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WATER-RESISTANT EXPLOSIVE COMPOSITIONS

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This invention relates to explosive compositions, and more particularly to improved ammonium nitrate blasting compositions resistant to the action of water and moisture, which comprises ammonium nitrate, a sensitizer, and solid fuels such as cellulosic or other carbonaceous materials.

Among the various types of blasting explosive compositions in use today are those comprising ammonium nitrate admixed in various proportions with sodium nitrate, various combustibles and a liquid explosive such as nitroglycerine, drip oil (dinitro-toluenes), and the like. For certain uses, these compositions containing ammonium nitrate are preferred over other blasting compositions. However, during storage and use, these compositions show certain disadvantages in that they deteriorate upon contact with moisture and water. In the handling and use of these compositions, often necessarily under adverse conditions, it is difficult to avoid contact with moisture or water. In contact with water, these explosive materials often absorb sufficient water either to show poor strength characteristics or to become progressively inert to detonation. This causes additional hazards and expense in blasting operations and this disadvantage becomes especially serious when the blasting composition is used in the wet bore holes often encountered in actual field conditions.

In the past many attempts have been made to improve the water resistance and overcome the disadvantages of ammonium nitrate containing explosive compositions. Most simply, the cartridges generally used as containers have been dipped in a paraffin wax or the like to seal them against water and moisture, but this has been only partly successful. Attempts have also been made to achieve water resistance by admixture of various water-repellent materials with the composition or by coating the particles with water-repellent substances or metallic soaps, resins and the like, but these have likewise been only partly successful. Incorporation of materials which swell when in contact with water is also a method used in these attempts. The increase in volume which results when such a material is in contact with water partly tends to seal up the crack or fissure through which the water has entered and prevents further entry of water. However, this, at best, affords a temporary seal against further deterioration by water, since the materials used in the past formed temporary gels which dispersed on further contact with water, thereby losing all the protection sought.

We have now found that ammonium nitrate blasting compositions can be made which show a surprisingly high degree of water resistance over greatly increased periods of time. These compositions contain an organic material which, in its polymerized form, upon contact with water, becomes a non-peptizable hydrophilic network resistant

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to further action of water. These networks are formed by cross-linking linear polymeric chains. The linear chains are formed from water-soluble ethylenic unsaturated monomers and not more than 50% of a water-insoluble ethylenic monomer, not less than 0.5 mol percent of the monomeric units of the copolymer chain being joined by cross-linkings. By the use of such non-peptizable, three-dimensional molecular networks in blasting compositions, we have achieved a great deal more life under extremely adverse conditions of exposure to water than has heretofore been possible. The property of being non-peptizable is the important necessary characteristic, for without this resistance to dispersion on exposure to much more water, the increased protection which is the essence of our invention will not be achieved. If peptization occurs, as in prior compositions, the initial protection is dispersed and the blasting composition rapidly deteriorates.

The high degree of water resistance is maintained even on prolonged periods of contact with water so that an extreme degree of permanence of water resistance is achieved. This high degree of permanence of water resistance is a most surprising feature of this invention. We believe that the high degree of permanence is due to the three-dimensional, non-peptizable hydrophilic network structure, but we do not wish to be limited to any theory thereon. Heretofore, water swelling agents, including various resins and gums, have given some degree of protection, but the protection is definitely limited since continued exposure to water results in peptization and deterioration of the swelling agent.

The water-resistant ammonia dynamite compositions of our invention are produced by admixing the hydrophilic network forming organic materials with known ammonium nitrate blasting compositions. The known ammonium nitrate blasting compositions may be varied to achieve properties appropriate for the various uses for which they are intended as practiced by those skilled in the art.

The water resistance of the blasting compositions of our invention is believed to be due to the swelling action which results when the material comes in contact with water. The exact structure of the water-resistant non-peptizable hydrophilic network is not known, but it is believed to result from the combined polymerization and cross-linking effect of the polymeric materials used, resulting in a three-dimensional network. The fact that it is three-dimensional is important since it is believed that it is due to this fact that the gels formed with water are non-peptizable.

