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NORMAL LEAD STYPHNATE AND A METHOD OF MAKING IT

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This invention relates to a new explosive and method of making the same.

It has heretofore been proposed to employ lead styphnate, the normal lead salt of trinitroresorcinol, as an initiator in priming mixtures for small arms ammunition in place of mercury fulminate. The adoption of this material has been retarded because of its hazardous characteristics and its tendency to detonate when detonation is not intended. We have found that the physical form of the material heretofore employed has been the cause of its unsafe characteristics and we have developed a new form, or crystalline structure, whereby a product may be produced which is relatively safe to use and is not subject to accidental detonation. In the method heretofore employed a suspension of trinitroresorcinol or styphnic acid was added to a solution of sodium carbonate or magnesium hydroxide and the lead styphnate precipitated therefrom at a high temperature, generally about 60° C. This resulted in the production of prismatic crystals having a relatively low ratio of surface area to volume. This material, when submitted to the burning test frequently employed to determine the safety of initiators, will burn indicating that it is unsafe for use in the manufacture of primers.

The burning test consists of taking a quantity of the material to be tested containing from 15 to 30 percent of water, placing black powder on it and lighting the powder. If the material does not burn, it is considered safe to use in the compounding of priming mixtures by the wet process, but if the material does burn under such conditions, it is an indication that it is apt to deflagrate or detonate in the wet state while being handled and is therefore considered unsafe.

In carrying out the process of our invention, we employ styphnic acid containing an impurity or adulterant. For this purpose we use the nitrated product or products of one or more of the compounds formed by reaction of nitrous and nitric oxides wth resorcine. These include the nitro derivatives of resorufin, the nitro derivatives of indo-phenol and the nitro derivatives of resazurin. Salts of these compounds may also be used, such as the lead salt of nitroresorufin. Mixtures of the above materials may also be used. Thus we have found that, under some conditions better results are obtained when a mxture of nitroresorufin and nitroindophenol or nitroresazurin is used than when either of them is used alone. In the commercial manufacture of styphnic acid, resorcine is first sulphonated with 90 percent sulphuric acid. After the sulphonation is complete, nitric acid is added, the material nitrated and the styphnic acid precipitated. When the material is manufactured on a commercial scale, it frequently happens that small amounts of nitrous and nitric oxides are present during the sulphonation. This produces a dark brown material which contains some or all of the above compounds as impurities. If pure sulphuric acid is used in the sulphonation, a very light product is obtained which is relatively pure styphnic acid. In practicing the process of the present invention, the dark brown material may be employed and the desired results obtained whereas if the light product is employed, a requisite amount of one or more of the nitrated products of the above mentioned compounds must be added to it.

In carrying out the process of the present invention and producing the product of the present invention, styphnic acid containing the requisite amount of one of the adulterants referred to above is suspended in water and then mixed with a solution of sodium hydroxide. One feature of the invention is the use of a suspension of styphnic acid and a solution of sodium hydroxide which will produce a relatively concentrated solution of sodium styphnate. In the preferred practice of the process as set forth herein, we employ sodium styphnate solutions of about twice the strength of those employed in the old process. The sodium styphnate solution which we employ is at slightly less than the saturation point at room temperature. As the process is carried out at an elevated temperature, no difficulty is experienced in keeping the sodium styphnate in solution. The temperature of the material is maintained at about 55° C. A solution of lead nitrate containing glacial acetic acid is then added to the first solution. The lead nitrate solution is first added slowly at a temperature between 54 and 56° C. and the temperature is then raised to 60° C. During the latter part of the precipitation the lead nitrate addition is speeded up. When this method of precipitating lead styphnate is followed, the material first begins to precipitate as a gel. With continuous stirring this gel, during the further addition of the lead nitrate solution, begins to break up and form a thick slurry which eventually changes from a yellow to a brown color and at the same time dissolves. The lead styphnate finally precipitates in the form of substantially hexagonal plate-like crystals. These crystals are thin and have a large ratio of surface area to volume. When subjected to the burning test, they do not burn when they contain

15 percent or more of water. Because of the safe condition of this product in the wet state in which it is normally used during the compounding of priming mixtures, it possesses a marked advantage over the old form of lead styphnate heretofore employed in priming mixtures.

While we do not wish to limit ourselves to the exact size of the plate-like crystals which we have produced, the following data is given as illustrative of the product obtained by the process of the present invention. The largest crystals measure .022 cm. along the longest axis, .020 cm. in width and approximately .003 cm. in thickness. The average size of the crystals in the batch from which the above measurements were obtained was .008 cm. x .006 cm. x .001 cm. The ratio of surface to volume in such crystals is more than twice that of the prismatic crystal of comparable size and this is a possible explanation of the difference in the burning properties of the two crystals. In the hexagonal plate-like crystal this ratio remains substantially constant because the smallest dimension, the thickness does not change greatly with increase in size, whereas in the prismatic crystal the ratio is an inverse function of the size, the shape of the crystal being the same for all sizes.

