PREPARATION OF EXPLOSIVE SUBSTANCES CONTAINING CARBOXYMETHYL CELLULOSE

22 Claims. (Cl. 149—24)

This application is a continuation-in-part of our application Serial Number 106,462, filed on May 1, 1961, now abandoned.

The invention relates to the manufacture of primary explosives, that is to say metal azides, metal fulminates and metal salts of various nitro derivatives of phenol and poly-hydroxyphenols.

Primary explosives are used for initiatory or delay purposes in detonators, fuses, primers and the like where ignition of the primary explosive is required in response to mild, low-energy stimuli, this ignition normally being required to produce a detonation wave capable of exploding quantities of a less sensitive secondary explosive, such as tetryl or pentaerythritol tetranitrate, or a relatively insensitive high explosive, such as ammonium nitrate. The inherent sensitiveness of primary explosives necessitates extreme care in their manufacture and handling to reduce accidental hazards even to acceptable levels. The primary explosive art is an art which advances slowly as no improvement can be theoretically predicted and even techniques used in the manufacture of other explosives cannot be applied and any modification of an established process or product cannot be made without exhaustive experimentation and testing.

The primary explosives with which the present invention is concerned are crystalline, essentially water-insoluble compounds which may generally be prepared by precipitating the primary explosive from aqueous solution, the precipitation resulting from the double decomposition reaction between two suitable reactants in aqueous solution or suspension, or from crystallisation of the primary explosive from solution. Primary explosives so produced usually tend to cake on drying, have poor flowing properties rendering them unsuitable for modern explosive filling machines, and possess undesirable crystal forms which make them very susceptible to accidental ignition.

Many attempts have been made to improve the properties of these primary explosives by varying the conditions under which the primary explosives are precipitated, and, most frequently, by incorporating adulterants in the primary explosive during precipitation. Considerable success has been achieved with certain primary explosives in reducing the sensitiveness of the explosive to accidental ignition by incorporating an adulterant, but this has usually resulted in an undesirable decrease in the initiating power (i.e. the available energy released by the explosive when ignited) generally due to the presence of a considerable proportion of non-explosive adulterant.

Particular attention has been paid to the manufacture of the primary explosive lead azide, which has a high energy content and is potentially an extremely powerful initiator. Pure lead azide precipitated from aqueous solution by double decomposition is such a dangerously sensitive material that it is difficult to isolate safely from its mother liquor and is thus of little practical value. It has been shown that the addition of dextrin to the solution from which the lead azide is precipitated results in the incorporation of a few percent of dextrin to form solution "dextrinated lead Azide" which is comparatively safe to handle, but which shows a marked decrease in initiating power and ignitability which necessitates the use of undesirably large quantities of the material to ensure effective functioning.

Dextrinated lead azide suffers from the further disadvantage that there is great difficulty in reproducing dextrinated lead azide of a particular grade of dextrin a natural product and varies widely in composition and causes variations in the properties of batches of dextrinated lead azide made in an identical fashion, but using different batches of dextrin. Further, dextrin is hygroscopic and dextrinated lead azides therefore tend to become damp on storage, resulting in decreased functioning reliability and the gradual decomposition of the primary explosive.

U.S. Patent No. 2,421,778 describes the preparation of lead azide using a synthetic organic polymer, in particular polyvinyl alcohol, instead of dextrin as additive and suggests that the use of these synthetic additives can be precisely formulated avoids the formulation problems associated with dextrinated lead azide. Lead azide prepared in a typical manner according to U.S. Patent No. 2,421,778 consists however predominantly of elongated crystals from which small sharp fragments are likely to break off during handling and filling and induce accidental ignition. Lead azide or any other primary explosive in such a crystalline form, as opposed to being in discrete granules, is more difficult to wash, filter and dry and cannot be so readily handled or pre-pelleted.

The general object of the present invention is to provide an improved process for the manufacture of a wide range of primary explosives in which the hereinbefore described defects of the prior art are overcome.

It is a further object of the invention to provide primary explosives in a granular, free-flowing form which is substantially free from crystal fragments and dust and in which well-defined crystal faces and projections likely to cause accidental ignition are virtually eliminated.

It is another object to provide primary explosives having a high bulk density which are eminently suitable to use in modern automatic explosive-filling machines.