The three-dimensional network may be achieved in a number of ways:

(1) It is possible to use monomers which are incorporated into the dynamite formulation along with polymerizing or complexing agents. These form on contact with water the non-peptizable hydrophilic network in the form of a three-dimensional hydrophilic network.

(2) A linear polymer, retaining functional groups presumably periodically placed, may be used for incorporation into the dynamite formulation, with or without a metal complexing agent. On contact with water, the linear polymer is cross-linked either by the metal complexing agent or, in the other type, by reaction of functional groups with one another to form this three-dimensional hydrophilic network.

(3) A copolymer, cross-linked by any means, is dried

and added in powdered form to the dynamite formulation. On contact with water, the hydrophilic network material then again takes up water and produces the non-peptizable seal.

(4) A monomer containing two or more ethylenic groups, together with a monomer containing only one ethylenic group, is incorporated together with a polymerization catalyst into the dynamite formulation. In the presence of water, polymerization to the three-dimensional hydrophilic network occurs. Polymerizing agents in the form of peroxy compounds and the like are usually used.

(5) Any combination of the 1, 2, 3, and 4, categories above with a metallic complexing agent or a polymerizing agent may also be present to accelerate the formation of the three-dimensional hydrophilic network.

Various types of polymer-forming materials may be used. The essential element in obtaining non-peptizable, gel-forming polymers is that the polymers must be based on a water-soluble monomer of the ethylenic type, that is, containing the group



The monomers of this type include acrylic acid, methacrylic acid, crotonic acid, itaconic acid, citraconic acid, maleic acid, maleic anhydride, acrylamide, methylacrylamide, methylene-bis-acrylamide, and other N-substituted acrylamides and similar compounds. In this group, also, is the theoretical compound vinyl alcohol (which is actually non-existent in the monomeric form since it tautomerizes to acetaldehyde). Polyvinyl alcohols and their copolymers are prepared from vinyl acetate and its copolymers by saponification of the ester groups. However, such polyvinyl alcohols are equally usable in our invention and the theoretical tautomeric monomer of vinyl alcohol is considered to be included in our term water-soluble monomers.

The water-soluble monomers can be used alone as homopolymers or can be copolymerized with up to 50% of relatively water-insoluble monomers. The limit of 50% is for the copolymers derived from water-soluble monomers having polar ionic groups such as the carboxylate group. When the water-soluble monomer has a less polar group such as the carboxamide group as, for example, acrylamide, the maximum allowable water-insoluble comonomer is decreased to about 25%. By water-insoluble monomer, it is not meant to imply that these show no water-solubility, although many are insoluble. Rather, it is meant that these monomers have relatively low solubility in water, as compared to the very soluble monomers included in the class of water-soluble monomers described above. As a rule of thumb, a solubility of less than 10% by weight should be regarded as insoluble. The water-insoluble monomers which may be used include most ethylenic compounds such as ethylene, vinyl acetate, acrylate esters, methacrylate esters, acrylonitrile, styrene, and similar compounds.

The copolymer chains are cross-linked to form a three-dimensional network of molecularly-bound atoms. The cross-linking must link at least 0.5 mol percent of the monomeric units of the polymer chains. Below this figure, the gels obtained will tend to peptize. Above 0.5 mol percent the gel becomes non-peptizing in the presence of excess water. It is thus usable for the protection of blasting material against exposure to water. Maximum results are obtained when the cross-linking joins 5-12 mol percent of the monomeric units. Too great an amount of cross-linking may reduce below desirable limits the ability of the cross-linked polymers to swell in water. The exact maximum of desired cross-linking depends on the cross-linking to be used since, with covalent cross-linking, a joining of 5-8% of the monomers is preferred, but when the cross-linking is ionic, good results are obtained when 10-12% is used.

