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## INITIATING EXPLOSIVES

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This invention relates to explosives and particularly to improvements in the manufacture of lead azide.

It has heretofore been known that crystalline lead azide of extremely high purity displays outstanding initiating power for high explosives. However, such lead azide has also been recognized as relatively hazardous, and its use has been limited because of the extraordinary precautions which are necessary in its handling and loading.

In order to improve the handling properties, it has been proposed that an adulterant such as glue, gelatin, or dextrin, be employed during the precipitation of lead azide to yield a product which is devoid of crystal faces and has a lowered azide content. Dextrin has been the most commonly used adulterant for this purpose, and the resulting product has generally contained less than 95% lead azide, the balance consisting of adsorbed adulterant and so-called basic lead azide.

While dextrinated lead azide displays appreciably improved handling properties as compared to crystalline lead azide of high purity, the ignitibility and the initiating power are simultaneously decreased. One result is that an auxiliary ignition agent such as lead styphnate has to be added to insure the ignition of lead azide initiating charges in blasting caps and shell detonators. Another consequence is that larger weights of azide must be used in detonators for initiating the relatively insensitive base charges of high explosive.

Furthermore, adulterated lead azides, such as that prepared with dextrin, have displayed variations in physical and explosive properties despite all precautions to insure uniformity. For example, supposedly identical lots differ appreciably in apparent density and in sensitivity to shock, and on occasion highly sensitive lots are obtained.

It is the object of this invention to overcome these difficulties by the provision of improvements in the manufacture of lead azide whereby a crystalline product may be obtained which possesses initiating power and ignitibility similar to those of pure lead azide, but at the same time displays no greater or less sensitivity to shock than the best dextrinated lead azide heretofore known. Another object is the provision of a class of ingredients for use in the manufacture of initiating explosives, such as lead azide, whereby the product is obtained in the form of crystals within a desired size range, characterized by the substantial absence of unduly coarse crystals or

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fine particles, and which display favorable handling and loading characteristics.

It has now been found that the foregoing desired results may be obtained by forming lead azide crystals in the presence of a dissolved synthetic organic polymer. Typical substances of this class which may advantageously be employed in the formation of desirable lead azide crystals from aqueous solution are the polyvinyl alcohols, polyethylene glycols, and the water-soluble polymers obtained by the interaction of an aldehyde and an amino compound, exemplified respectively by formaldehyde and urea. These materials have the property of promoting the formation of lead azide crystals of desirable physical and explosive properties. The effect thus differs markedly from that of the adulterants which have heretofore been employed in the preparation of lead azide.

Adulterants such as dextrin, glue, and gelatin tend to suppress the crystallinity of lead azide so that the resulting product consists essentially of minute particles, or agglomerates thereof, or of particles which are devoid of clearly defined crystal faces. Furthermore, appreciable amounts, up to several percent, of the adulterant employed are retained in the resulting lead azide product even after thorough washing.

It will furthermore be observed that the adulterants heretofore proposed for use in the manufacture of lead azide have consisted of materials obtained through partial decomposition of raw materials such as starch which are known to display variable composition. This may well be an important cause of the variations which have been observed in adulterated lead azides of the prior art. This factor does not exist in connection with the control ingredients of this invention, since they consist of polymers which are synthesized from simple compounds of controlled composition under reproducible conditions.

In accordance with this invention, therefore, desirable crystals of lead azide are formed in the presence of a dissolved synthetic organic polymer. When the precipitation of the lead azide is effected by the gradual addition of an aqueous solution of a soluble azide, for example, sodium or potassium azide, to an aqueous solution of a soluble lead salt, for example lead nitrate or acetate, the presence of an effective amount of the synthetic polymer may be insured by dissolving the same in either or both of the solutions prior to the precipitation. Likewise, if the precipation is carried out by the simultaneous addition of an azide solution and of a lead salt solution to a precipitation bath, the presence of syn-

thetic polymer to promote the formation of desirable crystals of lead azide may be assured by the addition of a solution thereof to the precipitation bath, or more conveniently, by dissolving the same in either or both the azide and the lead salt solution.

In order to illustrate the advantages obtainable in accordance with this invention, comparative tests were made on a series of lead azide samples prepared by the following procedure, some with and some without the improved crystal control ingredients.

A lead nitrate solution, containing 0.22 mole (72.87 grams) of lead nitrate and 0.073 grams of sodium hydroxide per liter, is heated to 59°±1° C. in a suitable vessel.

