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SAFE AQUEOUS SLURRIES OF PARTICULATE NITRATED EXPLOSIVES AND POLYACRYLAMIDES

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ABSTRACT OF THE DISCLOSURE

Aqueous dispersions of nitrostarch are provided in which the nitrostarch is prevented from settling out by a sufficient proportion of a water-soluble or water-dispersible polyacrylamide. The polyacrylamides employed in accordance with the invention have the remarkable and unusual property of maintaining a uniform suspension of the nitrostarch in water in the absence of any other ingredients.

This invention relates to aqueous slurries of particulate nitrated explosives, and particularly nitrostarch, that are safe to handle because of the presence of a sufficient amount of polyacrylamide to prevent the nitrostarch from settling out, and a process of preparing the same.

Slurried explosives based on an inorganic oxidizer such as ammonium nitrate and/or sodium nitrate, together with a fuel and an explosive sensitizer, are the subject of many recent patents, among them U.S. Patents Nos. 2,930,685 to Cook and Farnam, patened Mar. 29, 1960; 3,083,127 to Griffith and Wells, patented Mar. 26, 1963; 3,216,872 to F. B. Wells, patented Nov. 9, 1965; 3,147,163 to Griffith and Wells, patented Sept. 1, 1964; and 3,121,036 to Cook et al., patened Feb. 11, 1964. Such slurries have gained wide acceptance, because they are inexpensive and are readily loaded in bore holes. However, they present the problem that they contain substantial quantities of water as a result of which they are heavy, and costly to ship long distances. Accordingly, it has been proposed in World Mining, October 1965, pages 33 to 37, and 91, that aqueous explosive slurries be prepared at the blasting site by mixing and delivering the components of the explosive slurries there, slurrying them, and pumping the slurry directly into the bore holes from the mixing equipment. A truck or other mobile device is simply adapted to carry the mixing equipment normally used in the explosive plant for combining the ingredients of the explosive slurry. This system is the subject of U.S. application Ser. No. 315,908, filed Oct. 14, 1963, now abandoned to Robert B. Clay, Douglas H. Pack, L. L. Udy, and M. A. Cook, referred to in South Africa Patent No. 64/4735, filed Oct 5, 1964, and in French Patent No. 1,414,996, délivré Sept. 13, 1965.

The formulation of explosive slurries at the blasting site resolves the difficulty of transporting heavy slurries long distances, but it is complicated by the necessity of having to handle and mix dangerous explosive materials directly at the blasting site. This means that these must be brought to the blasting site in a safe form, and kept in that form until mixed in the explosive slurry, and that they must be safe to mix in that form, in preparing the slurry.

The transport of ammonium nitrate, fuel oil, and like ingredients represents no problem. However, the transport of explosive sensitizer, such as trinitrotoluene, nitrostarch, pentaerythritol tetranitrate, and similarly easily detonable materials, represents a special difficulty. In many

cases, these are not readily transportable in a dry condition. Nitrostarch, for example, is relatively sensitive to shock when dry. Even a damp nitrostarch which is insensitized by the water is not very safe to handle, particularly when it is remembered that it can dry out during storage, and that it must be blended in the slurry at the blasting site, using rather conventional mixing equipment, with no special provision possible for safety in handling.

In the presence of other slurry ingredients, such as in the compositions of Patent No. 3,083,127, nitrostarch presents no handling problem. Such slurries can also be thickened with conventional thickening agents, as disclosed in the patent, to form a thick mixture, in which the nitrostarch is prevented from settling out. However, nitrostarch cannot be shipped alone in this way, because it is impossible to maintain the suspension uniform during shipping. It separates out, forming a bottom concentrated stratum of nitrostarch.

For some reason which is not understood, conventional thickeners for aqueous explosive slurries do not maintain nitrostarch dispersed in a uniform suspension in the presence of water, absent the other explosive ingredients of the explosive slurry. Guar gum, hydrolyzed starch, carboxymethyl cellulose, psyllium seed mucilage, and like thickening agents mentioned in Patent No. 3,083,127, are not effective.

In accordance with the instant invention, aqueous dispersions of nitrostarch are provided in which the nitrostarch is prevented from settling out by a sufficient proportion of a water-soluble or water-dispersible polyacrylamide. The polyacrylamides employed in accordance with the invention have the remarkable and unusual property of maintaining a uniform suspension of the nitrostarch in water in the absence of any other ingredients. Such slurries can be made thick or thin in consistency, as desired, and can be safely shipped and safely blended with other explosive ingredients at the blasting site. They are thus particularly useful in the preparation on-site of explosive slurries.

