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3,326,733

GELLED EXPLOSIVE COMPOSITION CONTAINING A XANTHOMONAS HYDROPHILIC COLLOID

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This invention relates to a gelled explosive and a method for its preparation. More specifically, the invention relates to a gelled explosive containing a *Xanthomonas* hydrophilic colloid, borax, and a monovalent water-soluble explosive salt.

Various explosives are known which are supplied in the form of a gel. Such gelled explosives have not been entirely satisfactory because of gel instability. The gel instability has been manifested by syneresis and bleeding of the gel after a relatively short period of time.

An object of this invention is to provide gelled explosives which are characterized by their stability and the firm, tough and cohesive nature of their gel structure.

Another object of the invention is to provide a gelled explosive containing a *Xanthomonas* hydrophilic colloid, borax, and a monovalent explosive salt.

A further object of the invention is to provide a method of making a stable, tough, cohesive gelled explosive.

Additional objects will become apparent from a reading of the specification and claims which follow.

In accord with my invention, I form a gelled explosive by adding to water a *Xanthomonas* hydrophilic colloid, borax, and a water-soluble monovalent explosive salt. A gel is formed almost immediately which, on standing, becomes increasingly firm.

The monovalent explosive salt which is employed is soluble in water and can be an acid, basic or neutral salt. The practical explosive salts are those which contain a high quantity of oxygen so as to provide a favorable oxygen balance in the explosive. Typical of such salts are ammonium nitrate, sodium nitrate, and potassium nitrate.

The quantity of monovalent explosive salt which is employed can be varied widely while still obtaining a gelled explosive. To illustrate, I have obtained gels when employing as low as 5% by weight of monovalent salt. In order to obtain a favorable oxygen balance in the explosive, it is, of course, desirable to employ a much larger quantity of the explosive monovalent salt. A suitable quantity can, for example, be as high as about 90% by weight. The only limitation on the quantity of monovalent explosive salt which is used is its solubility in water. The water temperature is a factor affecting its solubility and increased solubility can be obtained simply by heating the water to which the salt is added. In my process, I have found that warming the water to a temperature such as about 40 to about 80° C. greatly improves the solubility of the salt, the quantity of which in turn determines the oxygen balance in the final explosive.

Also present in my explosive compositions is a soluble borate such as borax. Although other borate salts such as ammonium borate, sodium metaborate, and sodium tetraborate can be employed, I prefer to use borax since it is fairly cheap and readily available. The concentration of the borate compound employed can be varied in forming gelled explosives according to my invention. To illustrate, the content of borate salt can be varied from about 5 to about 50% by weight of the *Xanthomonas* hydrophilic colloid, as described later. Preferably, however, the concentration of borate compound ranges from about 10 to about 20% by weight of the *Xanthomonas* hydrophilic colloid.

The next ingredient required in my explosive composi-

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tions is a *Xanthomonas* hydrophilic colloid which is a colloidal material produced by bacteria of the genus *Xanthomonas*. In the practice of my invention, I employ a quantity of *Xanthomonas* hydrophilic colloid ranging from about 0.5 to about 3% by weight of the water contained in the explosive composition. Illustrative of such colloidal materials is the hydrophilic colloid produced by the bacterium *Xanthomonas campestris*. This colloidal material is a polymer containing mannose, glucose, potassium glucuronate and acetyl radicals. In such a colloid, the potassium portion can be replaced by several other cations without substantial change in the property of the said material for my purpose. The said colloidal, which is a high molecular weight, exocellular material, may be prepared by the bacterium *Xanthomonas campestris*, by whole culture fermentation of a medium containing 2-5% commercial glucose, organic nitrogen source, dipotassium hydrogen phosphate and appropriate trace elements. The incubation time is approximately 96 hours at 28° C., aerobic conditions. In preparing the colloid as aforesaid, it is convenient to use corn steep liquor or distillers' dry solubles as an organic nitrogen source. It is expedient to grow the culture in two intermediate stages prior to the final inoculation in order to encourage vigorous growth of the bacteria. These stages may be carried out in media having a pH of about 7. In a first stage a transfer from an agar slant to a dilute glucose broth may be made and the bacteria cultured for 24 hours under vigorous agitation and aeration at a temperature of about 30° C. The culture so produced may then be used to inoculate a higher glucose (3%) content broth of larger volume in a second intermediate stage. In this stage the reaction may be permitted to continue for 24 hours under the same conditions as the first stage. The culture so acclimated for use with glucose by the aforementioned first and second stages is then added to the final glucose medium. In the aforesaid method of preparation of *Xanthomonas campestris* hydrophilic colloid, a loopful of organism from the agar slant is adequate for the first stage comprising 200 milliliters of the said glucose media. In the second stage the material resulting from the first stage may be used together with 9 times its volume of a 3% glucose media. In the final stage the material produced in the second stage may be admixed with 19 times its volume of the final media. A good final media may contain 3% glucose, 0.5% distillers' dry solubles, 0.5% dipotassium phosphate, 0.1% magnesium sulphate having 7 molecules of water of crystallization and water. The reaction in the final stage may be satisfactorily carried out for 96 hours at 30° C. with vigorous agitation and aeration. The resulting *Xanthomonas campestris* colloidal material which I have found to be particularly suitable for my purpose can be recovered by precipitation in methanol of the clarified mixture from the fermentation. This resulting material may also be designated as a pseudoplastic, heteropolysaccharide hydrophilic colloid or gum produced by the bacterium species *Xanthomonas campestris*.