The cross-linking can be either ionic or covalent. Ionic cross-linking is achieved by causing the reaction of polyvalent cations with carboxylate groups on the polymer chains. Such polyvalent metal cations as aluminum, copper, chromium, iron, calcium, magnesium and the like, or organic polyamines such as ethylenediamine, diethylenetriamine, triethylenetetramine and the like can be used. In either case the polymer chains and a salt of the cation are usually mixed with the explosive. Contract with water produces cross-linkage by the formation of salts of the polyvalent cation or polyamine and the carboxylate groups of the polymer chains. It is also possible to form such salts by drying and then adding them to the blasting mixture. When water contacts such a blasting mixture, the dry salt reswells at the point of contact and protects the rest of the mixture. The use of ionic cross-linking is not limited to polymer chains and carboxylate groups since polyvinyl alcohol and copolymers of vinyl alcohol such as partly hydrolyzed polyvinyl acetate or hydrolyzed polyvinyl styrene copolymers can be used similarly. In this case the cross-linking is achieved by the use of boric acid.

Covalent cross-links may be prepared by forming derivatives of the monomer to give a bifunctional monomer. As examples of this type, one can use N,N'-alkylenebis-acrylamides such as methylenebisacrylamide, vinyl esters of dibasic acids such as divinyl succinate and the like. Covalent cross-linking can be formed also by using monomers substituted by functional groups capable of reacting with other groups or with unlike groups to form other chains in situ. As examples of this type one can mention N-methylol acrylamide. In the presence of an acid catalyst the methylol groups of this monomer inter-react with other such groups or with amide groups to form cross-linkage between the acrylamide units. Another possibility is to form cross-links from polymer chains and other molecular materials included in the mixture. An example of this would be the reaction of polyketone or glyoxal with polyvinyl alcohol. Such a compound can be prepared in situ on contact with water or can be preformed and dried for inclusion in the explosive composition.

Any of these cross-links can be used in an explosive composition in which the monomers to be copolymerized are included in the explosive together with a polymerization catalyst. They may also be used as uncross-linked polymers to be cross-linked in situ on exposure to water or as completely formed, dried, three-dimensional networks which swell on contact with water. When polymerization is to take place on contact with water, a persalt peroxide or similar compound must be included in the mixture to catalyze the polymerization. Usually, one uses potassium persulfate or ammonium persulfate for this purpose, and very often to achieve a fast polymerization a bisulfite or thiosulfate is also included. When the cross-linking is to occur in situ as, for example in the presence of methylol groups, an acid catalyst, usually an organic acid such as oxalic or benzoic, or a substance like diammonium hydrogen phosphate, is included in the mixture.

While our invention can use many different kinds of polymers, as described, the dynamite compositions containing acrylic polymers or polymer-forming materials are the preferred embodiment of our invention. It is with polymers of this type that we have achieved the best protection of blasting compositions from water deterioration. By acrylic polymers or polymer-forming materials we refer to polymers of the acrylic type made up of units which in their unpolymerized form are acrylic acid and its functional derivatives such as acrylamide, acrylonitrile, and the like, possibly combined with other derivatives like methylene bisacrylamide, methylol acrylamide and the like. These materials as polymer units may be used as such or may be used in a partially polymerized or cross-linked form as explained above to achieve the hydrophilic network of our dynamite composition.

