment grade aluminum powder, 1 percent finely ground gilsonite, 1 percent guar gum and 16 percent water. The hexamethylenetetramine was dissolved in water 15 prior to mixing in order to facilitate uniform distribution throughout the composition. The guar gum was dry blended with ammonium nitrate prior to mixing with water.

Composition B was prepared in the same manner as com-Commonly hydroxylated polymers such as galactomannan 20 position A and contained 59.3 percent ammonium nitrate, 10 percent sodium nitrate, 4 percent hexamethylenetetramine, 8 percent coarse granular aluminum, 1.7 percent pigment grade aluminum powder, 1 percent guar gum and 16 percent water.

A peristaltic pump which squeezes a neoprene hose by gelled explosive in place by injecting the gelling agent into the 25 means of two rollers carried on a rotor was employed to pump slurry. This type of pump is available commercially, being commonly used to pump mixed concrete or grout into place.

#### EXAMPLE 1

Two aqueous solutions were prepared for injection into the exit stream from the slurry pump. One solution contained only 2.25 percent borax in water. The other solution contained 2.25 percent borax and 0.45 percent polyacrylamide in water. To the exit side of the pump was attached one 50-foot section of 2-inch inside diameter hose, followed by a 50-foot section of 1.5-inch inside diameter hose.

The pump was started with composition A at a flow rate of 700 lbs. per minute. Gelling solution containing 2.25 percent borax and 0.45 percent polyacrylamide was injected into the exit stream of the pump at 14 lbs. per minute. The exit pressure on the pump was 90 p.s.i.g. on startup, reaching a steady value of 30 p.s.i.g. in continuous operation.

The pump was stopped and the gelling solution was changed to 2.25 percent borax with no polyacrylamide. Composition A 45 was then pumped at a rate of 700 lbs. per minute, with injection of gelling solution into the exit stream at 14 lbs. per minute. The exit pressure on the pump was 325 p.s.i.g. on startup reaching a steady pressure of 200 to 225 p.s.i.g. during 50 continued pumping.

This example demonstrates the reduction in resistance to flow through the hose which is obtained by addition of polyacrylamide to the explosive gel.

#### EXAMPLE 2

Composition B was pumped at 700 lbs. per minute with injection of the gelling solution into the exit stream at 10 lbs. per minute. When using the gelling solution containing polyacrylamide, the startup pressure on the pump was 125 p.s.i.g., settling to a steady value of 90 p.s.i.g. during continuous pumping. When gelling solution containing only 2.25 percent borax was used, startup pressure was 250 p.s.i.g., settling to a steady value of 180 to 200 p.s.i.g. during continuous

The viscosity of an aqueous slurry explosive varies greatly with temperature, mainly because a change in temperature changes the percent of suspended solids. It is therefore advantageous to keep the slurry warm to facilitate mixing and pumping. In U.S. Pat. application Ser. No. 691,949 there is disclosed the use of a small amount of ammonium perchlorate in slurries to overcome the variation of sensitivity with changing temperature. However, if the slurry is kept hot for an extended period of time to facilitate pumping, more ammonium low viscosity and substantially neutral pH and are not gelled 75 perchlorate may be required to obtain the desired stabilizing

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effect. We have found that by putting the ammonium perchlorate in the gelling solution, as illustrated in the following example, as little as 0.5 percent of the total composition is a sufficient quantity to stabilize against loss of sensitivity at low temperatures.

#### EXAMPLE 3

A slurry explosive was made up by mixing the following ingredients in the indicated proportions by weight: 59.3 percent ammonium nitrate, 10 percent sodium nitrate, 4 percent hexamethylenetetramine, 8.0 percent granular aluminum, 1.7 percent pigment grade powdered aluminum, 1.0 guar gum and 16 percent water. An aqueous gelling solution was prepared containing 10 weight percent ammonium perchlorate, 2.25 percent borax and 0.45 percent polyacrylamide. 15

The slurry was heated to  $80^{\circ}$  F. to facilitate pumping and gelling and was then pumped under the same conditions as in example 2, with injection of the gelling solution at 10 lb. per minute. Pumping pressure was substantially the same as obtained in example 2. Portions of the finished product were 20 pumped into cardboard tubes of 4.5 and 5 inches inside diameter. After aging for 2 weeks, these charges were fired with the use of blasting caps and primers and they detonated successfully at 42° F. Corresponding charges made up with use of a gelling solution containing no ammonium perchlorate 25 failed to detonate at 42° F.

This example illustrates the combination of gelling, lubrication and temperature stabilization of sensitivity in the same process step, employing aqueous slurry explosive maintained above ambient temperature.

The improvement of extrudability of aqueous slurry explosives stabilized with gelled hydroxylated polymers is readily accomplished by addition of from 0.001 percent to 0.02 percent by weight of water-soluble noncrosslinked polyacrylamide. Preferably this is accomplished by injecting into a stream of aqueous slurry explosive stabilized with a polysaccharide gum from 0.5 percent to 3.0 percent of an aqueous solution containing at least 1.0 percent borax and from 0.2 percent to 0.6 percent noncrosslinked polyacrylamide.

We claim:

1. Forming in place a stable, gelled suspension explosive composition by pumping into a hole an aqueous slurry comprising:

a. at least 15 weight percent water,

- b. at least 40 weight percent ammonium nitrate,
- c. at least 0.5 weight percent finely divided solid fuel, and
- d. a stabilizing amount of a water-soluble hydroxylated polymer thickening agent and injecting into the exit stream from the pump in aqueous solution a combination of sufficient gelling agent to produce an immediate gelling of the hydroxylated polymer and sufficient noncrosslinked polyacrylamide to reduce the resistance of the gelled composition to extrusion through a tubular conduit.

2. The step of injecting an aqueous solution of borax and noncrosslinked polyacrylamide into a stream of aqueous ammonium nitrate slurry explosive stabilized with a water-soluble hydroxylated polymer thickening agent.

3. The step of injecting into a stream of aqueous slurry explosive stabilized with a polysaccharide gum from 0.5 percent to 3.0 percent of an aqueous solution containing at least 1.0 percent borax and from 0.2 percent to 0.6 percent noncross-linked polyacrylamide.

30 4. The step of injecting into a stream of aqueous slurry explosive stabilized with a polysaccharide gum and maintained above ambient temperature, from 0.5 percent to 3.0 percent of an aqueous solution containing at least 10 percent ammonium perchlorate, at least 1.0 percent borax and from 0.2 per-

35 cent to 0.6 percent noncrosslinked polyacrylamide.

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