Other *Xanthomonas* colloidal materials may be prepared by repeating the procedure used for producing the *Xanthomonas campestris* colloidal material described above by substituting known *Xanthomonas* bacterium or organisms, i.e., *Xanthomonas carotae*, *Xanthomonas incae*, *Xanthomonas begoniae*, and *Xanthomonas malvacearum*, for the bacterium, *Xanthomonas campestris*.

In addition to the ingredients set forth above, my gelled explosives also contain water. In forming a gelled explosive according to my invention, the various ingredients are added to water. The order of addition of the ingredients is not critical. Thus, for example, the *Xanthomonas* hydrophilic colloid may be first dissolved in the water after

which the monovalent explosive salt may be added or conversely, the *Xanthomonas hydrophilic* colloid may be dissolved directly in an aqueous solution of the monovalent explosive salt. Further, the *Xanthomonas hydrophilic* colloid may be co-dissolved with either the soluble borate compound or with the soluble monovalent explosive salt.

To facilitate formation of my explosives, it is, of course, desirable that the various ingredients employed be in a finely divided form. As stated previously, it is oftentimes desirable to heat the water which also facilitates solution of the various ingredients therein. In order to obtain a homogeneous explosive, it is also desirable to agitate the water mixture. I have found that best results are obtained when the borax or soluble borate compound is added to the aqueous solution of *Xanthomonas hydrophilic* colloid and the soluble monovalent explosive salt. Following addition of the last ingredient, whether soluble borate, monovalent explosive salt, or *Xanthomonas hydrophilic* colloid, a gel is immediately formed which becomes increasingly firm on standing.

To further illustrate the scope of my invention, there are presented the following examples in which all parts and percentages are by weight unless otherwise indicated.

Example I

A solution containing 120 grams of ammonium nitrate and 78 grams of water (60.6% of ammonium nitrate), was warmed to 50° C. at which point 2 grams of a finely divided *Xanthomonas campestris* hydrophilic colloid was added with agitation. After *Xanthomonas campestris* hydrophilic colloid had dissolved in the warm ammonium nitrate solution, there was added with agitation 0.2 gram of borax. A gel was immediately formed on addition of the borax which gel became more firm on standing.

When Example I is repeated utilizing sodium nitrate or potassium nitrate in lieu of ammonium nitrate, a satisfactory explosive gel is obtained. Similarly, explosive gels are obtained by utilizing a larger quantity of the monovalent explosive salt, e.g., ammonium nitrate, at total concentrations ranging up to as high as about 90% by weight.

Example II

To 150 grams of a 60% ammonium nitrate aqueous solution at 60° C. was added 1.5 grams of a finely divided *Xanthomonas campestris* hydrophilic colloid with stirring. After the colloid had dissolved, 0.37 gram of borax was added with stirring and there was immediately formed a soft gelled explosive.