In the practice of our invention, the hydrophilic net-

work materials are added to the ordinary ammonia dynamite formulations and the resulting mixtures are then handled and processed by the ordinary methods in the art. Various concentrations of the hydrophilic network materials may be used, from about 0.2% to 8%. However, we prefer to use from about 1-4%. As such agents there may be used various combinations of monomeric units either in the form of monomers containing only one ethylenic group, or of these mixed with monomers containing more than one ethylenic linkage (i. e. cross-linked before polymerization), or as chains to be cross-linked in situ, or as already formed cross-linked, three-dimensional polymers which have been dried. Examples of the preferred ethylenic polymer- or polymer-forming materials which may be used are acrylic acid, acrylamide, methylolacrylamide, methylenebisacrylamide and the like as water-soluble monomers, the latter two being examples of monomers capable of organic cross-linking and the acrylic acid being an example of a monomer capable of ionic cross-linking. Acrylonitrile, acrylate esters and the like are the preferred examples of water-insoluble monomers. These are used in the proportions of monomers and cross-linking previously described.

More specifically, in achieving the hydrophilic network in the composition of our invention according to the five categories above, there may be described as examples, the following combinations of the acrylic products which, when present in the dynamite, form an increased volume non-peptizable hydrophilic network upon contact with water.

(1) A mixture of acrylamide and acrylic acid together with a metal salt, preferably those with polyvalent cations such as aluminum, chromium, copper, iron, calcium, magnesium, and the like is used together with potassium persulfate and sodium thiosulfate to catalyze polymerization. Organic polyvalent cations may also be used such as those formed from triethylene tetramine, ethylene diamine, and similar polyamines. In the presence of water this forms the non-peptizable hydrophilic network; the metal here probably takes part in the structure as a complexing agent or chelating agent to form the cross-links.

(2) A polyacrylamide-polyacrylic acid (either a copolymer formed by partial hydrolysis of polyacrylonitrile or a mixture of homopolymers) containing in part carboxyl groups and in part carboxamide groups is used together with a metal salt, such as aluminum sulfate, etc., in the blasting compositions. The metal ion, on contact with water, cross-links the polymer chains by salt formation and/or chelation.

(3) Acrylamide and methylene-bis-acrylamide is copolymerized in aqueous solution, for example, using sodium thiosulfate and potassium persulfate as the catalyst system. This forms the three-dimensional polymer which is then dried and pulverized and used as such in the blasting composition, to reswell when contacted by water. The metallic ions here function as polymerization catalysts and do not function as complexing or chelating agents. N-methylol polyacrylamide is also an example of polymers in this category usable in our process, but with this there must also be included an acid catalyst to effect cross-linking through the methylol groups when water comes in contact with the polymer chains or the cross-linking must have been previously achieved.

(4) A mixture of acrylamide and methylenebisacrylamide, along with various proportions of such catalysts as sodium thiosulfate and potassium persulfate, is used. This is incorporated into the dynamite formulation and forms the three-dimensional polymer, in contact with water, by polymerization in situ.

(5) Any combination of categories 1-4 may be used.

The compositions of our invention show greatly improved water-resistance properties which have a remarkable degree of permanence. By the use of the methods available in the art for measuring the water resistance of dynamite compositions, it is extremely difficult to

obtain reproducible results. Moreover, the methods used afford at best a determination merely of whether or not the deterioration caused by water has reached such a state as to result in the composition being completely or in part inert to detonation. By the means known in the art, it is difficult if not impossible to obtain quantitative measurements as to the degree of water deterioration resulting from contact with water with varying amounts of time, as shown by loss of strength of the explosion. In order to demonstrate this surprising degree of water resistance of our dynamite compositions, we have devised a method by means of which we can reproducibly determine the degree of deterioration, that is, the relative loss of strength of the explosion resulting from exposure to water with varying periods of time and the limit of water exposure before the composition becomes inert to detonation. Described most simply, we determine the relative strength of the explosion on partially deteriorated samples of the composition by measuring the intensity of the noise of the explosion; we have found that this gives a measurement of the relative strength of the explosion which is dependent upon the degree of deterioration by exposure to water. This is further explained below.

Our invention is further illustrated in more detail by the following examples.