It is important that the slurries in accordance with the invention be in a fluid flowable condition, so that they can be blended with other explosive ingredients in conventional mixing equipment. Slurries of a thickened thixotropic consistency can be employed, since such slurries become fluid under pressure, and can be readily broken down and dispersed in conventional mixing equipment. However, gelled aqueous slurries of nitrostarch are not contemplated by the invention. Such stable gels are formed by incorporation of a cross-linking agent for the polyacrylamide, which results in setting of the dispersion to form a stable solid gel. Such gels cannot be broken down in conventional mixing equipment, and thus in effect render the nitrostarch unavailable for mixing in explosive slurries. Gelled exploseive slurries of this type are described in U.S. Patent No. 3,097,120, patented July 9, 1963, to Hoffman and Bowkley.

The reason for the effectiveness of the polyacrylamides in this connection, whereas other thickening agents are not effective, is not understood. However, the effectiveness may be related in some way to the chemical structure of the nitrostarch, because the polyacrylamides have now been found to display a similar effectiveness with other particulate solid nitrated explosives, among them, trinitrotoluene, pentaerythritol tetranitrate, nitrocellulose, dinitrotoluene, pentolite (an equal parts by weight mixture of pentaerythritol tetranitrate and trinitrotoluene), Cyclonite (RDX, cyclotrimethylene trinitramine), Composition B (a mixture of up to 70% RDX, up to 40% TNT, and 1 to 4% wax), Cyclotol (Composition B without the wax), tetryl, and sorbitol hexanitrate. Accordingly, the invention contemplates slurries in water of any particulate nitrated explosive material, as a class, alone or in

admixture, with a sufficient amount of a polyacrylamide to prevent the explosive suspended in the water from settling out, but essentially no other ingredients.

The polyacrylamides that are employed in accordance with the invention are hydrophilic in character, due to the presence of free carboxylic acid groups, which can, if desired, be neutralized by alkali metal, alkaline earth metal, or ammonium bases, in whole or in part. Such free acid groups are introduced into the polymer by hydrolysis of the amide group from a proportion of the acrylamide units. These polyacrylamides consequently can be characterized as partially hydrolyzed polyacrylamides. There should in general be at least 0.1% and in many cases as much as 10% to 50%, of the acrylamide units hydrolyzed to such acid groups, in free acid or salt form. The greater the proportion of free acid groups, the more hydrophilic the polyacrylamide, and therefore the more readily dispersible in water. However, polyacrylic acids are not effective in accordance with the invention. Apparently, a balanced combination of free acid groups and acid amide groups is required for effectiveness; for optimum effectiveness, at least 50% of the acrylamide units should be in the form of acid amide groups, and a maximum of 50% free acid groups.

The molecular weight of the polyacrylamides is in no way critical, so far as is presently known, except that as the molecular weight increases, the polyacrylamide becomes less dispersible in water. However, polyacrylamide becomes less dispersible in water. However, polyacrylamides having a molecular weight as high as 25,000,000 are still effective. Preferred polyacrylamides have a molecular weight within the range from about 1,000,000 to about 8,000,000.

These partially hydrolyzed polyacrylamides are known compounds. They are described in U.S. Patents Nos. 3,341,383 to Bergwerk, issued Sept. 12, 1967, and 3,355,336 to Lyerly, issued Nov. 28, 1967. Any of the partially hydrolyzed polyacrylamides of these patents can be employed in the instant invention.

Many polyacrylamides useful in the slurries of the invention are available commercially. A preferred material is Polyhall 295. This polyacrylamide has the following properties:

Molecular weight	3,000,000 to 8,000,000.
Acid groups	15 to 30%.
Viscosity in 1% aqueous solution	3000 to 7000 cps. Brookfield at 20 r.p.m. at 20° C.
Ash content	8 to 11%, free from polyvalent metal cations.

Very small amounts of the hydrophilic polyacrylamides are effective. The amount used, of course, depends to some extent upon the amount and nature of the particulate nitrated explosive that is to be dispersed in the slurry. An amount of polyacrylamide of as little as 0.05% is effective to produce a stable, nonsettling dispersion, containing as much as 60% nitrostarch, and 40% water. This composition is stable against settling, even when undergoing the bumping and jolting normally encountered in transportation by truck or rail. Larger amounts of the polyacrylamide produce dispersions of even greater stability, containing higher proportions of the nitrated explosive. The upper limit of the polyacrylamide concentration is in no way critical, and will be established by economic considerations and the limit of the amount of polyacrylamide that the slurry will tolerate without settling out. This limit is not usually reached even when the amount of polyacrylamide is as much as 10%, but this limit depends to some extent upon the hydrophilicity of the polyacrylamide.

