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**CRYSTALLINE DOUBLE SALT OF LEAD  
NITROAMINOTETRAZOLE AND LEAD  
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Virginia****No Drawing. Filed Apr. 9, 1962, Ser. No. 185,851  
1 Claim. (Cl. 260-299)**

This invention relates to a novel compound displaying improved explosive properties combined with extraordinary thermal stability.

Although many proposals have been made in the past for the obtaining of improved initiating compounds in priming charges for ammunition and detonators, the prior art compositions have been deficient with respect to certain performance characteristics. In particular, they have displayed an inadequate extent of thermal stability, so that attempts to increase the sensitivity to initiation by percussion have been accompanied by a decrease in the thermal stability. Furthermore, extensive research has continued for many decades for an initiating compound displaying an improved combination of stability in storage with desirable explosive properties. Desirably, these include the rapid onset of explosive decomposition when the compound is subjected to the desired minimal range of mechanical or thermal energy and also, an extent of explosive decomposition characterized by great vigor and brisance. Such performance is essential for accomplishing the improved ignition of propellant powders by ammunition primers and the initiation of secondary explosive charges by detonator primer charges.

The principal object of this invention has been to provide a novel compound having the stability and effectiveness of a greatly improved initiating explosive. A further object has been to provide such compound in crystalline form. Another object has been to enable the production of primer compositions of superior thermal stability and of increased brisance as compared with prior art compositions thereby to accomplish better ignition of propellant powder charges. Another object has been to furnish a process for the preparation of an improved initiating explosive. Other objects will be apparent from the following detailed description.

The foregoing objectives have been accomplished in accordance with the present invention by the provision of a novel crystalline explosive double salt of lead trinitroresorcinat (styphnate) and lead nitroaminotetrazole.

It has been found that desirable crystals of the above double salt are formed by reacting a solution of soluble lead salt, desirably in excess, with a solution of an alkali or an alkaline earth salt of styphnic acid and of nitroaminotetrazole.

The following specific examples constitute illustrative embodiments of preferred procedures for the preparation of the novel crystalline double salt.

*Example I*

One molar aqueous solutions of magnesium styphnate and of potassium nitroaminotetrazole are prepared, the solutions having, respectively, a pH of  $4.5 \pm 0.5$  and of  $7 \pm 0.5$ . A volume of 5 ml. of one solution is added to 5 ml. of the other in a suitable beaker and the resulting solution is diluted to a total volume of 50 ml., the pH being adjusted to a value of  $6.3 \pm 0.3$  by the addition, as required, of magnesium oxide or of styphnic acid. The solution is heated in a water bath to a temperature of  $75^\circ$ – $80^\circ$  C. While the solution is well stirred at this temperature, 15 ml. of 1 molar lead nitrate solution, which has been diluted with water to a volume of 50

ml., is added dropwise thereto over a period of 15 to 25 minutes, resulting in the precipitation of the crystalline double salt. Following the addition of the lead nitrate solution, the agitation is continued for a period of 5 to 10 minutes. The crystalline product settles rapidly to relatively small bulk, the supernatant liquid is decanted and the product is washed four to six times by agitation with water, followed by decantation. The moist product, amounting to 90% to 95% of the theoretical yield, may then be transferred to suitable containers for storage until required for use in wet-mixed compositions. When a dry product is desired, the moisture may be removed by drying in the air or under vacuum at a temperature of  $25^\circ$  to  $80^\circ$  C.

The above procedure is preferred when a product having an apparent density of 0.80 to 0.85 gram per ml. is desired. A product of somewhat higher apparent density, about 1 gram per ml., may be obtained by effecting the precipitation at a higher temperature,  $85^\circ$  C. to the boiling point of the solution, and by lengthening the precipitation period to about an hour.

When the novel double salt is desired in a form having an apparent density in the range of 1 to 1.85 grams per ml., the precipitation is preferably carried out in accordance with the following example.

*Example II*

The precipitation is carried out in a stainless steel or other suitable vessel, provided with a mechanical stirrer and maintained at about  $60^\circ$  C. in a water bath or other convenient heating means. A lead nitrate solution is prepared in the vessel by mixing 2500 ml. of one molar lead nitrate solution with 1 liter of water. While the solution is stirred at about the maximum rate without the occurrence of splashing, a caustic soda solution containing one mole of sodium hydroxide is added in a slow stream, for example by adding a solution containing 480 ml. of a 2.084 normal sodium hydroxide solution further diluted with water to a volume of 1500 ml. This results in a finely dispersed white precipitate of basic lead nitrate or lead hydroxide or both.

