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(54) Title: EXPLOSIVE COMPOSITION

(57) Abstract: An aqueous explosive composition, particularly a water gel explosive composition which contains chemically generated gas bubbles, contains an amount of a protein, preferably an undenatured vegetable protein, to stabilize the gas bubbles against migration and agglomeration.

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"EXPLOSIVE COMPOSITION"

This invention relates to aqueous explosive compositions containing chemically generated gas bubbles which include an amount of a protein to stabilize the gas bubbles against migration and agglomeration.



In many aqueous explosive compositions it is necessary to provide a means of voiding in order to make the explosive sufficiently sensitive to detonation by means of conventional primers or boosters. Over the years many systems have been used to provide the necessary degree of voiding in the final product. Techniques have varied from chemical gassing or mechanical air entrainment to the addition of void containing particles to the mixture. Examples of the latter are Perlite and glass or plastic microballoons. Where chemical gassing and mechanical air entrainment are used, the coalescence of the very small bubbles into larger ones has a marked desensitizing effect, and where this method has been used in the past, a technique has been either partially or completely to solidify the mass shortly after gassing to ensure minimum migration and agglomeration of the gas bubbles. One area of particular interest is in water gel explosives where it is desirable to provide a means of stabilising void spaces against migration and agglomeration.

The following patents indicate the importance of including small gas bubbles in explosive compositions.

United States Patent No 3,400,026 to E I du Pont De Nemours & Company discloses a water bearing explosive composition containing an inorganic oxidising salt, a fuel, a thickener and water and a proteinaceous material which is soluble in the aqueous explosive composition of pH 3 to 10 and, preferably, foamable therein. The explosive composition containing this proteinaceous material is rendered soft and pliable and consistently sensitive to detonation by means of a primer at low temperatures. It is preferable that the proteinaceous material is also foamable so that the result is the incorporation of small gas bubbles in the gel structure when the mixture is sufficiently agitated thus providing further sensitivity to the explosive composition. It is stated that the proteinaceous material is any protein or protein derivative such as those obtained by hydrolysis,



amidation, acylation or other chemical reaction applied to a protein. Representative proteinaceous materials that can be used in the explosive composition include proteins, conjugated proteins and protein derivatives, i.e. derived proteins, namely products formed by the action of heat or other physical forces or by hydrolytic agents such as denatured proteins or peptides. The preferred proteins are albumins such as ovalbumin and lactalbumin, globulins such as ovoglobulin and lactoglobulin, conjugated proteins, such as the glycoprotein mucin, protein derivatives such as partially hydrolized milk protein and extracted collagen derivatives.

United States Patent No 3,678,140 to E I Du Pont De Nemours & Company teaches passing a thickened protein-containing water-bearing blasting agent through a plurality of orifices at a pressure from about 40 to 160 psi to create a vacuum in the area where the blasting agent exits from the orifice, incorporating air or other gas in the blasting agent and, thereafter, reducing the velocity of the blasting agent to provide a foamed product. The proteinaceous material contained in the explosive is any protein or protein derivative as disclosed in US Patent No 3,400,026. The amount of proteinaceous material in the blasting agent to be formed can be varied within a wide range, generally it contains about 0.01% to 10% by weight proteinaceous material.

United States Patent No 3,582,411 to Ireco Chemicals discloses the use of a foam promoting agent, in an explosive blasting slurry, which is effective substantially to entrap and retain fine gas bubbles produced by the intimate blending of a liquid solution with a gas. The foam promoting agent contained in the explosive may comprise a small amount of gel forming thickener, a salt water foamer or a foam promoting gum such as a guar gum to which hydroxyl groups have been added by some treatment.

United States Patent No 3,886,010 to Ireco Chemicals discloses a blasting composition of the aqueous gel or slurry type employing a decomposable nitrite gassing agent and containing an oxidizer salt, fuel, water and a



thickener as well as thiourea which is used to accelerate the decomposition of the nitrite gassing agent while concomitantly stabilizing the thickening effectiveness of the galactomannan thickener.

It is desirable for a water gel explosive to contain evenly distributed gas bubbles of an average size (diameter) in the range 10 - 40 microns, and to have bubbles of relatively uniform size. It has been found that mechanical air entrainment does not result in the desired fine bubble structure required to yield optimum sensitivity. However the optimum size of the bubbles and the desired distribution can be attained by selecting the appropriate pH and catalyst content, thereby controlling the rate of the chemical gassing reaction. Once generated the optimally sized bubbles have to be stabilised against migration or agglomeration. It is often necessary that the gas bubbles be sufficiently stabilised, such that neither prolonged agitation of the explosive mixture, nor prolonged standing prior to crosslinking, results in the loss of the optimal bubble dispersion.