For the purpose of formulation blasting slurries on-site, it is of course desirable to have as concentrated a nitrated explosive slurry as possible. In this way, the amount of water that is shipped with the explosive is kept to a minimum, thus reducing transportation costs, and at the same time the formation of concentrated slurries at the blasting site is facilitated. For this reason, usually the slurries prepared in accordance with the invention will contain the minimum proportion of water required for safety in handling, and the formation of a uniform dispersion.

Solid particulate nitrated explosives, particularly in finely-divided form, are capable of absorbing unusually large amounts of water. Nitrostarch, for example, can absorb approximately 25% water. The amount of water that is employed in the slurries of the invention is in all cases enough in addition to the amount absorbed in the nitrated explosive to form a slurry. As little as 9% water in excess of that which is absorbed by the explosive is usually sufficient. However, larger amounts can be used. Slurries of acceptable consistency are obtained when the amount of water in excess of that absorbed by the explosive ingredients is within the range from about 10 to about 50%.

The effect of the polyacrylamide in general is to thicken the slurry, more or less, but still leave it readily flowable. Occasionally, a thixotropic slurry is obtained. The slurries of the invention are in no way describable as gels, or even as gel-like.

The nitrated explosives are employed in finely-divided particle form. Nitrostarch is available in the form of a very fine powder. Trinitrotoluene is available in a wide range of particle sizes, and all of these are readily suspended in water in the slurries of the invention. Pentaerythritol tetranitrate is also available in various particle sizes.

In general, it can be said that the smaller the particle size, the more readily the explosive can be made in the form of a stable suspension. A larger particle size will usually require a larger proportion of polyacrylamide, in order to prevent settling.

The compositions of the invention are usually prepared by simple blending of the nitrated explosive, water and polyacrylamide. These can be added in any order. It is usually preferred, however, to disperse the polyacrylamide in the water, and then add the nitrated explosive. The components can be combined at room temperature, but in some cases, an elevated temperature will facilitate mixing and dispersion.

The following examples illustrate preferred embodiments of the invention.

EXAMPLE 1

A slurry was prepared from dry mill nitrostarch and polyacrylamide, having the following composition:

	Percent
Nitrostarch, dry	65
Water	34.9
Polyacrylamide (Polyhall 295)	0.1

A similar composition was prepared composed of 65% of the nitrostarch, and 35% water.

The compositions were each thoroughly mixed, and then placed in five gallon drums and allowed to stand overnight. The composition without the polyacrylamide separated, and the nitrostarch formed a layer below the water. The composition containing the polyacrylamide was perfectly stable, and no settling out of nitrostarch was evident.

The polyacrylamide dispersion was stored for two months. At intervals during the storage period, the slurry was examined. However, no evidence of settling was observed at any time. During this period, the composition was subjected to temperatures ranging from 20° F. to 65° F.

At the completion of the storage period, the slurry was removed from the drum, and blended with ammonium nitrate, sodium nitrate, zinc oxide, bagasse, corn starch, Hydroseal 3B, and water, to form a composition in accordance with Example 2 of Patent No. 3,083,127. This

composition was poured into a bore hole and shot, with good detonation and rock breakage, showing that the polyacrylamide had no effect on the explosive properties of the nitrostarch in the blasting slurry.

EXAMPLE 2

A slurry was prepared from dry mill nitrostarch and polyacrylamide, having the following composition:

	Percent
Nitrostarch, dry	57
Water	42.8
Polyacrylamide (Polyhall 295)	0.2

A similar composition was prepared composed of 57% of the nitrostarch, and 43% water.

The compositions were each thoroughly mixed, and then placed in five gallon drums and allowed to stand overnight. The composition without the polyacrylamide separated, and the nitrostarch formed a layer below the water. The composition containing polyacrylamide was perfectly stable, and no settling out of nitrostarch was evident.

The polyacrylamide dispersion was stored for two months. At intervals during the storage period, the slurry was examined. However, no evidence of settling was observed at any time. During this period, the composition was subjected to temperatures ranging from 40° F. to 70° F.