It is a further object to provide a granular, free-flowing lead azide which can be readily washed and filtered, and which can be conveniently dried by a current of cold air or on a hot table without causing caking or aggregation of the granules.

It is another object to provide a granular lead azide which can be pre-pelleted and which when loaded by a press into a detonator or fuse case will adhere to the sides of the case and consolidate well.

It is an additional object of the invention to provide a granular, free-flowing lead azide having the above superior properties and still having an azide value between 95 and 99 percent; azide value being the actual azide radical content compared with the azide radical content of pure lead azide expressed as a percentage.

It is a further object to provide a process for the manufacture of lead azide having the above superior properties which can yet be carried out at temperatures at which dangerous quantities of toxic hydrazoic acid fumes are not evolved and hazards which would arise on cooling the mother liquor are substantially reduced.

Other objects and advantages of the present invention will be hereinafter apparent in the course of the following description.

In accordance with the invention, a process for the manufacture of water-insoluble primary explosives comprises precipitating the primary explosive from an aqueous solution containing carboxymethyl cellulose, separating the primary explosive from the said solution and drying the primary explosive, whereby the primary explosive is pro-
duced in a granular, free-flowing form which incorporates carboxymethyl cellulose from the solution.

The addition of carboxymethyl cellulose in accordance with the present invention is capable of producing water-insoluble primary explosives in a superior physical form and with better explosive properties than primary explosives produced with prior known additives.

The superiority of physical form of the explosives of the present invention is believed to be due to the formation of an insoluble metal salt of carboxymethyl cellulose in the solution from which the primary explosive is precipitated. This metal salt appears to provide nuclei around which the precipitating primary explosive may aggregate to yield characteristic, compact granules of primary explosive in which the metal salt of the carboxymethyl cellulose is evenly dispersed throughout the granule. This is in contradistinction to the effect of such additives as dextrin and polyvinyl alcohol which do not contain salt-forming groups and act as crystal-modifying agents by adsorption on crystal faces during the precipitation process.

The present invention is outstanding in providing a process for the production of a primary explosive which can be widely applied to diverse types of essentially water-insoluble primary explosives.

The precipitation of the primary explosive from solution is generally achieved by reaction between two substances dissolved or suspended in an aqueous solution containing carboxymethyl cellulose, but precipitation may also be achieved by crystallisation and recrystallisation of the explosive from aqueous solution. In carrying out a process in accordance with the invention when the precipitation of the primary explosive is by crystallisation, carboxymethyl cellulose may be added to the crystallisation liquor before the crystallisation commences, or to one or more of the solutions which are admitted to form the precipitant. When the precipitation of the primary explosive is by reaction, carboxymethyl cellulose may be added to one or to both of the solutions interacting to produce the precipitation, or the interacting solutions may be introduced, preferably substantially simultaneously, into a solution containing carboxymethyl cellulose.

Carboxymethyl cellulose, which is water-soluble throughout the commercially available range of carboxymethyl content 12-35%, is preferably employed in the form of its sodium salt, and is conveniently used as a 0.5% solution, a measured volume of which is added to the appropriate solution or solutions.

The particular procedure adopted in carrying out a process in accordance with the invention has an effect on the physical characteristics of the product. Thus the proportion of carboxymethyl cellulose in the mixture of the product. The rate of admixture of the solutions or the rate of crystallisation, the temperature of the reaction, as well as the nature of the explosive substance itself, all influence to a greater or lesser degree the properties of the final product. Carboxymethyl cellulose is often effective when present in the solution in a quantity as low as 0.01% of the weight of the explosive substance and for initiatory purposes up to 1% is generally used, a generally useful range being 0.1-1%. Larger amounts, however, up to 3% and occasionally up to 5% may be used especially for delay purposes. The addition of carboxymethyl cellulose gives very effective control of the rate of burning by regulating the crystal growth as well as the inertness of the explosive. Generally speaking, as the amount of carboxymethyl cellulose employed is increased bulk density will increase to a maximum, the optimum amount depending upon the particular primary explosive used.