The precise aggregate of bubbles required varies with each explosive formulation and the required function and application of the explosive. The total bubble content is inversely proportional to the density of a particular formulation. A greater requirement for sensitivity to detonation can usually be satisfied by the formulation having a lower density. However, without proper stabilisation, the lower density (i.e. greater quantity of gas bubbles) usually encourages the undesired agglomeration of the bubbles as a result of their proximity to one another, thereby reducing the sensitivity. Thus for optimum sensitivity efficient stabilisation is necessary.

It should be noted that the use of monomethylammonium nitrate (MMAN) increases the tendency of the migration and agglomeration of the gas bubbles. The use of proteinaceous material in explosive compositions including MMAN without the use of a gassing agent, allows the incorporation of very fine gas bubbles, however the use of a standard

turbine mixer does not allow sufficient gas incorporation for cap sensitivity, unconfined in small diameters and at low temperatures. Alternatively, the use of a nitrite gassing agent in the absence of proteinaceous material yields sufficient gas incorporation and may even attain the correct density, but it does not prevent the agglomeration and migration of said bubbles and the required sensitivity is not achieved; the density also increases with time unless the composition is immediately cross-linked, thereby also losing sensitivity with time. The use of a modified guar gum with hydroxyl groups, either with or without the use of a nitrite gassing agent, allows sufficient gas incorporation to attain the desired density, but again does not sufficiently prevent the agglomeration and migration of said bubbles, with time, to achieve cap sensitivity under the desired conditions.

Thus, the prior art has taught that in an aqueous explosive composition, a foam promoting agent or a proteinaceous material may be incorporated to entrap and retain gas bubbles produced by agitation or blending of the explosive composition or a solution thereof. The prior art has also taught the use of a nitrite gassing agent and a thiourea for the aeration of a blasting slurry. It is an object of the present invention to provide an aqueous explosive composition which contains a chemical gassing agent as well as an amount of a protein to stabilize the gas bubbles formed by the chemical gassing agent, against migration and agglomeration.

According to a first aspect of the invention there is provided the use, in an aqueous explosive composition containing chemically generated gas bubbles, of an amount of a protein to stabilize the gas bubbles against migration and agglomeration.

The aqueous explosive composition may be a water gel explosive composition.



Thus according to a second aspect of the invention there is provided a water gel explosive composition which comprises one or more oxidizing salts at least partially dissolved in water, a fuel and a thickener and which contains chemically generated gas bubbles which is characterized in that it includes 0,03 to 0,5% by weight of the composition of a protein.

The protein is preferably an undenatured protein, more preferably an undenatured vegetable protein. Most preferably, the thickener is a bean gum, for example guar gum, and the protein is bean protein, for example guar protein.

Preferably, the water gel explosive composition of the invention contains 12% or more, more preferably 15% or more by weight of the composition of monomethylammonium nitrate (MMAN) and, as a chemical gassing agent, sodium nitrite and thiourea as a catalyst. It has been found that the addition of an amount of a protein to such a composition stabilizes the gas bubbles generated by the chemical gassing agent against migration and agglomeration sufficiently to render the composition sensitive to detonation by a standard detonator (strength No 6), unconfined, in diameters from 15 mm at temperatures from 0°C.

The crux of the invention is the use of a protein in an aqueous explosive composition to stabilize chemically generated gas bubbles contained in the composition against migration and agglomeration, so that the composition is sensitive to initiation using a standard detonator (strength No 6).

The aqueous explosive composition may be a water gel explosive composition consisting of one or more oxidizing salts partially or completely dissolved in water, one or more fuels and a thickener as well as other optional ingredients such as a metallic fuel, e.g. pigment flake aluminium, or a halide salt, as well as a plurality of gas bubbles.

The oxidizing salt or salts, usually comprising about 30 to 90% by weight of the total composition, can be any of the salts conventionally used in water gel explosive compositions such as alkali metal, alkaline earth metal or ammonium nitrates or perchlorates or mixtures of two or more thereof.

The fuel may be for example the nitrate or perchlorate salts of amines. Other examples are alcohols, glycols, glycerols and the like.

The thickener may be any thickener conventionally used in water gel explosive compositions such as guar gum, locust bean gum, polyacrylamide and xanthan gum.

The water gel explosive composition may also contain additional ingredients such as a metallic fuel, e.g. atomised aluminium or pigment flake aluminium, a halide salt, carbohydrates, ground rubber, coal dust and the like.

The water gel explosive composition also contains reagents designed to generate gas bubbles in situ such as sodium bicarbonate, hydrogen peroxide or preferably sodium nitrite. It may be desired to add a catalyst for the chemical gassing reaction such as urea or preferably thiourea.