We have found several features of the process which are of importance in obtaining the desired product. One is that the gel form quickly and completely and that it break up soon after forming. This gel is probably a hydrated salt and if it forms only partially and does not thicken entirely, the final product does not have the desired properties found when the reaction goes smoothly. If the gel persists too long in the "solid" form the final product is not as uniform as otherwise.

The factors which control the precipitation of the lead styphnate as a hydrated gel are apparently the control of temperature and regulation of the addition of the lead nitrate-acetic acid solution together with the correct ratio of sodium hydroxide to acetic acid. After the complete precipitation of the lead salt as a hydrated gel, a rapid transformation to the crystalline state is necessary. This may be controlled by either an increase in the concentration of acetic acid or an increase in temperature or both.

Another factor is the strength of the sodium styphnate solution. As stated, we preferably employ a solution slightly less than the saturation point at room temperature. This may be varied, however. A concentration one-half as strong as that set forth herein is unsuitable and a concentration 50 percent higher, while workable, tends to become too stiff during the gel stage and is therefore not as convenient to handle. The principal controlling factors are, therefore, concentration of the sodium styphnate solution, time of addition of solutions, temperatures, and ratio of acetic acid to sodium hydroxide. If one of these factors is changed, the other three may be varied to compensate for this change. It is necessary in all cases, however, to employ a strength of sodium styphnate solution and a ratio of acetic acid to sodium hydroxide which will cause the precipitation to form first as a gel and then as the plate-like crystals as additional lead nitrate, acetic acid solution is added. The acetic acid increases the solubility and therefore permits the formation of the separate plate-like crystals without further growth into the prismatic crystals.

In carrying out a typical example of the invention a suspension of styphnic acid in water is first prepared. If the styphnic acid is the relatively impure material characterized by dark brown color, the desired results can be obtained without any additional material being added to it. If it is relatively pure styphnic acid characterized by a light color, 8 grams of nitroresorufin are added to each 450 grams of styphnic acid. Instead of nitroresorufin any of the other materials mentioned above may be used. A typical example may consist of the addition of 450 grams of styphnic acid to 5 liters of water. This is placed in a pail or container and preferably located in a water bath to control the temperature. A solution of 1500 cc. of water containing 500 grams of sodium hydroxide is then prepared. This solution is stirred until the sodium hydroxide is completely dissolved and 520 grams of it is added to the styphnic acid suspension. The sodium hydroxide solution is added slowly to the styphnic acid suspension with a temperature of the latter at about 50° C. The sodium hydroxide solution is at a temperature of about 60° C. and upon its addition to the suspension the temperature of the pail or container rises. It should be maintained at about 55° C.

A solution of lead nitrate is prepared by adding 13,800 grams of lead nitrate to 36 liters of water. This solution is prepared without agitation and is preferably placed in the tank containing the water in a leaching box and allowed to stand over night. When the lead nitrate solution is complete, 2280 cc. of glacial acetic acid are added for a period of one minute with stirring. The solution is then stirred for about five minutes and quantities of 2500 cc. each are run into calibrated delivery flasks.

With the lead nitrate solution prepared as described and with the sodium styphnate solution at a temperature of about 55° C., precipitation of lead styphnate is begun. The lead nitrate solution is allowed to drip into the sodium styphnate solution slowly. The first 600 cc. of lead nitrate solution is added in approximately twelve minutes and the remainder in about thirty-five minutes. The temperature is maintained between 54° C. and 56° C. for the first twelve minutes and is then raised to 60° C. for the remainder of the addition. When from 400 to 500 cc. of the lead nitrate solution has been added to the sodium styphnate solution, a gel begins to form which changes quickly in color from black to brown and to a bright yellow until a point is reached at which all surface motion ceases. At that time the containers apparently contain only masses of thick yellow flocs, non-crystalline in appearance. At this time the addition of lead nitrate is speeded up and the temperature of the water bath must be raised to about 70° C. to keep the container at a temperature of 60° C.

In from two to ten minutes, depending upon the efficiency of stirring, the gel begins to break up and form a thick slurry which eventually changes from a yellow to a brown color and at the same time dissolves. Solution of the gel is apparently complete when approximately 2000 cc. of the lead nitrate solution has been added and no visible change occurs from this point to the end of the addition.