An equal volume of a sodium azide solution at room temperature, containing 0.40 mole (26.01 grams) of sodium azide and 0.527 gram of sodium hydroxide per liter, is added at a uniform rate with constant stirring to the lead nitrate solution in 28½ minutes.

The precipitated lead azide is allowed to settle and the mother liquor is decanted. The precipitate is then washed by decantation, three times in each case, successively using water, alcohol, and ether. The product, after being dried at 30°–40° C., is passed through a 100 mesh screen.

The following table lists the results which were obtained. The weight of crystal control ingredient is the amount used per liter of the combined solutions.

TABLE I

| | Control Agent | Apparent Density | Impact Sensitivity | Product |
|---|---|---|---|---|
| | | G./c. c. | | |
| Prior Art | None | 1.27 | 23 | Crystalline. |
| Do | 5 g. dextrin | 1.37 | 55 | Non-crystalline. |
| This Invention | 0.1 g. Polyvinyl alcohol | 1.23 | 17 | Crystalline. |
| Do | 0.2 g. Polyvinyl alcohol | 1.23 | 20 | Do. |
| Do | 1.0 g. Polyvinyl alcohol | 1.25 | 30 | Do. |
| Do | 0.2 g. Polyvinyl alcohol (High Viscosity) | 1.19 | 34 | Do. |
| Do | 0.2 "Carbo wax 4000" | 1.36 | 41 | Do. |
| Do | 1.0 "Carbo wax 4000" | 1.46 | 27 | Do. |
| Do | 2.0 "Carbo wax 4000" | 1.46 | 34 | Do. |
| Do | 4.0 "Carbo wax 4000" | 1.50 | 32 | Do. |
| Do | 0.2 "Carbo wax 1500" | 1.43 | 21 | Do. |
| Do | 1.0 "Carbo wax 1500" | 1.40 | 21 | Do. |
| Do | 2.2 Hexaethylene glycol | 1.37 | 23 | Do. |
| Do | 4.4 Hexaethylene glycol | 1.45 | 31 | Do. |
| Do | 0.5 "Uformite" | 1.81 | 45 | Do. |
| Do | 1.0 "Uformite" | 1.77 | 42 | Do. |

In Table I, the "apparent density" gives the weight in grams per cubic centimeter which the product will occupy when poured into a container without pressing. The "impact sensitivity" gives the total number of samples which fired when struck by a 200 gram weight falling from heights of 10, 15, 20, and 25 centimeters (20 trials at each height). The hexaethylene glycol and the "Carbowaxes" are representative polyethylene glycols, while "Uformite" is an example of a water-soluble urea-formaldehyde polymer.

While in the first two samples listed (prior art), appreciable quantities of both coarse and fine particles are present following the precipitation step, the products prepared with the water-soluble organic polymers are remarkably free therefrom. The crystalline lead azides dry more rapidly and flow much more freely than the dextrinated product.

The data in Table I are average values and therefore do not bring out a further important advantage of the synthetic polymer control agents. This is the significantly increased reproducibility of successive lots of lead azide, which is illustrated by the data of Table II, which lists the apparent density of successive lots prepared (*a*) without control agent, (*b*) with dextrin, and (*c*) with a soluble synthetic polymer exemplifying this invention.

TABLE II

*Apparent density (grams/cc.)*

| Control agent | None | Dextrin | Polyvinyl alcohol |
|---|---|---|---|
| | 1.11 | 1.35 | 1.29 |
| | 1.42 | 1.34 | 1.23 |
| | 1.24 | 1.36 | 1.22 |
| | 1.36 | 1.29 | 1.19 |
| | 1.28 | 1.41 | 1.19 |
| | 1.23 | 1.49 | 1.25 |
| Average | 1.27 | 1.37 | 1.23 |
| Extreme Variation | 0.31 | 0.20 | 0.10 |

The increase in the uniformity of the apparent density of the lead azide which is effected in accordance with this invention is of great significance, since it is reflected in more uniform charge weights measured out by the volumetric charging devices commonly used in the art for loading detonators. It is known that the presses employed in the compression of detonator initiating charges of lead azide are sometimes destroyed by the explosion of charges while being pressed. The variation in weight of volumetrically measured charges is believed to be one of the principal causes of such explosions. In fact, certain lots of lead azide may display low sensitivity to impact and to friction, but still be impractical for loading by automatic machinery because of frequent press explosions, which can be ascribed to appreciable variations in the apparent density.