At the completion of the storage period, the slurry was removed from the drum, and blended with ammonium nitrate, flake aluminum, and water, to form a composition in accordance with Example 1 of Patent No. 3,083,127. This composition was poured into a bore hole and shot, with good detonation and rock breakage, showing that the polyacrylamide had no effect on the explosive properties of the nitrostarch in the blasting slurry.

EXAMPLE 3

A slurry was prepared from dry mill nitrostarch and polyacrylamide, having the following composition:

	Percent
Nitrostarch, dry	45
Water	54.5
Polyacrylamide (Polyhall 295)	0.5

A similar composition was prepared composed of 45% of the nitrostarch, and 55% water.

The compositions were each thorouhgly mixed, and then placed in five gallon drums and allowed to stand overnight. The composition without the polyacrylamide separated, and the nitrostarch formed a layer below the water. The composition containing polyacrylamide was perfectly stable, and no settling out of nitrostarch was evident.

The polyacrylamide dispersion was stored for two months. At intervals during the storage period, the slurry was examined. However, no evidence of settling was observed at any time. During this period, the composition was subjected to temperatures ranging from 40° F. to 70° F.

At the completion of the storage period the slurry was removed from the drum, and blended with ammonium nitrate, sodium nitrate, zinc oxide, bagasse, corn starch, Hydroseal 3B, oil No. 5, and water, to form a composition in accordance with Example 3 of Patent No. 3,083,127. This composition was poured into a bore hole and shot, with good detonation and rock breakage, showing that the polyacrylamide had no effect on the explosive properties of the nitrostarch in the blasting slurry.

EXAMPLE 4

A slurry was prepared from dry mill nitrostarch and polyacrylamide, having the following composition:

	Percent
Nitrostarch, dry	60
Water	39.8
Polyacrylamide (Polyhall 295)	0.2

A similar composition was prepared composed of 60% nitrostarch, and 40% water.

The compositions were each thoroughly mixed, and then placed in five gallon drums and allowed to stand overnight. The composition without the polyacrylamide separated, and the nitrostarch formed a layer below the water. The composition containing polyacrylamide was perfectly stable, and no settling out of nitrostarch was evident.

The polyacrylamide dispersion was stored for two months. At intervals during the storage period, the slurry was examined. However, no evidence of settling was observed at any time. During this period, the composition was subjected to temperatures ranging from 50° to 80° F.

At the completion of the storage period, the slurry was removed from the drum, and blended with ammonium nitrate, flake aluminum, and water, to form a composition in accordance with Example 1 of Patent No. 3,083,127. This composition was poured into a bore hole and shot, with good detonation and rock breakage, showing that the polyacrylamide had no effect on the explosive properties of the nitrostarch in the blasting slurry.

EXAMPLE 5

A slurry was prepared from dry mill nitrostarch and polyacrylamide, having the following composition:

	Percent
Nitrostarch, dry	55
Water	44.75
Polyacrylamide (Polyhall 295)	0.25

A similar composition was prepared composed of 55% nitrostarch, and 45% water.

The compositions were each thoroughly mixed, and then placed in five gallon drums and allowed to stand overnight. The composition without the polyacrylamide separated, the nitrostarch forming a layer below the water. The composition containing polyacrylamide was perfectly stable, and no settling out of nitrostarch was evident.

The polyacrylamide dispersion was stored for two months. At intervals during the storage period, the slurry was examined. However, no evidence of settling was observed at any time. During this period, the composition was subjected to temperatures ranging from 60 to 90° F.

At the completion of the storage period, the slurry was removed from the drum, and blended with ammonium nitrate, sodium nitrate, zinc oxide, bagasse, corn starch, Hydroseal 3B, and water, to form a composition in accordance with Example 2 of Patent No. 3,083,127. This composition was poured into a bore hole and shot, with good detonation and rock breakage, showing that the polyacrylamide had no effect on the explosive properties of the nitrostarch in the blasting slurry.

EXAMPLE 6

A slurry was prepared from pentaerythritol tetranitrate and polyacrylamide, having the following composition:

	Percent
Pentaerythritol tetranitrate	70
Water	29.8
Polyacrylamide (Polyhall 295)	0.2

A similar composition was prepared composed of 70% of the pentaerythritol tetranitrate and 30% water.

The compositions were each thoroughly mixed, and then placed in five gallon drums and allowed to stand overnight. The composition without the polyacrylamide separated, and the pentaerythritol tetranitrate formed a layer below the water. The composition containing polyacrylamide was perfectly stable, and no settling out of pentaerythritol tetranitrate was evident.