The water gel explosive composition of the invention is characterised in that it also includes 0,03% to 0,5% by weight of the composition of a protein which may be any protein or protein derivative such as those obtained by hydrolysis, amidation, acylation or other chemical reaction applied to a protein. The protein which may be used in the explosive composition of the invention includes simple proteins, conjugated proteins and protein derivatives such as denatured proteins. Both animal and vegetable proteins can be used for example egg white, soya protein or guar protein.



The preferred water gel explosive composition of the invention includes guar gum as the thickener and guar protein, preferably undenatured guar protein in an amount of 0,03% or more by weight of the total composition.

Further preferably, the water gel explosive composition of the invention contains 12% or more, preferably 15% or more by weight of the composition of MMAN as well as sodium nitrite as the gassing agent and thiourea as the catalyst. The presence of the protein in this composition stabilizes the gas bubbles against migration and agglomeration sufficiently to render the composition sensitive to detonation by a standard detonator (strength No 6), unconfined, in diameters as small as 15 mm at temperatures as low as 0°C. This is in spite of the fact that the use of MMAN increases the tendency of the migration and agglomeration of the gas bubbles. With the use of both a chemical gassing agent and a protein, large quantities of very fine gas bubbles are not only entrapped in the water gel explosive composition but stabilized as such to the extent where the explosive composition retains sensitivity even if kept un-crosslinked for prolonged periods, even greater than 24 hours. No special mixing technique or equipment need be used to result in efficient sensitisation, and any mixer which will adequately combine the reagents can be used, such as a standard turbine mixer.

The water gel explosive composition may also include a crosslinking agent.

The water gel explosive composition may be made as follows:

The one or more oxidizing salts and any soluble fuel are partially or completely dissolved in water and charged into a suitable mixer. The catalyst of the chemical gassing reaction and any additional ingredients, e.g. other fuels, are added to the mixer and agitated. The thickener and the protein are added to the mixture and the mass is allowed to develop an adequate viscosity. If it is desired, optional ingredients such as pigment flake aluminium and/or a halide salt can be added to the mixture at this stage. Thereafter, there is added to the mixture a gassing agent or

a solution thereof for the generation of gas bubbles in situ, followed by the addition of a crosslinking agent.

Examples of water gel explosive compositions of the invention will now be given.



Various explosive compositions were prepared containing the components set out in the following Tables 1 and 2.

TABLE 1

Formulation No	1	2	3	4	5
Ammonium Nitrate	46.51	50.47	53.25	39.89	41.76
Sodium Nitrate	6.0	7.35	4.8	10.1	13.0
Monomethylammonium Nitrate	28.95	24.18	22.46	23.62	27.3
Atomised Aluminium	2.84	1.7	3.2	0.0	0.0
Pigment Flake Aluminium	0.0	0.7	0.7	1.5	0.0
Ground Rubber	0.0	0.91	1.0	0.8	1.4
Adipic Acid	0.2	0.1	0.1	0.2	0.2
Thiourea	0.12	0.12	0.12	0.12	0.12
Guar Gum	1.2	1.0	1.0	1.0	1.2
Guar Protein	0.06	0.06	0.06	0.06	0.06
Potassium Chloride	0.0	0.0	0.0	12.0	0.0
Sodium Chloride	0.0	0.0	0.0	0.0	3.0
Sodium Nitrite	0.06	0.03	0.03	0.05	0.08
Stearic Acid	0.00	0.04	0.04	0.04	0.00
Water	14.06	13.38	13.28	10.66	11.88
Density (gcm⁻³)	1.06	1.20	1.20	1.15	1.00
Critical Diameter	25	25	25	29	29

TABLE 2

Formulation No	6	7	8	9	10
Ammonium Nitrate	24.00	53.11	59.23	43.6	48.7
Sodium Nitrate	26.9	7.20	7.0	10.0	6.4
Monomethylammonium Nitrate	26.60	23.51	17.85	23.51	24.92
Atomised Aluminium	10.00	1.0	2.02	0.0	3.0
Pigment Flake Aluminium	0.0	0.7	0.0	1.5	1.5
Ground Rubber	0.0	1.20	2.09	1.0	0.0
Adipic Acid	0.2	0.1	0.15	0.2	0.2
Thiourea	0.13	0.13	0.13	0.13	0.13
Guar Gum	1.0	1.0	0.7	1.0	1.0
Guar Protein	0.06	0.06	0.04	0.06	0.06
Calcium Carbonate	0.36	0.36	0.36	0.36	0.36
Sodium Chloride	0.0	0.0	0.0	7.0	0.0
Sodium Nitrite	0.02	0.02	0.04	0.03	0.09
Stearic Acid	0.00	0.04	0.00	0.04	0.04
Water	10.69	11.57	10.35	11.51	13.6
Density (gcm⁻³)	1.30	1.20	1.20	1.15	0.95
Critical Diameter	50	25	80	29	15

The critical diameter is the critical diameter for detonation at 0°C with a No 6 cap in mm.

