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LEAD STYPHNATE CONTAINING METHYL CELLULOSE

George William Charles Taylor, Waltham Abbey, Essex, and Stanley Edward Napier, Tilehurst, Reading, England, assignors to Minister of Aviation in Her Britannic Majesty's Government of the United Kingdom of Great Britain and Northern Ireland, London, England
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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 the primary explosive lead styphnate.

Primary explosive such as lead styphnate 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 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 accident 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 experiment and testing.

Lead styphnate, the primary explosive with which the present invention is concerned, is a crystalline essentially water-insoluble compound which may generally be prepared by precipitating the primary explosive from aqueous solution, the precipitation resulting from a double decomposition reaction between two suitable reactants in aqueous solution or suspension, or from the crystallisation of the primary explosive from solution. Such products tend to be variable in crystal size and shape and frequently contain very small crystal particles and fragments which increase the danger of accidental mechanical and electrostatic ignition.

Attempts have been made to improve the properties of certain primary explosives by varying the conditions under which the primary explosives are precipitated, or by incorporating adulterants in the primary explosive during precipitation, but little attention has hitherto been paid to lead styphnate. The sensitiveness of various primary explosives to accidental ignition has been reduced 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) and generally has other disadvantages.

For example, the primary explosive lead azide is a powerful initiator and is dangerously sensitive when pure, but 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 "dextrinated lead azide" which although comparatively safe to handle, shows a marked decrease in initiating power and ignitability and also lack of consistency and good storage properties because dextrin is a natural product which is hygroscopic and varies widely in composition from batch to batch. Because of this marked reduction in initiating power, dextrin is only of practical use in the preparation of the powerful lead azide.

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 sug-

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gests that the use of these synthetic additives which can be precisely formulated avoids the formulation problems associated with dextrinated lead azide and can be applied to the manufacture of other primary explosives including lead styphnate. Lead azide prepared in a typical manner according to U.S. Patent No. 2,421,778 however consists 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 such as lead styphnate in such a crystalline form is furthermore not easily washed or dried and cannot be readily handled or pre-pelleted.

U.S. Patent No. 2,295,104 suggests that gum arabic may be used as an additive in the preparation of lead styphnate, but lead styphnate so manufactured would be inconsistent and unreliable because gum arabic is a natural product subject to bacterial degradation and which is very hydrophilic, and therefore renders the lead styphnate hygroscopic to an objectionable extent.

An object of the present invention is to provide a process for the manufacture of lead styphnate in a granular free-flowing form which is particularly suited to use in modern automatic filling machines.

It is another object to provide a process for the manufacture of lead styphnate in high yield and in which the characteristics of the lead styphnate so produced show no significant variation from batch to batch.

A further object is to provide a granular lead styphnate which is substantially free from crystal fragments and dust and in which well-defined crystal faces and projections likely to cause accidental ignition of the explosive are virtually eliminated.

Another important object is to provide lead styphnate in a granular form which when pressed on to bridge wires in electric detonators breaks down into a finely-divided form which functions reliably and consistently.

Other objects and advantages of the present invention will be hereinafter apparent.

In accordance with the invention lead styphnate is manufactured in a desired physical form by precipitating lead styphnate from an aqueous solution containing methyl cellulose.

A process for the manufacture of lead styphnate thus usually comprises reacting an aqueous solution of a salt of styphnic acid with an aqueous solution of a soluble lead salt in the presence of methyl cellulose to form a precipitate of lead styphnate, and separating and drying the precipitate, whereby lead styphnate is obtained in a granular, free flowing form which incorporates methyl cellulose, which is found to be evenly distributed throughout the granules. It should be noted however that the mode of action of the methyl cellulose in the precipitation of lead styphnate is in contrast to the action of carboxymethyl cellulose, as it does not form an insoluble metal salt in the precipitation medium and thus cannot provide insoluble salt nuclei around which the granules of primary explosive might form.

An important feature of granular lead styphnate produced in accordance with the present invention is that although the size of the granules is especially suitable for loading processes the constituent crystals in each granule are extremely small and comparable in size with ball-milled explosive. Thus for electric priming purposes the superior igniting properties of finely-divided lead styphnate are obtained without the disadvantages of ball-milling and without the difficulties entailed in handling ball-milled explosive.

The precipitation of lead styphnate from solution is generally achieved by reaction between two reactants dissolved or suspended in an aqueous solution containing methyl cellulose, but it may also be possible to achieve

precipitation by crystallisation or recrystallisation of the explosive from an aqueous solution containing methyl cellulose. In carrying out a process in accordance with the invention, where the precipitation of lead styphnate is by reaction, methyl cellulose may be added to one or both of the solutions interacting to produce the precipitation, or the interacting solutions may be introduced, preferably substantially simultaneously, into a solution containing methyl cellulose.