Example III

To 100 grams of a 60% ammonium nitrate solution containing 0.8 gram of finely divided *Xanthomonas campestris* hydrophilic colloid was added 1 gram of borax. The addition was made at room temperature with mixing of the ammonium nitrate solution. On addition of the borax, a firm, rubbery gelled explosive was immediately formed.

Example IV

An aqueous ammonium nitrate solution containing 60 grams of ammonium nitrate and 40 milliliters of water was heated to 80° C. at which point there was added 0.5 gram of deacetylated *Xanthomonas campestris* hydrophilic colloid. The addition was made with stirring in order to assist the solution of the colloid. Following this, there was added 0.5 gram of borax with stirring. On addition of the borax, there was immediately formed a firm, rubbery gelled explosive.

As shown in Example IV, a deacetylated *Xanthomonas hydrophilic* colloid may be employed in the same manner as the *Xanthomonas hydrophilic* colloid itself in practicing my invention. The deacetylated colloids and their method of preparation are described in U.S. Patents 3,000,790, 3,054,689, and 3,096,293 which are incorporated herein by reference. In terms of cost and avail-

ability, I prefer to use the *Xanthomonas hydrophilic* colloid rather than the deacetylated derivative thereof.

Example V

When Example I was repeated using 0.25% by weight of a finely divided *Xanthomonas campestris* hydrophilic colloid and 0.1% by weight of borax, a gelled explosive was formed. Due to the decreased quantities of *Xanthomonas campestris* hydrophilic colloid and borax which were used, the gelled explosive which formed had a softer consistency than that obtained in Example I.

Example VI

Two grams of finely divided *Xanthomonas malvacearum* hydrophilic colloid were dissolved with stirring in 196 grams of an aqueous solution containing 60% by weight of ammonium nitrate. The solution was warmed to 50° C. with stirring and 2 grams of borax were added and mixed in. There was produced a firm, rubbery gelled explosive.

In the foregoing examples, I have illustrated my invention with regard to use of ammonium nitrate as the monovalent soluble explosive salt. It should be understood, however, that other explosive salts, such as sodium perchlorate, and the like, may be employed in the practice of my invention. Due to its low cost and availability, ammonium nitrate is the preferred explosive salt for use in my invention. My explosive compositions can also, of course, contain conventional explosive additives, such as finely divided aluminum to increase the energy output.

As illustrated by the foregoing, my invention relates primarily to the formation of gelled explosives. In a broader sense, however, my invention has general application to forming aqueous gels containing a *Xanthomonas hydrophilic* colloid, a soluble borate salt, and a soluble monovalent salt. In forming explosives, the soluble monovalent salt is one which contains a large quantity of oxygen to provide a suitable oxygen balance in the explosive. However, it is not necessary that the soluble salt contain a large quantity of oxygen in order to form an aqueous gel. For example, the soluble salt can be sodium chloride, potassium chloride, ammonium chloride, sodium acetate, potassium acetate, ammonium acetate, sodium sulfate, potassium sulfate, ammonium sulfate, sodium phosphate, potassium phosphate, ammonium phosphate, ammonium citrate, or potassium pyrophosphate. Preferably, the soluble salt is an ammonium salt of a strong acid, especially a nitrate or sulfate. Certain of the above salts which may be used in forming gels according to my invention are di- or trivalent. However, the soluble salts which I generally employ are monovalent.

The gelation mechanism involved in forming gels according to my invention is not clearly understood. However, whatever the mechanism, it apparently involves the co-joint action of both a soluble borate and a soluble monovalent salt with a *Xanthomonas hydrophilic* colloid. Soluble borate salts do not, by themselves, form a gel when added to an aqueous solution of a *Xanthomonas hydrophilic* colloid. Likewise, soluble monovalent salts do not, by themselves, form gels when added to a solution of a *Xanthomonas hydrophilic* colloid. Thus, the co-joint action of a soluble borate salt with a soluble monovalent salt in forming gels with an aqueous solution of a *Xanthomonas hydrophilic* colloid is highly unexpected and can only be attributed to some synergistic coaction between the various ingredients.

My invention is illustrated in the foregoing specification by reference to specific concentrations, temperatures, and the like. However, it should be understood that these references are solely for the purpose of illustration and that I desire to be limited only by the lawful scope of the appended claims.