In addition to its other advantages, the crystalline lead azide prepared with the use of a soluble synthetic polymer in accordance with this invention has been shown to function efficiently as an initiator of high explosives. The following table lists typical comparative data which have been obtained.

TABLE III

*Initiating tests*

| Type of lead azide | Per cent $PbN_6$ | | Minimum weight required to initiate tetryl | Detonator function test—No. firing in 20 trials |
|---|---|---|---|---|
| | Range | Specific | | |
| | | | *Grains* | |
| Dextrinated lead azide | 90 –95 | 93.5 | .37–.41 | 10–14 |
| Pure lead azide | 99.2–99.9 | 99.9 | 0.17 | 18 |
| Lead azide of this invention | 95 –97 | 95.0 | 0.21 | 17 |

The "Detonator function test," referred to in Table III, involved the charging of detonators with the different azides, loading the same in explosive projectiles, shooting the projectiles against a standard target, and observing the number out of twenty which exploded properly.

The determination of the minimum initiating charge is a standard test, in which increasing weights of explosive are loaded over a compressed tetryl base charge in fuse-type blasting caps. The latter are fired on lead plates and checked for complete detonation of the base charge by observation of the extent of perforation produced.

The results of comparative ignitibility tests are listed in Table IV. These values were obtained by subjecting the samples to the flame from a standard safety fuse at different distances and recording the percent which fired for each sample.

TABLE IV

*Ignitibility test—% firing*

| Type of lead azide | Distance From Fuse, inches | | | | | |
|---|---|---|---|---|---|---|
| | ½ | 4 | 12 | 16 | 20 | 22 |
| | *Per-cent* | *Per-cent* | *Per-cent* | *Per-cent* | *Per-cent* | *Per-cent* |
| Dextrinated | 100 | 20 | 0 | ------ | ------ | ------ |
| Pure | ------ | ------ | 100 | 80 | 0 | ------ |
| This Invention | ------ | ------ | 100 | 60 | 40 | 0 |

Electrostatic characteristics of different lead azides were determined by means of measurements with an electroscope. Each sample was allowed to stand for sixteen hours and its electrostatic charge was determined. The charge was again measured immediately after each sample had been subjected to the same amount of tumbling. The data which were obtained are given in Table V.

TABLE V

*Electrostatic charge measurements*

| Type of Lead Azide | Before Tumbling | After Tumbling | Increase |
|---|---|---|---|
| | *Volts* | *Volts* | *Volts* |
| Dextrinated | 2.0 | 9.6 | 7.6 |
| Pure | 1.8 | 5.8 | 4.0 |
| This Invention | 0.2 | 0.7 | 0.5 |

The electrostatic characteristics of initiating explosives are of significance with respect to the possible effect on the uniformity in the weight of charges measured out volumetrically. Also, in many cases, the tendency of explosives to detonate during handling appears to parallel the extent to which electrostatic charges can be developed.

It will be seen from the foregoing data that this invention enables the production of lead azide in a form which provides essentially the ignitibility and initiating power of pure lead azide and at the same time greatly improved handling characteristics. Other advantageous features which are obtainable by the described use of water-soluble synthetic organic polymers are the production of crystals within a desirable size range, substantially free from both fine and coarse particles; a desirable apparent density of the product, well adapted for the volumetric measurement of charges intended for subsequent pressing; and in particular, the reproducibility of the desired physical and explosive properties in successive lots which are manufactured.



The fact that the obtainment of the foregoing advantages is peculiarly a function of the soluble synthetic organic polymers has been indicated by comparative experiments showing the ineffectiveness of compounds such as glycerine, sucrose, methyl cellulose, and non-polymeric wetting agents. In order to promote the formation of the desired crystals of initiating explosive from aqueous solution, it is essential in accordance with this invention to utilize as control agent a water-soluble synthetic organic polymer characterized by a molecule containing a repeated unit such as

(—$CH_2$—CHOH—) in polyvinyl alcohols, or
(—$CH_2$—O—$CH_2$—) in polyethylene glycols, or
(—NH—CO—NH—$CH_2$—) in polymethylol ureas.

Inasmuch as the polymers referred to contain terminal hydroxyl groups, they may further be characterized as polyhydroxy compounds.