The temperature at which the precipitation is carried out is important in determining the characteristics of the lead styphnate produced. Precipitation temperatures in accordance with the invention may be in a range of about 50° to 100° C. and are preferably between about 70° to 90° C. In general, a low precipitation temperature in the given range yields a lead styphnate product with a greater burning rate than the product produced at a higher precipitation temperature and it is therefore possible to select precipitation temperatures to yield lead styphnate having a chosen burning rate. Thus lead styphnate precipitated at 70° C. as described in Example 2 of the following examples has a sufficiently slow burning rate for the product to be an excellent fast delay composition, whereas the product precipitated at 90° C. as described in Example 3 has a higher burning rate and is very suitable as a priming composition.

The choice of precipitation temperatures may affect the grade of methyl cellulose selected for use in the precipitation and the properties of the methyl cellulose itself form an important aspect of the present invention. Methyl cellulose which is water-soluble with a methoxyl content of 16–30% is unusual in that its solubility in water decreases with increasing temperature and consequently a particular concentration of a given grade of methyl cellulose possesses a "coagulation temperature" above which the methyl cellulose will not remain completely dissolved. Commercially, water-soluble grades of methyl cellulose are identified by their molecular weight (i.e. viscosity) and coagulation temperature. The coagulation temperature of the methyl cellulose should roughly be of the same order as the temperature of precipitation, that is within about 15° C. of the precipitation temperature, and a grade of methyl cellulose having a coagulation temperature of 70°–75° C. may conveniently be used in the preparation of lead styphnate in accordance with the invention. The inverse solubility characteristics of methyl cellulose are of particular advantage in the preparation of the lead styphnate of the present invention as any methyl cellulose deposited on the surface of the lead styphnate granules during precipitation will be dissolved as the precipitation liquor is cooled without affecting the methyl cellulose dispersed within the granules. In this way no coating of non-explosive methyl cellulose is left upon the granules of lead styphnate and the readiness of the primary explosive containing methyl cellulose to ignite is thus advantageously not greatly less than that of pure lead styphnate. Also there is a reduced tendency of the granules to stick together and form aggregates which would impair their highly satisfactory free-flowing properties.

The proportion of methyl cellulose of whatever grade used, whether it is added to one or more of the reacting solutions involved and the rate of admixture of the solutions or the rate of crystallisation, besides the temperature of the reaction, all influence to a greater or lesser degree the properties of the final product.

Methyl cellulose is often effective when present in the solution in a quantity as low as 0.05% of the weight of the yield of lead styphnate and for initiatory purposes up to 1% is generally used; but larger amounts, e.g. up to 10% in solution may be used especially for delay purposes. Generally speaking, the greater the amount of methyl cellulose employed the higher is the bulk density and particle size of the product.

Methyl cellulose is generally more effective in a form

having a relatively high molecular weight which produces more viscous solutions so that a given modification of physical properties of lead styphnate is usually obtained by using a lower proportion of a higher molecular weight methyl cellulose than is required when a lower molecular weight methyl cellulose is used.

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 methyl cellulose, or using a lower viscosity grade increases the time of burning of the product. Thus for example, if it is desired to obtain products of increased bulk density and improved flowing properties without concomitant modification of the burning time, the addition of the minimum quantity of methyl 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. Methyl celluloses differing with regard to properties such as viscosity characteristics have the same general effect (depending of course on the proportion thereof added) so that an extensive range of available products can be used.

In general, not all the methyl cellulose present in solution is incorporated in the lead styphnate product, a certain proportion being retained in the mother liquor throughout precipitation and a further proportion being dissolved from the methyl cellulose coating on the precipitated granules as the mother liquor cools. The unincorporated portion increases with increasing methyl cellulose concentration in the precipitation solution, thus for example when the methyl cellulose concentration in solution is 10% only about half of this quantity of the methyl cellulose is actually incorporated into the lead styphnate product.

Typical examples of the preparation of granular, free-flowing lead styphnate in accordance with the invention will now be given.

Example 1

19 mls. of aqueous methyl cellulose solution (containing 1% by weight of methyl cellulose having a coagulation temperature of 70°–75° C. and a viscosity of 87 centipoises in 1% by weight aqueous solution at 25° C.) are added with stirring to 205 mls. of aqueous magnesium styphnate solution containing 10.0 g. of styphnic acid and 0.747 g. of magnesium. The mixture is heated to 80° C. and 51.8 mls. of aqueous lead nitrate solution (containing 13.57 g. of lead nitrate per litre) are added with stirring over a period of 30 minutes. Stirring is continued for a further 5 minutes and the precipitated lead styphnate is allowed to settle. The mother liquor and precipitate is cooled to 30° C., the mother liquor is decanted off and the precipitate is washed with water and alcohol. After drying at 40°–45° C., the product is obtained in the form of characteristic compact granules which are very free-flowing and have good priming properties.