Nearly all of the added carboxymethyl cellulose used in the process of the invention becomes incorporated in the product, there remaining in the mother liquor only a small proportion. Carboxymethyl celluloses are available in a range of molecular weights, relatively high molecular weight grades producing more viscous solutions so that a given modification of physical properties of a primary explosive is usually obtained by using a lower proportion of a higher molecular weight carboxymethyl cellulose than is obtained when a lower molecular weight carboxymethyl cellulose is used. Thus, for example, granular lead azide of a given grade can be prepared either by incorporating 0.6% by weight of a low molecular weight carboxymethyl cellulose, having a viscosity of 400 centipoises in 4% aqueous solution at 20°C, or by incorporating 0.2% of a high molecular weight carboxymethyl cellulose, having a viscosity of 6,000 centipoises in 4% aqueous solution at 20°C.

In applying the invention, the optimum conditions for obtaining the desired results may be arrived at in specific cases by means of a few preliminary experiments carried out under controlled conditions. Increasing the amount of carboxymethyl cellulose, or using a lower viscosity grade (made from degraded celluloses of relatively low molecular weight) normally increases the time of burning of the product. Thus for example, it is desired to obtain products of increased bulk density and improved handling properties without concomitant modification of the burning time, the addition of the minimum quantity of carboxymethyl cellulose to give the desired result should be the first object. Preliminary experiments should therefore start at the minimum end of the aforesaid range of additions. Carboxymethyl celluloses differing with regard to properties such as viscosity characteristics have the same general effect (depending on course on the proportion thereof added) so that an extensive range of available products can be used.

Temperatures up to boiling temperature, e.g. up to about 100°C, may generally be used, the higher temperatures normally yielding primary explosives having higher bulk densities than those prepared at lower temperatures. However, in the preparation of metal azides such as lead azide it is very advantageous to maintain the temperatures of the solution from which the primary explosive is precipitated close to ambient temperatures, i.e. below about 30°C, since above this first temperature toxic and explosive vapours of volatile hydroscopic acid are evolved, presenting a hazard to operating personnel which can be overcome only by the use of costly ventilating and heating equipment. Furthermore, when the process is carried out at temperatures approximately above ambient temperature, lead azide crystals will form and can explode as the mother liquor cools for example, in gulleys and tanks into which the mother liquor is discharged for disposal. In contradistinction to the present invention, it shall be clear that it is within the scope of the invention to add lead azide according to U.S. Patent No. 2,421,778, as described in the range 30°-80°C and preferably at 50°, and that a precipitation temperature of more than 70°C is required to obtain the desirable value for bulk density achieved by the present invention at a safe precipitation temperature of only 25°C.

The solutions and/or suspensions employed in the precipitation may be used over a wide concentration range. Stirring is preferably maintained throughout the operation. As a rule the conditions normally obtaining for the precipitation operation in respect of a particular primary explosive will broadly hold for the preparation of that explosive in accordance with the invention, except of course that the operation will be carried out in the presence of carboxymethyl cellulose.

The control of bulk density which is afforded by the invention may be utilised for the preparation of products of consistent bulk density from starting materials of variable impurity contents, without the necessity of purifying the latter, since by suitably adapting the conditions of the preparation process, more particularly by appropriately choosing the amount of carboxymethyl cellulose used, in relation to the amount of impurity present in each individual instance, the effect of the impurity on the bulk
density of the explosive product may be compensated for.

In accordance with a feature of the invention, the process for producing a primary explosive compound involves the formation of the primary explosive compound in the presence of a solution containing a carboxymethyl cellulose and also a non-ionic surface-active agent, for example, Enipal A.Q.100 (an ethylene derivative of lauryl and alcohol made by Marchon Products Ltd.) or Laponin N (Imperial Chemical Industries Ltd.).

The presence of the surface-active agent aids the mechanical inter-mixing of the ingredients involved in the formation of the explosive substance and is particularly useful in larger scale processes in increasing further the effectiveness of mechanical stirring. The surface-active agent also advantageously reduces the surface tension of the mother liquor and further increases the effectiveness of the filtering and washing of the product.

By way of example, a description will now be given of the preparation of various primary explosives by processes in accordance with the invention.