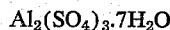
EXAMPLE 1

Water-resistant explosive compositions

These are prepared by adding from 1 to 4 parts of the indicated acrylic type hydrophilic network-forming materials to about 100 parts of various ammonium nitrate dynamite compositions. Examples of such compositions are:

A

12.4% nitroglycerin
1.5% drip oil
0.1% nitro cotton
35.0% NH_4NO_3
35.0% NaNO_3
8.0% starch
1.0% of a mixture of a copolymer of 10% acrylic acid and 90% acrylamide with 20% of its weight



+ other minor ingredients such as absorbents, combustibles, etc.

B

7.8% nitroglycerin
75.0% NH_4NO_3
4.3% NaOH
1.5% NaCl
3.0% of a mixture of 3% methylenebisacrylamide, 95% acrylamide, and 2% potassium persulfate
solid fuels, such as corn starch or bagasse

C

9.5% nitroglycerin
71.5% NH_4NO_3
1.2% NaNO_3
4.0% of a mixture of a dried copolymer of methylolacrylamide (10%), acrylamide (75%), and methylmethacrylate (15%) with oxalic acid (3% of the mixture)
and the usual combustibles

D

10.0% nitroglycerin
47.3% fine NH_4NO_3
20.4% coarse NH_4NO_3
0.4% NaNO_3
2.0% of mixture of a copolymer of 50% acrylic acid and 50% styrene with about 15% of its weight of chromic chloride

16.7% nitroglycerin
2.0% drip oil
0.3% nitro cotton
66.5% NH_4NO_3
5.0% NaNO_3
2.0% of a dried copolymer of 5% methylenebisacrylamide, 70% acrylamide, and 25% acrylonitrile
and the usual combustibles like wood flour, corn starch, etc.

EXAMPLE 2

An explosive composition is prepared by adding from 1 to 4 parts of the hydrophilic network forming material to a dynamite formulation in substitution of the parts of starch as indicated. A typical formula is as follows:

	Parts
Ammonium nitrate-----	37.0
Sodium nitrate-----	36.7
Corn starch-----	8.0
Granulated coal-----	2.3
Wood pulp-----	1.0
Ground chalk-----	1.0
Nitro cotton-----	0.1
Drip oil-----	1.5
Nitroglycerin-----	12.4

Thus, if 4 parts of the hydrophilic network forming material are added, only 4 parts of starch are used. The usual means of mixing as employed in the art are used.

The composition is then machine packed uniformly into $1\frac{1}{4}$ " x 8" dynamite cartridges and subjected to the following testing methods, the results of which are given in the table below.

The water resistance of these formulations is determined by the following procedure: The cartridges are completely sealed with a wax coating (microcrystalline wax is preferable). The whole cartridge is first dipped in the wax. Then each end is dipped again and finally wax is ladled into the depressions in the ends. Holes, 2 mm. in diameter, and 17.5 mm. deep, are then punched into the cartridge perpendicular to its longitudinal axis; 16 holes are placed in the cartridge in four staggered longitudinal rows of four punch holes each, each row being at 90° of arc to the other, the distance between holes in any one row being $1\frac{3}{4}$ " and from a given end of the cartridge, the nearest holes for alternate rows being 1" and $1\frac{1}{8}$ ", respectively.

The punched cartridges are then placed in a water bath, 9" from the surface and firmly supported at the ends and middle in a level and horizontal position, being so placed that the holes point in vertical and horizontal directions in the tank. After being thus exposed to the action of water for various periods of time, the cartridges are removed and then detonated with a standard No. 6 blasting cap. The intensity of the sound from the explosion of the immersed cartridges is compared with the intensity of the sound from a "control" non-immersed cartridge of the same formulation. The ratio of the sound intensity from an immersed cartridge to the sound intensity of a non-immersed "control" cartridge is designated the "relative sound intensity" (RSI).

The sound intensity of each explosion is determined in a shooting house, 75 feet uphill from the shooting pit, both shooting pit and shooting house being located outdoors in a convenient place such as in a ravine. Practically any sound measuring device may be used. When the readings are in decibels, which are equal to ten times log of the sound intensity, they are converted to sound intensity for calculation of the relative intensity.