I claim:

1. A gelled explosive comprising water, a *Xanthomonas hydrophilic* colloid in an amount ranging from about 0.5

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to about 3% by weight of said water, a water-soluble borate salt in an amount ranging from about 5 to about 50% by weight of said *Xanthomonas hydrophilic* colloid, and a water-soluble monovalent explosive salt.

2. The composition of claim 1 wherein said monovalent explosive salt is ammonium nitrate.

3. The composition of claim 1 wherein said *Xanthomonas hydrophilic* colloid is produced by the bacterium *Xanthomonas campestris*.

4. The composition of claim 1 wherein said *Xanthomonas hydrophilic* colloid is produced by the bacterium *Xanthomonas malvacearum*.

5. The composition of claim 1 wherein said borate salt is borax.

6. The composition of claim 1 wherein said borate salt is present in a concentration ranging from about 10 to about 20% by weight of said *Xanthomonas hydrophilic* colloid.

7. A gelled explosive comprising water, a hydrophilic colloid selected from the group consisting of *Xanthomonas hydrophilic* colloid and deacetylated *Xanthomonas hydrophilic* colloid, said hydrophilic colloid being present in an amount ranging from about 0.5 to about 3% by weight of said water, a soluble borate in an amount ranging from about 5 to about 50% by weight of said hydrophilic colloid, and a water-soluble monovalent explosive salt.

8. A gelled explosive composition comprising water, a *Xanthomonas campestris* hydrophilic colloid in an amount ranging from about 0.5 to about 3% by weight of said water, borax in an amount ranging from about 10 to about 20% by weight of said *Xanthomonas campestris* hydrophilic colloid, and ammonium nitrate.

9. An aqueous gel comprising water, a *Xanthomonas hydrophilic* colloid in an amount ranging from about 0.5 to about 3% by weight of said water, a soluble borate in an amount ranging from about 5 to about 50% by weight of said *Xanthomonas hydrophilic* colloid, and a water-soluble monovalent salt.

10. The composition of claim 9 wherein said monovalent salt is an ammonium salt of a strong acid.

11. An aqueous gel comprising water, a *Xanthomonas hydrophilic* colloid in an amount ranging from about 0.5 to about 3% by weight of said water, a soluble borate in an amount ranging from about 5 to about 50% by weight of said *Xanthomonas hydrophilic* colloid, and a water-soluble salt selected from the class consisting of chlorides, acetates, sulfates, phosphates, citrates and pyrophosphates.

12. A method for forming a gelled explosive composi-

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tion comprising mixing water, a hydrophilic colloid selected from the group consisting of *Xanthomonas hydrophilic* colloid and deacetylated *Xanthomonas hydrophilic* colloid, said colloid being present in an amount ranging from about 0.5 to about 3% by weight of said water, a soluble borate salt in an amount ranging from about 5 to about 50% by weight of said hydrophilic colloid, and a monovalent explosive salt.

13. The method of claim 12 wherein said hydrophilic colloid is a *Xanthomonas hydrophilic* colloid.

14. The method of claim 13 wherein said explosive salt is ammonium nitrate.

15. The method of claim 13 wherein said *Xanthomonas hydrophilic* colloid is produced by the bacterium *Xanthomonas campestris*.

16. The method of claim 13 said *Xanthomonas hydrophilic* colloid is produced by the bacterium *Xanthomonas malvacearum*.

17. The method of claim 12 wherein said soluble borate salt is borax.

18. A method of producing an aqueous gel comprising mixing water, a *Xanthomonas hydrophilic* colloid in an amount ranging from about 0.5 to about 3% by weight of said water, a soluble borate salt in an amount ranging from about 5 to about 50% by weight of said *Xanthomonas hydrophilic* colloid, and a water-soluble monovalent salt.

19. A method of producing an aqueous gel comprising mixing water, a *Xanthomonas hydrophilic* colloid in an amount ranging from about 0.5 to about 3% by weight of said water, a soluble borate salt in an amount ranging from about 5 to about 50% by weight of said *Xanthomonas hydrophilic* colloid, and a water-soluble salt selected from the class consisting of chlorides, acetates, sulfates, phosphates, citrates, and pyrophosphates.

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