**Example 1.**—Sparingly soluble barium stypnate (monohydrated barium salt of trinitroresorcinol) is normally prepared by a double decomposition reaction between aqueous solutions of a barium salt and a salt of trinitroresorcinol consisting of small individual crystals of varying habit according to the precipitation conditions. By carrying out the precipitation in the presence of carboxymethyl cellulose, the product may be obtained in the form of rounded granules possessing exceptionally free-flowing properties and other characteristics of value in an explosive composition. One suitable procedure is as follows:

345.6 ml. of 85% aqueous solution of sodium carboxymethyl cellulose are mixed with 800 ml. of aqueous magnesium stypnate solution containing 196 gms. of stypnic acid and 19.4 gms. of magnesium. The mixture, at normal temperature, is then added during a period of 20 minutes to a stirred solution of 194.5 gms. of barium chloride dihydrate in 800 ml. of water, the temperature of the latter solution being 85°C and this temperature is maintained throughout the addition. Stirring is continued for 15 minutes after completion of the addition, the temperature of 85°C being maintained all the time; the mother liquor is then removed by decantation, e.g., while hot, the product washed twice with water and once with alcohol, dried at 30–40°C, and finally sieved through a No. 5 mesh screen. The product contains 249 gms. equivalent to 80% based on the stypnic acid; the product consists of very free-flowing rounded granules of average particle size 0.22 mm. and bulk density 1.20 gms./ml. This product has excellent properties as a filling for electricity fired gas producers.

**Example 2.**—The process provided by the invention enables a large number of compositions to be prepared from the lead salt of 2,4-dinitroresorcinol, giving a range of products with selected rates of burning and bulk density.

668.6 mls. of aqueous sodium hydroxide solution, containing 70 gms. sodium hydroxide per litre, are slowly added to 780 ml. of stirred aqueous lead acetate solution containing 284.4 gms. of lead acetate trihydrate per litre. The resulting lead hydroxide suspension is washed with water and mixed with 400 ml. of 0.85% aqueous sodium carboxymethyl cellulose solution. The mixture is added during 30 minutes to a stirred solution of 439.3 ml. of aqueous lead acetate solution containing 70 gms. of lead acetate trihydrate per litre and after completion of the addition and after cooling to 20°C the mother liquor is removed by decantation and the product washed with water and alcohol, dried at 40–45°C, and finally sieved through a No. 5 mesh B.S.S. sieve. A granular, free-flowing lead 4:6-dinitroresorcinate suitable for use as a delay and priming composition may be prepared as follows:

439.3 ml. of aqueous sodium hydroxide solution, containing 70 gms. of sodium hydroxide per litre, are added slowly to 512.5 ml. of stirred aqueous lead acetate solution containing 284.4 gms. of lead acetate trihydrate per litre. The resulting suspension of lead hydroxide is washed with water and mixed with 104 ml. of 0.85% aqueous solution of sodium carboxymethyl cellulose. The resulting mixture is then added during a period of 30 min. to a stirred suspension of 35 gms. of 4:6-dinitroresorcinol in 2 litres of water maintained at a temperature of 90°C. Stirring is continued at this temperature for after completion of the addition and after cooling to 20°C.

The mother liquor is removed by decantation and the product washed with water and alcohol, dried at 40–45°C and sieved through a No. 50 mesh B.S.S. sieve.

**Example 4.**—Lead stypnate (normal lead trinitroresorcinate monohydrate), commonly obtained in the form of individual crystals, may, by the process of the invention, be obtained in the form of free-flowing rounded granules, one method of affecting this being as follows:

18 ml. 0.85 per cent aqueous sodium carboxymethyl cellulose is added to 64.3 ml. of an aqueous solution of 15 gms. of 10.1 gms. of stypnic acid and 0.98 g. magnesium having a pH of 4.6. The mixture is stirred and heated to 65°C ±1°C. and 52 ml. lead nitrate solution containing 13.5 g. lead nitrate is added dropwise during 26 minutes the temperature being maintained at 65°C. After further stirring for 5 minutes, cooling to 40°C, and allowing the precipitated lead stypnate to settle, the mother liquor is removed by decantation and the product is washed twice with 120 ml. water. It is finally washed with alcohol, dried on a hot table at 45°C and sieved through a 40 B.S.S. sieve. The product is obtained in a yield of 14.5 g. and consists of free-flowing granules of bulk density 0.7 g./ml. This granular form of lead stypnate has excellent consolidation properties on pressing into sleeves or in pellet form.

**Example 5.**—A solution of magnesium trinitrophloroglucinate was prepared by dissolving 5.22 g. of trinitrophloroglucinate and 2.52 g. of magnesium carbonate in 50 ml. of water at 40°C, filtering and diluting to 200 mls. This solution was added to a stirred solution containing 7.83 g. of barium nitrate and 0.32 g. of sodium carboxymethyl cellulose in 100 ml. of water over a period of ten minutes, the temperature remaining at 40°C. The resulting precipitate of barium trinitrophloroglucinate is washed three times by decantation and dried. 9 g. of granular, free-flowing barium trinitrophloroglucinate containing about 2% of incorporated carboxymethyl cellulose are obtained.