Examples of suitable apparatus are the following.

(1) General Radio Sound Survey Meter, type 1555-A. Here the maximum needle deflection is measured. Readings are in decibels.

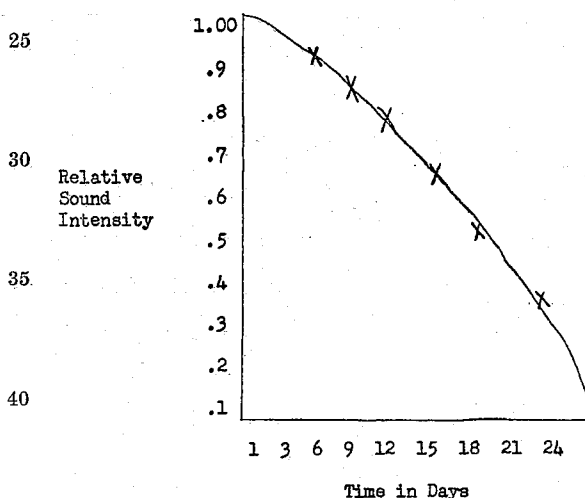
(2) General Electric Sound Survey Meter, Catalog

4980178-G1. Here, also, the maximum needle deflection is measured. Readings are also in decibels.

(3) Brush Electronic equipment, pen-recording type of sound measuring apparatus using a microphone, Brush BA 106; amplifier, Brush BL 905; recorded through a Brush recording oscillograph, Brush BL 202. Here the displacement of the pen as shown on the tracing is proportional to the sound intensity.

The noise of the blasting cap can be ignored since this is negligible compared with the noise of the exploding dynamite composition.

The cartridges are immersed for different periods of time and are then detonated. The relative sound intensities as defined above and as obtained by detonating one or more immersed cartridges and comparing with one or more dry cartridges, are then plotted against time (the relative intensity for no immersion is 1) to give a curve from which may be read the degree of failure from immersion in water at any particular time up to the time of being inert to detonation. An example of such a curve where six cartridges are immersed for periods of 3, 6, 9, 12, 16, and 22 days is shown in the following figure:



The extent of deterioration for any given time may be determined from the curve. Thus, for example, the time of $\frac{1}{2}$ deterioration (on the basis of relative sound intensity equal to 0.66) is 12 days.

Any particular point may be designated as the failure point; as time progresses, even though an explosion takes place, the decreased relative sound intensity indicates loss of strength of the explosion.

Evidence of stub, i. e. incomplete detonation, is noted by observation; thus, even when only part of the charge detonates there may still be a measurable sound intensity. For convenience for comparison purposes, the time when $\frac{1}{2}$ deterioration has taken place, as determined from the curve, is used as the basis of comparison. This is an extremely useful test for showing the degree of permanence of water resistance which is achieved, it being possible to follow the actual rate of deterioration.

The results of this test showing the rate of deterioration cannot be directly compared with the results in previously published tests since the other tests as carried out simply indicate the point in hours after exposure to water at which the cartridge fails to detonate completely. Also these cartridges have been completely waxed to hermetically seal them except for punched openings, while cartridges in previous tests have not always been so treated. There may be considerable deterioration of the composition before detonation fails completely. As stated, the evidence of stub has been the only endpoint designated in previous tests. In the new test described it is possible to follow the progress of deterioration with time of exposure to water.

In the following table are shown the results of tests on typical compositions.