Example 2

0.257 l. of aqueous methyl cellulose solution (containing 1% by weight of methyl cellulose having a coagulation temperature and viscosity as given in Example 1) are added to 2.167 litres of aqueous magnesium styphnate solution (containing 125 g. of styphnic acid and 15.5 g. of magnesium oxide per litre) and 1.569 l. distilled water. The temperature of the resulting solution is raised to 70° C. and 1.4 l. of aqueous lead nitrate solution (containing 262 g. lead nitrate per litre) is added with stirring during 20 minutes. Stirring is maintained for a further 15 minutes and the solutions are cooled to 40° C. The precipitated lead styphnate is allowed to settle and the mother liquor is decanted. The precipitate is washed successively with water and alcohol and dried at 50° C. on a hot table. 245 g. of granular, free flowing lead

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styphnate obtained having a bulk (apparent) density of 0.46 g./ml. This product is an excellent fast delay composition.

Example 3

0.276 l. of an aqueous methyl cellulose solution (containing 1% by weight of methyl cellulose having a coagulation temperature and viscosity as given in Example 1) are added to 2.320 litres aqueous magnesium styphnate solution (containing 125 g. styphnic acid and 15.5 g. magnesium oxide per litre) and 1.636 l. distilled water. The mixture is heated to 90° C. and 1.5 l. aqueous lead nitrate solution is added with stirring during 20 minutes. Stirring is continued for a further five minutes and the precipitated lead styphnate is allowed to settle. The mother liquor is decanted and the lead styphnate product is washed successively with water and alcohol and dried at 50° C. 260 g. of granular, free-flowing product having a bulk density of 0.46 g./ml. is obtained which is an excellent priming composition. In addition, when the product is pressed on to bridge wires in electrical detonators it breaks down to a finely divided form which has very good functioning properties. It may thus be used as a replacement for the form of finely-divided lead styphnate at present commonly used in electrical detonators which is manufactured by the hazardous and time-consuming process of ball-milling coarser grades of lead styphnate to the required size.

The manufacture of lead styphnate, in accordance with the processes given in the foregoing examples, with appropriate modifications for changes in scale as required, may be carried in a stainless steel tilting pan fitted with a smoothly-finished paddle-type stirrer, rotatable at a variable speed. The desired operating temperature is maintained by providing the jacket round 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 tilting the pan. Alternatively, the stirrer may be fixed and the pan made removable. The pan is fitted with gravity feed tubes from storage vessels arranged above the level of the liquid in the pan.

The general procedure is to add steadily the reactant solution or simultaneously the reactant solutions stored on the operating side of a protecting wall to a prepared base solution in the pan. At the end of the precipitation or crystallisation 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

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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 lead styphnate which comprises precipitating the lead styphnate from an aqueous solution containing methyl cellulose, separating the precipitated lead styphnate from the said solution and drying the precipitate, whereby lead styphnate is produced in a granular, free-flowing form which incorporates methyl cellulose.

2. A process for the manufacture of lead styphnate which comprises forming an aqueous solution of methyl cellulose and two reactant compounds which can react with each other to form lead styphnate, reacting the said two reactant compounds to form a precipitate of lead styphnate having methyl cellulose from the solution incorporated therewith, separating the precipitated lead styphnate and drying the separated lead styphnate, whereby free-flowing granules of lead styphnate containing methyl cellulose are obtained.

3. A process according to claim 2 wherein the said two reactant compounds are a soluble lead salt and a soluble metal salt of styphnic acid.

4. A process according to claim 2 wherein the soluble lead salt is lead nitrate and the soluble metal salt of styphnic acid is magnesium styphnate.

5. A process according to claim 2 wherein the said aqueous solution of methyl cellulose contains between about 0.05 to 10% methyl cellulose by weight.

6. A process according to claim 2 wherein the said aqueous solution contains between about 0.1 to 2% methyl cellulose by weight.

7. A process according to claim 2 in which the temperature at which the reaction is carried out is between about 50°–100° C.

8. A process according to claim 7 wherein the temperature is within the range 70°–90° C.

9. A granular lead styphnate having a small proportion of methyl cellulose incorporated therewith.

10. A granular lead styphnate according to claim 9 wherein the proportion of methyl cellulose incorporated is between 0.05–5% by weight.

11. A granular lead styphnate according to claim 9 wherein the proportion of methyl cellulose incorporated is between about 0.1 to 1%.

References Cited by the Examiner

FOREIGN PATENTS

849,101 9/1960 Great Britain.

BENJAMIN R. PADGETT, *Primary Examiner*.

L. A. SEBASTIAN, *Assistant Examiner*.