If no carboxymethyl cellulose is present, the product consists of small needle-shaped crystals which are very difficult to process.

**Example 6.**—15 litres of an aqueous solution containing 12 gms. of sodium carboxymethyl cellulose is vigorously stirred in a vessel of 50 litres capacity. 6 litres of aqueous lead acetate solution at a concentration of 315 gms. of lead acetate trihydrate per litre and 6 litres of aqueous sodium azide solution at a concentration of 108 gms. litre are added simultaneously during 60 minutes. All solutions are kept at 20–25°C. After a further 10 minutes stirring, the mother liquor is decanted and the product washed first with water and then with alcohol. The granulated lead azide is finally dried by a current of cold dry air in a porous gutta percha pot. The yield is 1400 grams of dust free and free flowing lead azide of high purity and excellent binding properties when compressed.

**Example 7.**—The use of a non-ionic surface-active agent enables a larger quantity of lead azide to be produced in a 50-litre vessel by an otherwise similar process to that given in Example 6.

14 litres of the lead acetate solution and 14 litres of the sodium azide solution are added simultaneously over
The yield is 3.2–3.3 kg. (i.e., 74.3 g. lead azide per litre of reactant solutions) of lead azide in the form described in the previous example. The lead azide thus produced has an azide value of 96.3 with a mean variation over ten consecutive production runs of 0.2 and has a bulk density of 1.62±0.05 over ten consecutive production runs at a precipitation temperature of 25°C.

Example 8.—Lead azide of very high bulk density can be produced in a 50 litre vessel by a process which is a modification of that described in Example 7.

14 litres of the lead acetate solution and 14 litres of sodium azide solution, containing 108 gms./litre of sodium azide and also about 1 gms./litre of added sodium hydroxide (to give a hydroxide concentration of 0.9–1.3 gms./litre) are added to simultaneously over 60–70 minutes to 15 litres of aqueous solution containing 12 gms. of sodium carboxymethyl cellulose. No surface-active agent is used as foaming would occur. The lead azide obtained has a bulk density of 1.6 gms./ml.

The superiority of lead azide in accordance with the invention over dextrinized lead azide is also shown by the fact that in a given detonator, the length of charge of lead azide in accordance with the invention required to initiate tetryl is only two-thirds of the length of charge of dextrinized lead azide required. Furthermore, whereas dextrinized lead azide requires a pressure of about 24,000 lbs./sq. in. to form pellets and thus very high pressures to be then consolidated into a detonator, lead azide in accordance with the invention forms good pellets with a wide range of pressing loads of 2,650–14,000 lbs./sq. in. on a diameter of 0.23 in. and can then be readily consolidated at a relatively moderate pressure in a detonator or sleeve.

The superior product obtained from a process for manufacturing lead azide in accordance with our invention is demonstrated by test results which compare the lead azide produced in accordance with Example 7 and lead azide produced by the process using polyvinyl alcohol additive as described in U.S. Patent No. 2,421,778, column 3.

The yield per litre of reactant solution is 74.3 g. in our Example 7 whereas the yield obtained by a process in accordance with U.S. Patent No. 2,421,778 is only 27.1 g/litre. The azide value is 95–99 (specific 97.3), whereas in U.S. Patent No. 2,421,778 (Table III) it is 95–99 (specific 95.0), and is thus more consistently above the critical azide value of about 95.

The bulk density of the lead azide prepared as in Example 6 is 1.6 g/ml. at a precipitation temperature of 25°C. Table VI in U.S. Patent No. 2,421,778 shows that the apparent density (i.e., bulk density) is less than 1.0 g/ml. at this precipitation temperature and that even at the unsafe precipitation temperature of 60°C the density rises to only 1.29±0.1 g/ml.

The results show that the present invention produces a considerably higher yield of lead azide with a reproducibly higher azide value and with a higher bulk density and this is much more suitable for automatic filling machines than the prior art product. Furthermore, this high density may be achieved at a safe precipitation temperature of 25°C.

At which dangerous hydrazoic acid fumes are not evolved and the mother liquor cools down from a higher temperature are avoided, whereas the prior art uses a temperature of about 60°C to produce a product with a bulk density of only 1.29.