Hydrophilic Network Forming Material Used	Percent of Hydrophilic Network Forming Material Used	Percent Cornstarch Used In Formulation	Time of $\frac{1}{2}$ Deterioration (RSI equal to 0.667)	Evidence of Stub
Polyacrylamide-polyacrylic acid prepared by partial hydrolysis of polyacrylamide mixed with alum in ratio of 80 parts of polymer to 20 parts of alum ($Al_2(SO_4)_3 \cdot 7H_2O$)	1	7	11.5	26
Same as above	2	6	6.5	15.5
Same as above	4	4	9.0	22
Polyacrylamide (95%)—Methylene Bis Acrylamide (5%)	2.5	5.5	7.0	17
Polyacrylamide (95%)—Methylene Bis Acrylamide (5%)	4	4	10.0	22
Methylol polyacrylamide	3	5	6.5	16
None used—"Control"	0	8	1.8	7

We claim:

1. An explosive composition resistant to deterioration on contact with water which comprises ammonium nitrate, a sensitizer, a solid fuel and at least 0.5% by weight of materials which, in their polymerized form, are a hydrophilic, non-peptizable, three-dimensional network of molecularly bound atoms, said network being composed of chains of a linear polymer of an unsaturated monomer of the ethylenic type, at least 50% of said monomeric units having at least one substituent group chosen from the group consisting of carboxyl, carboxamide, N-methylol carboxamide, N,N'-methylene bis-carboxamide, carboxylic anhydride, and lower alkyl chains having a carboxylic acid substituent, said polymer chains being cross-linked by short chemically bound atom chains, said cross-linkings joining a minimum of 0.5 mol percent of the monomeric units of said polymer.

2. Compositions according to claim 1 in which the materials which in their polymerized form are a hydrophilic, three-dimensional network comprising 0.5-8% of the explosive composition.

3. Compositions according to claim 1 in which the materials which in their polymerized form are a hydrophilic, three-dimensional network comprising 1-4% of the explosive composition.

4. The compositions according to claim 3 in which the monomers have been polymerized but have not been cross-linked.

5. The compositions according to claim 4 in which the polymer chain contains carboxyl substituents and the cross-linking means is a polyvalent cation.

6. The compositions according to claim 5 in which the polymer chain contains acrylic acid units and the polyvalent cation is aluminum.

7. The compositions according to claim 4 in which the polymeric chain is a poly-N-methylolacrylamide and an acid catalyst is included to effect cross-linking.

8. The product according to claim 7 in which the methylolacrylamide is copolymerized with acrylamide.

9. The compositions according to claim 3 in which the monomers have been polymerized and cross-linked and the resultant hydrophilic network has been dried.

10. The compositions according to claim 9 in which the dry hydrophilic molecular network is a polyvalent cation salt of polyacrylic acid.

11. The compositions according to claim 10 in which the hydrophilic network is an aluminum salt of a copolymer of acrylic acid and acrylamide.

12. The compositions according to claim 9 in which the hydrophilic, three-dimensional molecular network contains units of an N-N'-alkylene acrylamide.

13. The compositions according to claim 12 in which the said network is a copolymer of acrylamide with methylene bis-acrylamide.

14. The compositions according to claim 9 in which the said network is a chain cross-linked through N-methylolacrylamide units.

15. The compositions according to claim 14 in which the said network is a copolymer of acrylamide with methylolacrylamide.

16. An explosive composition resistant to deterioration on contact with water which comprises ammonium nitrate, a sensitizer, a solid fuel and from 1-4% by weight of unsaturated ethylenic monomers, at least 50% of said monomers having at least one substituent group chosen from the group consisting of carboxyl, carboxamide, N-methylol carboxamide, N,N'-methylene bis-carboxamide, carboxylic anhydride, and lower alkyl chains having a carboxylic acid substituent, a polymerization catalyst and a means for cross-linking the ultimate polymer, said cross-linking to join a minimum of 0.5 mol percent of the monomeric units of said polymer.

17. The product according to claim 16 in which one of the monomers is an alkylene bis-acrylamide.

18. The compositions according to claim 17 in which the alkylene bis-acrylamide is methylene bis-acrylamide.

19. The compositions according to claim 18 in which there is also included acrylamide.

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