With the contents of the vessel maintained under vigorous agitation at a temperature of  $55^\circ$  to  $57^\circ$  C., one mole of the hydrated acid barium salt of nitroaminotetrazole ( $233 \text{ g. Ba (NAT)}_2 \cdot 4\text{H}_2\text{O}$ ) is added. Also, the slow controlled addition of 1 liter of one molar magnesium styphnate solution, having a pH in the range of 5.4 to 5.8, is started and continued over a period of about 20 minutes, the reaction mixture being maintained at  $53^\circ$  to  $57^\circ$  C. One completion of this addition, agitation is continued for an additional period of about 10 minutes. The dense crystalline product settles quickly when stirring is discontinued and the mother liquor is removed by decantation. After washing with water at least five times, the wash liquid being separated by decantation, the product, obtained at a 90% to 95% of theoretical yield is ready for use, for drying, or for wet or dry storage. The space yield of the process conducted as described above is approximately 120 grams of product per liter of batch volume. The space yield may be increased further, when this is desirable, by eliminating the water used to dilute the lead nitrate and sodium hydroxide solution (a total volume of 2 liters), wholly or in part. By this means the space yield may be increased to approximately 180 grams per liter of batch volume when no dilution is involved. Although further increase in space yield is technically possible through use of more concentrated solution, control of the process and maintenance of product quality become more difficult. From the standpoint of space yield, however, the process as described above is efficient and commercially practicable for the production of a product of highly desirable properties. It is also possible

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to conduct this process under conditions of greater dilution. If the dilution is too great, as in the preparation of 0.1 mole in a total batch volume of 4 liters, product formation is sluggish and complete conversion of raw materials to product requires a reaction period of an hour or more. However, the reaction temperature may be increased to 90–100° C. to compensate for dilution, and product formation is accelerated so that a satisfactory product may be obtained. At such dilution, the yield is somewhat reduced because of the solubility of the product in the added volume of water.

In a preparation following the procedure set forth in this example, the crystalline product settles rapidly after agitation is stopped to a volume such that the apparent density on the dry basis is about 1.65 grams per ml. However, the apparent density may be controlled at any desired value between about 0.7 and 1.85 grams per ml. by appropriate modifications. For example, raising the precipitation temperature and slowing down the rate of addition tend to increase the apparent density, while lowering the temperature and decreasing the precipitation period tend to decrease the apparent density.

While lead nitrate is the preferred lead salt used in the preparation, other soluble lead salts may be substituted therefor in whole or in part, particularly soluble inorganic lead salts such as the chloride or bromide. Likewise, any soluble salt of nitroaminotetrazole may be used in the preparation, preferably an alkali or alkaline-earth metal salt such as of lithium, sodium, potassium, magnesium, calcium, barium or strontium.

While the above specific examples constitute preferred embodiments of procedure, the temperature may be varied according to the product properties desired from about room temperature to about the boiling point of the reaction mixture. Generally, it is desirable to operate between about 35° to 95° C.

In order to insure the production of pure crystalline double salt, the amount of reagents should be controlled to provide molar equivalents of styphnate and nitroaminotetrazole groups and at least two molar equivalents of divalent lead ions, with preferably an excess of the latter. For many purposes, exactly equivalent amounts of the anions are not essential, and either may be used in excess of up to about 5% to 25%. The presence of an

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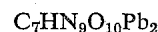
in a slightly acid to neutral reaction mixture, alkaline conditions leading to the formation of basic lead salts. When the lead salt solution is added to effect the precipitation, as in Example I, the reaction mixture should generally be maintained at a pH of 6.0 to 6.6 for best results. When the precipitant is added to the lead salt solution, as in Example II, the reaction mixture is preferably maintained at a pH of about 3 during the precipitation of the crystalline double salt product. If the pH should be found to vary from the optimum value during the course of a preparation, adjustment may readily be effected by adding an acid, preferably styphnic acid, or an alkali, preferably an alkali or alkaline-earth hydroxide, as required. Excellent product is obtainable by the use of more acidic reaction mixtures, at values of pH less than 3, but generally with some sacrifice in yield.

Nitroaminotetrazole may be derived from nitroaminoguanidine by reaction with nitrous acid, as described by Lieber et al., JACS, vol. 73, 2327 (1951), or by the nitration of aminotetrazole, for example as described by Herbst and Garrison in J. Org. Chem., vol. 18, 941–5 (1953).

Analyses of the novel lemon yellow crystalline double salt conform to the composition.