The manufacture of essentially water-insoluble primary explosives, in accordance with the processes given in the foregoing examples, with appropriate modifications for changes in scale as required, may be carried out in a stainless steel tilting pan fitted with a smoothly-finished paddle-type stirrer, rotatable at a variable speed. For certain primary explosives, for example, lead azide, the stirrer is preferably covered with rubber or plastics material. The desired operating temperature is maintained by providing the jacket around the pan with cold or hot water, or steam as required.

For remote operation there must be provided an arrangement for lifting the stirrer assembly before filling the pan. Alternatively, the stirrer may be fixed and the pan made movable. The pan is fitted with gravity feed tubes from storage vessels arranged above the level of the liquid in the pan. For lead azide preparations feed tubes may be made of gutta-percha.

The general procedure is to add steadily the reactant solution or simultaneously the reactant solutions stored on the underlying side of a protecting wall to a prepared base solution in the pan. At the end of the precipitation or crystallization the stirrer is removed and the mother liquor decanted. The product is washed by stirring in water, removing the wash liquors in the same manner. It is finally transferred by means of a water spray into a filter box or drying pot. Drying is effected by washing with alcohol (methylated spirits) and exposing on a hot table, or alternatively, by passing cold dry air through the drying pot. Final sieving is recommended as a check on drying and to ensure freedom from any oversize aggregations.

The shape and dimensions of the precipitating vessel may be rather critical with respect to stirrer speed but adjustment of stirrer speed will usually compensate for minor differences between various pans and stirrers. For a 10-litre pan, for example the stirrer speed should generally be around 200–250 rev./min. Arrangements for washing, drying and sieving the product are not critical and may be modified to suit the equipment used.

We claim:

1. A process for the manufacture of an essentially water-insoluble primary explosive which comprises precipitating the primary explosive from an aqueous solution containing carboxymethyl cellulose and sodium azide and also about 1 g/litre of added sodium hydroxide (to give a hydroxide concentration of 0.9–1.3 g/litre) at a precipitation temperature of 25°C. The primary explosive comprises primary explosives, for example, lead azide, the stirrer is styphnate to form a precipitate of barium styphnate, preferably covered with rubber or plastics material. The desired operating temperature is maintained by providing the jacket around the pan with cold or hot water, or steam as required.

2. For remote operation there must be provided an arrangement for lifting the stirrer assembly before filling the pan. Alternatively, the stirrer may be fixed and the pan made movable. The pan is fitted with gravity feed tubes from storage vessels arranged above the level of the liquid in the pan. For lead azide preparations feed tubes may be made of gutta-percha.

3. The general procedure is to add steadily the reactant solution or simultaneously the reactant solutions stored on the underlying side of a protecting wall to a prepared base solution in the pan. At the end of the precipitation or crystallization the stirrer is removed and the mother liquor decanted. The product is washed by stirring in water, removing the wash liquors in the same manner. It is finally transferred by means of a water spray into a filter box or drying pot. Drying is effected by washing with alcohol (methylated spirits) and exposing on a hot table, or alternatively, by passing cold dry air through the drying pot. Final sieving is recommended as a check on drying and to ensure freedom from any oversize aggregations.

4. The shape and dimensions of the precipitating vessel may be rather critical with respect to stirrer speed but adjustment of stirrer speed will usually compensate for minor differences between various pans and stirrers. For a 10-litre pan, for example the stirrer speed should generally be around 200–250 rev./min. Arrangements for washing, drying and sieving the product are not critical and may be modified to suit the equipment used.

We claim:

1. A process for the manufacture of an essentially water-insoluble primary explosive which comprises precipitating the primary explosive from an aqueous solution containing carboxymethyl cellulose and sodium azide and containing about 108 gms./litre of sodium azide and also about 1 g/litre of added sodium hydroxide (to give a hydroxide concentration of 0.9–1.3 g/litre) at a precipitation temperature of 25°C.

2. A process according to claim 1 wherein the said aqueous solution contains between about 0.01 to 5% carboxymethyl cellulose by weight of product.

3. A process according to claim 1 in which the said primary explosive is a primary explosive selected from the group consisting of metal azide, metal styphnate and metal salts of dimoyl the said primary explosive, whereby the primary explosive is produced in a granular, free-flowing form which incorporates carboxymethyl cellulose from the said aqueous solution.