The proportion of control agent to be used is preferably between 0.1 and 5% by weight of the precipitation bath, but amounts beyond these limits may at times be used effectively. It is furthermore to be understood that the specific directions given above for carrying out the preparation are illustrative and not limiting, the specified control agents being effective in other precipitation procedures. For example, variations may be made in the amounts of reagents, order of mixing, and time and temperature of precipitation.

As illustrative of the fact that advantage may at times be taken of such modifications, reference may be made to the data of the following table, showing the effect of precipitation temperature on the apparent density of crystalline lead azide produced with polyvinyl alcohol (0.2 gram per liter) as the control agent. Since other properties remained essentially constant, the possibility of controlling the apparent density by adjusting the temperature of precipitation is indicated.

TABLE VI

| Precipitation Temperature, degrees | Apparent Density |
|---|---|
| 30 | 1.00 |
| 40 | 1.05 |
| 50 | 1.15 |
| 60 | 1.29 |
| 70 | 1.38 |
| 80 | 1.75 |

A further advantage of the specified class of control agent is that a smaller amount is retained in the product than has been the case with the adulterants heretofore used in the manufacture of lead azide. One result is that the crystalline product of this invention, containing from a trace to not more than about one percent of synthetic organic polymer, has substantially the non-hygroscopicity of pure lead azide. This is in contrast to dextrinated, and other adulterated, lead azides which contain several percent of the adulterant and display appreciable hygroscopicity. The product of this invention is therefore characterized by the presence of a trace to about one percent of a water-soluble synthetic organic polymer, which is probably uniformly absorbed throughout the crystals.

While the advantages of the specified control agents have been described particularly with reference to lead azide, they may be beneficially employed in the formation in aqueous solutions of suitable crystals of other initiating explosives. For example, they may be utilized in the production of other azides, such as of silver, and espe-

cially in the manufacture of other explosive lead salts, such as lead styphnate, picrate, and polynitrocresylates.

Having now described the invention, what is claimed as new and is desired to be secured by Letters Patent, is:

1. In the art of making explosives, a process comprising the step of forming crystals of lead azide in an aqueous solution in the presence of polyvinyl alcohol.

2. In the art of making explosives, a process comprising the step of forming crystals of lead azide in an aqueous solution in the presence of polyethylene glycol.

3. In the art of making explosives, a process comprising the step of forming crystals of lead azide in an aqueous solution in the presence of polymethylol urea.

4. In the art of making explosives, a process comprising the step of forming crystals of an initiating explosive of the group consisting of heavy metal azides and lead salts of nitroaromatic compounds in an aqueous solution in the presence of a water-soluble synthetic organic polymer of the group consisting of polyvinyl alcohol, polyethylene glycol, and amine-aldehyde polymers.

5. In the art of making explosives, a process comprising the step of forming crystals of lead azide in an aqueous solution in the presence of a water-soluble synthetic organic polymer of the group consisting of polyvinyl alcohol, polyethylene glycol, and amine-aldehyde polymers.

6. As a new product, crystalline particles of an initiating explosive of the group consisting of heavy metal azides and lead salts of nitroaromatic compounds, characterized by the current throughout the particles of a minor proportion of a water-soluble synthetic organic polymer of the



group consisting of polyvinyl alcohol, polyethylene glycol, and amine-aldehyde polymers, said particles having been formed in an aqueous solution containing said polymer.

7. As a new product, crystalline particles of lead azide characterized by the content throughout the particles of a minor proportion of a water-soluble synthetic organic polymer of the group consisting of polyvinyl alcohol, polyethylene glycol, and amine-aldehyde polymers, said particles having been formed in an aqueous solution containing said polymer.

8. As a new product, crystalline particles of lead azide characterized by the content throughout the particles of a minor proportion of polyvinyl alcohol and comprising substantially 95 to 97% $PbN_6$, said particles having been formed in an aqueous solution containing said polyvinyl alcohol.

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## Certificate of Correction

Patent No. 2,421,778. June 10, 1947.

JOSEPH FLEISCHER ET AL.

It is hereby certified that errors appear in the printed specification of the above numbered patent requiring correction as follows: Column 6, line 67, for "absorbed" read *adsorbed*; column 7, line 37, claim 6, for "current" read *content*; and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 16th day of September, A. D. 1947.

[SEAL]

THOMAS F. MURPHY,
*Assistant Commissioner of Patents.*

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