When nitroresorufin is added to the light colored styphnic acid, the procedure is slightly varied. The quantity of sodium hydroxide is increased slightly and 25 cc. of glacial acetic acid is added to the sodium styphnate solution. The starting temperature is about 56° C. and during

the gel stage the temperature drops to about 51 to 52° C. but as stirring becomes more efficient, the temperature rises to approximately 55° C. The time of addition is ten minutes for the first 500 cc. of lead nitrate-acetic acid solution. This rate is continued until about 750 cc. has been added. At this point the gel begins to break up and the addition is speeded up so that the entire solution is added in 30 to 35 minutes.

As stated above, the process heretofore outlined produces a new product in that the lead styphnate is in the form of plate-like crystals having a large ratio of surface area to volume, as distinguished from the prismatic crystals heretofore produced. By following the process and obtaining complete precipitation of the lead styphnate as a hydrated gel followed by a rapid transformation to the crystalline state, this desirable product is obtained. Among its many advantages over previous methods the following may be noted:

1. The product is more uniform. The crystals are either uniformly large or uniformly small within a given batch, the extreme variation is quite small.

2. The product passes the burning test regardless of crystal size.

3. The method allows the precipitation of larger quantities in each working batch.

4. An increase in the percentage yield is obtained.

5. Control of the method is much easier than in previous methods, a greater leeway in the time, temperature and concentration factors is possible without seriously affecting the product.

Perhaps the greatest advantage, however, of the plate-like crystals over the prismatic crystals is the greater safety of the product and the consequent lesser possibility of injury to workmen in the handling of it. This is probably due to the fact that the larger surface area allows a more effective wetting of the crystals. This permits a much wider range of crystal size and still be within the limitation of satisfactory functioning when subjected to the burning test.

The data given above with respect to the size of crystals relates to crystals from a single batch. Typical average size crystals obtained from many batches is .007 cm. along the longest axis, .005 cm. in width and approximately .0015 cm in thickness. In a crystal of such size the ratio of square centimeters of area to cubic centimeters of volume is approximately 24 to 1. This is more than twice that in the prismatic crystal. In a prismatic crystal of comparable size, the ratio of square centimeters of area to cubic centimeters of volume is approximately 10 to 1. The ratio for the prismatic decreases as the size of the crystals increases but remains substantially the same for all size of crystals of the hexagonal type.

In the claims the term "sodium styphnate" is intended to include the commercial product which is a dark brown material containing as impurities or adulterants one or more of the nitro derivatives of resorufin, indophenol and resazurin.

We claim:

1. As a new product, normal lead styphnate in the form of plate-like crystals.

2. As a new product, normal lead styphnate in the form of plate-like crystals of approximately .003 cm. thickness.

3. As a new product, normal lead styphnate in the form of plate-like crystals of an average thickness of .001 cm.

4. As a new product, normal lead styphnate in the form of plate-like crystals of an average size of approximately .007 cm. x .005 cm. x .0015 cm.

5. As a new product, normal lead styphnate in the form of plate-like crystals wherein the ratio of square centimeters of surface to cubic centimeters of volume is approximately 24 to 1.

6. The herein described method which comprises forming a solution of sodium styphnate, adding a solution of lead nitrate and acetic acid, concentrated with regard to lead nitrate and dilute with regard to acetic acid, thereto at such temperature that a gel is precipitated, and continuing the addition of the lead nitrate-acetic acid solution until lead styphnate is precipitated in crystalline form.

7. The process of claim 6 wherein the sodium styphnate solution is prepared from styphnic acid containing an adulterant from the group consisting of the nitro derivatives of resorufin, indophenol and resazurin.

8. The herein described process which comprises adding sodium hydroxide to styphnate acid at a temperature of substantially 55° C., then adding a solution of lead nitrate and acetic acid, concentrated with regard to lead nitrate and dilute with regard to acetic acid, thereto at such temperature that a gel is precipitated and then continuing the addition of the lead nitrate-acetic acid solution until lead styphnate is precipitated in crystalline form.

9. The herein described process which comprises preparing a solution of sodium styphnate, adding a solutions of lead nitrate and acetic acid, concentrated with regard to lead nitrate and dilute with regard to acetic acid, thereto at a temperature of substantially 55° C. until a gel is precipitated, and adding additional lead nitrate-acetic acid solution thereto at a temperature substantially 60° C. until lead styphnate is precipitated in the form of crystals.

10. In the process of manufacturing lead styphnate, the steps comprising precipitating a gel from a solution of sodium styphnate, and then adding a concentrated lead nitrate-dilute acetic acid solution thereto at a temperature of substantially 60° C. to precipitate the lead styphnate in crystalline form.

11. In the process of manufacturing lead styphnate, the steps comprising precipitating a gel from a solution of sodium styphnate and then adding a concentrated lead nitrate-dilute acetic acid solution thereto to precipitate the lead styphnate in crystalline form.

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