All the formulations contain 0,01% by weight of the formulation of a cross-linking agent, the active component of which is potassium pyroantimonate.

The formulations were prepared as follows:

Into a turbine mixer was placed the ammonium nitrate and the monomethylammonium nitrate, both in solution form. Thiourea and stearic acid, where present, were added and the whole mass was agitated with cooling. At a suitable temperature the guar gum, the guar protein and the adipic acid premixed with the sodium nitrate or with solid ammonium nitrate were added. After allowing the guar sufficient time to thicken, the pigment aluminium and the sodium nitrite were added, followed by the ground rubber and the atomised aluminium. Sodium chloride (where it was used) was then added.

The calcium carbonate, where present, was added followed by the crosslinking agent (potassium pyroantimonate). After these were thoroughly mixed, the product was packed into plastic tubing.

The formulations Nos 1 to 10 set out above all contain guar protein as the protein material. Various explosive compositions were also prepared containing other types of protein and the components of these compositions are set out in the following Tables 3 and 4.

TABLE 3

Formulation No	11	12
Ammonium Nitrate	46.51	46.51
Sodium Nitrate	6.0	6.0
Monomethylammonium Nitrate	28.95	28.95
Atomised Aluminium	2.84	2.84
Pigment Flake Aluminium	0.0	0.0
Ground Rubber	0.0	0.0
Adipic Acid	0.2	0.2
Thiourea	0.12	0.12
Guar Gum	1.2	1.2
Egg White Protein	0.2	0.2
Potassium Chloride	0.0	0.0
Sodium Chloride	0.0	0.0
Sodium Nitrite	0.06	0.06
Water	14.06	14.06
Density (gcm⁻³)	1.04	1.04
Critical Diameter	32	32

TABLE 4

Formulation No	13	14
Ammonium Nitrate	48.5	39.0
Sodium Nitrate	5.5	10.0
Monomethylammonium Nitrate	28.63	34.8
Atomised Aluminium	1.8	0.0
Pigment Flake Aluminium	0.0	0.0
Ground Rubber	0.0	0.0
Adipic Acid	0.2	0.3
Thiourea	0.12	0.12
Guar Gum	1.2	0.4
Egg White Protein	0.2	0.25
Polyacrylamide	0.0	0.6
Calcium Carbonate	0.0	0.0
Sodium Nitrite	0.06	0.03
Water	13.79	14.50
Density (gcm⁻³)	1.04	1.15
Critical Diameter	25	32

Formulations 11, 13 and 14 contained powdered egg white protein or albumin while formulation 12 contained fresh egg white protein.

All the formulations contain 0,01% by weight of the formulation of a cross-linking agent, the active component of which is potassium pyroantimonate.

The formulations were prepared as described above.

It is important to note that all the formulations 1 to 14 could be left for more than twenty four hours in an un-crosslinked state without any apparent gas bubble migration at all. This was demonstrated by the fact that the formulations retained the required density and sensitivity.

Claims:**1.**

An aqueous explosive composition containing chemically generated gas bubbles is characterized in that it contains an amount of an undenatured protein to stabilize the gas bubbles against migration and agglomeration.

2.

A water gel explosive composition which comprises one or more oxidising salts at least partially dissolved in water, a fuel and a thickener and which contains chemically generated gas bubbles includes 0,03 to 0,5% by weight of the composition of an undenatured protein to stabilize the gas bubbles against migration and agglomeration.

3.

A composition according to either of claims 1 or 2 wherein the undenatured protein is an undenatured vegetable protein.

4.

A composition according to claim 2 wherein the thickener is a bean gum and the protein is a bean protein.

5.

A composition according to claim 4 wherein the bean gum is guar gum and the bean protein is guar protein.

6.

A composition according to claim 5 wherein the guar protein is undenatured guar protein.

7.

A water gel explosive composition comprising one or more oxidizing salts at least partially dissolved in water, 12% or more by weight of the composition of monomethylammonium nitrate, optionally another fuel, a thickener, sodium nitrite as a chemical gassing agent to generate gas bubbles, and thiourea as a catalyst for the sodium nitrite includes 0,03 to 0,5% by weight of the composition of an undenatured protein.

8.

A composition according to claim 7 which contains 15% or more by weight of the composition of monomethylammonium nitrate.

9.

A composition according to claim 7 wherein the undenatured protein is an undenatured vegetable protein.

10.

A composition according to claim 9 wherein the thickener is a bean gum and the protein is a bean protein.

11.

A composition according to claim 10 wherein the bean gum is guar gum and the bean protein is guar protein.