4. A process according to claim 1 and in which a non-ionic surface-active agent is present in the aqueous solution containing carboxymethyl cellulose.

5. A process according to claim 4 wherein the non-ionic surface-active agent is an ethylene derivative of lauric acid.

6. A process for the manufacture of an essentially water-insoluble primary explosive in a granular, free-flowing form which comprises forming an aqueous solution of carboxymethyl cellulose and containing two compounds which can react with each other to form an essentially water-insoluble primary explosive, with the said two compounds to form a precipitate of the said primary explosive having carboxymethyl cellulose from the solution incorporated therewith, separating the precipitated primary explosive and drying the primary explosive, whereby the primary explosive containing carboxymethyl cellulose are obtained.

7. A process according to claim 6 wherein the said aqueous solution contains between about 0.01 to 5% carboxymethyl cellulose by weight of the product.

8. A process for the manufacture of barium styphnate which comprises forming an aqueous solution of carboxymethyl cellulose, internitrosating this solution with reactive aqueous solutions of barium chloride and magnesium styphnate to form a precipitate of barium styphnate,
separating and drying the precipitated barium styphnate, whereby barium styphnate is obtained in a granular, free-flowing form which incorporates carboxymethyl cellulose.

9. A process for the manufacture of lead 2:4-dinitroresorinate which comprises forming an aqueous solution of carboxymethyl cellulose, intermixing this solution with reactant aqueous suspensions of 2:4-dinitroresorcinol and lead hydroxide to form a precipitate of lead 2:4-dinitroresorinate, and separating and drying the precipitated lead 2:4-dinitroresorinate, whereby lead 2:4-dinitroresorinate is obtained in a granular, free-flowing form which incorporates carboxymethyl cellulose.

10. A process for the manufacture of lead 4:6-dinitroresorinate which comprises forming an aqueous solution of carboxymethyl cellulose, intermixing this solution with reactant aqueous suspensions of 4:6-dinitroresorcinol and lead hydroxide to form a precipitate of lead 4:6-dinitroresorinate, separating and drying the precipitated lead 4:6-dinitroresorinate, whereby lead 4:6-dinitroresorinate is obtained in a granular, free-flowing form which incorporates carboxymethyl cellulose.

11. A process for the manufacture of lead azide which comprises forming an aqueous solution of carboxymethyl cellulose, intermixing this solution with reactant aqueous solutions of sodium azide and lead acetate to form a precipitate of lead azide, whereby lead azide is obtained in a granular, free-flowing form which incorporates carboxymethyl cellulose.

12. A process for the manufacture of lead styphnate which comprises forming an aqueous solution of carboxymethyl cellulose, intermixing this solution with reactant aqueous solutions of magnesium styphnate and lead nitrate to form a precipitate of lead styphnate, separating and drying the precipitated lead styphnate, whereby lead styphnate is obtained in a granular, free-flowing form which incorporates carboxymethyl cellulose.

13. A process for the manufacture of barium trinitrophloroglucinate which comprises forming an aqueous solution of carboxymethyl cellulose, intermixing this solution with reactant aqueous solutions of magnesium trinitrophloroglucinate and barium nitrate to form a precipitate of barium trinitrophloroglucinate, separating and drying the precipitated barium trinitrophloroglucinate, whereby barium trinitrophloroglucinate is obtained in a granular, free-flowing form which incorporates carboxymethyl cellulose.

14. An explosive composition which comprises a water-insoluble primary explosive containing from about 0.05 to 3 percent of carboxymethyl cellulose incorporated therewith.

15. An explosive composition according to claim 14 which contains 0.1 to 1 percent of carboxymethyl cellulose.

16. An explosive composition according to claim 14 wherein the primary explosive is barium styphnate.

17. An explosive composition according to claim 14 wherein the primary explosive is lead 2:4-dinitroresorinate.

18. An explosive composition according to claim 14 wherein the primary explosive is lead 4:6-dinitroresorinate.

19. An explosive composition according to claim 14 wherein the primary explosive is lead azide.

20. An explosive composition according to claim 15 wherein the primary explosive is lead azide.

21. An explosive composition according to claim 14 wherein the primary explosive is barium trinitrophloroglucinate.

22. An explosive composition according to claim 14 wherein the primary explosive is lead styphnate.

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