The polyacrylamide dispersion was stored for two months. At intervals during the storage period, the slurry was examined. However, no evidence of settling was observed at any time. During this period, the composition

was subjected to temperatures ranging from 60° F. to 80° F.

At the completion of the storage period, the slurry was removed from the drum, and blended with ammonium nitrate, sodium nitrate, flake aluminum, sodium carboxymethyl cellulose, wood flour, guar gum, zinc oxide, and water, to form a thixotropic composition in accordance with Example 4 of Patent No. 3,238,074. This composition was pumped into a bore hole and shot, with good detonation and rock breakage, showing that the polyacrylamide had no effect on the explosive properties of the pentaerythritol tetranitrate in the blasting slurry.

EXAMPLE 7

A slurry was prepared from trinitrotoluene (35 mesh) and polyacrylamide, having the following composition:

	Percent
Trinitrotoluene	60
Water	39.8
Polyacrylamide (Polyhall 295)	0.2

A similar composition was prepared composed of 60% trinitrotoluene and 40% water.

The compositions were each thoroughly mixed, and then placed in five gallon drums and allowed to stand overnight. The composition without the polyacrylamide separated, and the trinitrotoluene formed a layer below the water. The composition containing polyacrylamide was perfectly stable, and no settling out of trinitrotoluene was evident.

The polyacrylamide dispersion was stored for two months. At intervals during the storage period, the slurry was examined. However, no evidence of settling was observed at any time. During this period, the composition was subjected to temperatures ranging from 50° F. to 80° F.

At the completion of the storage period, the slurry was removed from the drum, and blended with ammonium nitrate, sodium nitrate, bagasse, zinc oxide, cornstarch, Hydroseal 3B, and water, to form a composition in accordance with Example 1 of Patent No. 3,216,872. This composition was poured into a bore hole and shot, with good detonation and rock breakage, showing that the polyacrylamide had no effect on the explosive properties of the trinitrotoluene in the blasting slurry.

EXAMPLE 8

A slurry was prepared from pentolite (granular) and polyacrylamide, having the following composition:

	Percent
Pentolite, granular	55
Water	44.75
Polyacrylamide (Polyhall 295)	0.25

A similar composition was prepared composed of 55% pentolite, and 45% water.

The compositions were each thoroughly mixed, and then placed in five gallon drums and allowed to stand overnight. The composition without the polyacrylamide separated, the pentolite forming a layer below the water. The composition containing polyacrylamide was prefectly stable, and no settling out of pentolite was evident.

The polyacrylamide dispersion was stored for two months. At intervals during the storage period, the slurry was examined. However, no evidence of settling was observed at any time. During this period, the composition was subjected to temperatures ranging from 50° F. to 75° F.

At the completion of the storage period, the slurry was removed from the drum, and blended with ammonium nitrate, sodium nitrate, zinc oxide, silica, flake aluminum, water and 100 SSU paraffin oil, to form a composition in accordance with Example 2 of Patent No. 3,147,163, substituting the pentolite for the pentaerythritol tetranitrate. This composition was poured into a bore hole and shot, with good detonation and rock breakage, showing that the polyacrylamide had no effect on the explosive properties of the pentolite in the blasting slurry.

Having regard to the foregoing disclosure, the following is claimed as the inventive and patentable embodiments thereof:

1. An aqueous slurry consisting essentially of water, an organic particulate nitrated explosive in uniform dispersion, and a sufficient amount of a hydrophilic polyacrylamide containing at least 0.1% free acid groups, and at least 50% acid amide groups, to prevent the particulate nitrated explosive from settling out.

2. An aqueous slurry in accordance with claim 1, in which the organic nitrated explosive is nitrostarch.

3. An aqueous slurry in accordance with claim 1, in which the organic nitrated explosive is trinitrotoluene.

4. An aqueous slurry in accordance with claim 1, in which the organic nitrated explosive is pentaerythritol tetranitrate.

5. An aqueous slurry in accordance with claim 1, in which the organic nitrated explosive is a mixture of pentaerythritol tetranitrate and trinitrotoluene.

6. An aqueous slurry in accordance with claim 1, in which the amount of polyacrylamide is within the range from about 0.05% to about 10%.

7. An aqueous slurry in accordance with claim 1, in which the polyacrylamide has a molecular weight within the range from about 1,000,000 to about 25,000,000.

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