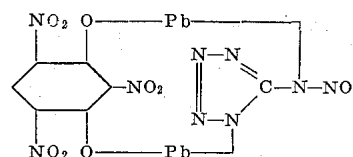


or the formula



the determined values of lead and nitrogen content being within about 0.1 to 0.2% of the theoretical values of 52.75% lead and 16.05% nitrogen.

The corresponding structural formula of the double salt may be represented as follows:



The following table lists the indicated properties of of normal lead styphnate (PbTNR), which has been widely used as a priming explosive, and of the novel double salt (PbNATNR).

TABLE I

	PbTNR	PbNATNR
Specific gravity.....	3.03	3.60.
Color.....	Amber to brown	Lemon yellow.
Solubility in Water.....	0.75 g./l. (25° C.) 1.71 g./l. (70° C.)	0.32g./l. (25° C.) 1.75 g./l. (70° C.)
Heat of Explosion, Cal./g.....	410	425.
Ignition Temperature (Instantaneous Flash Point).....	320° C. ± 10°	340° C. ± 10°.
Impact Sensitivity, 100 g. weight.....	16 cm	14 cm.
Weight Loss after 24 hrs. at 210° C.....	24.3%	0.5%.

appreciable proportion of a lead salt of styphnic acid or of nitroaminotetrazole is not disadvantageous while the product consists preponderantly of the novel double salt.

If desired, the novel double salt may be produced by digestion of individually precipitated lead salts of styphnic acid and of nitroaminotetrazole in water or aqueous solutions, preferably at temperatures of about 35° to 95° C. Likewise, litharge, styphnic acid, and nitroaminotetrazole in substantially theoretical proportions may be suspended in water or suitable aqueous solutions and converted to the novel double salt by digesting the stirred mixture for up to several hours at about 35° to 95° C., the period required for conversion being less as the temperature is raised.

Another factor which may advantageously be used in the control of desired crystal formation is the pH of the reaction mixture. Preferably, the precipitation is effected

As compared to the lead salt of nitroaminotetrazole, the novel double salt displays far greater, and more desirable, sensitivity to impact and explodes with far greater force and vigor.

As shown in the above table, the novel double salt displays satisfactory properties in all respects and is particularly outstanding in thermal stability. After storage at 210° C. for 24 hours, the crystals of normal lead styphnate had disintegrated and the residual material was no longer explosive. In contrast, the crystals of double salt were only slightly darkened and the explosive properties were not perceptibly impaired. Further, the crystals withstand boiling with water or storage under water at 65° C. for several months without evidence of decomposition.

The novel double salt generally crystallizes in the form of tabular prismatic crystals. The crystals tend

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to be elongated or needle-like and more clustered when the apparent density is low. With increased apparent density, the crystals tend to broaden and thicken relative to length. Thus, at an apparent density of 0.70 g./ml., the crystals may be 0.01 to about 0.03 mm. long and 0.0025 to 0.0060 mm. wide, while at an apparent density of 1.85 g./ml., the crystal lengths may vary from 0.035 to 0.050 mm. and the widths from 0.015 to 0.030 mm.

Study of the double salt by X-ray diffraction yielded the following data:

Interplanar spacing:	Relative intensity
11.1 A. -----	6
7.50 A. -----	10
5.50 A. -----	9
3.45 A. -----	7

X-ray studies of single crystals indicated monoclinic crystals, with B approximately 81° and unit cell of about 7.9×11.1×16.9 A. Infrared and ultraviolet spectrographic studies provided further confirmation that the novel crystalline product of this invention does not consist of a physical mixture of the individual lead salts.

Comparative brisance measurements by Sand Tests were made in accordance with "Standard Laboratory Procedures for Sensitivity, Brisance and Stability of Explosives" by A. J. Clear, January 1961 (O.T.S., 171,326 U.S. Dept. of Commerce), pages 15-21 and 24. In concordant 5-shot series, 0.4 g. charges crushed the following average weights of 20/30 mesh Ottawa sand to particles finer than 30 mesh:

	G.
Lead azide -----	14.2
Mercury fulminate -----	18.9
Lead styphnate -----	16.1
Novel double salt -----	24.0

Thus, the novel product of this invention substantially exceeds the other three in brisance or crushing power, these being the primary explosives used most extensively in the past as initiating explosives.

The improved sensitivity, brisance and other explosive properties of the novel double salt has enabled the preparation of priming compositions of enhanced stability and performance.

Superior performance was substantiated qualitatively by firing tests of rimfire blanks in a pistol, using blanks primed with (a) a standard commercial priming mixture based on lead styphnate and (b) a priming mixture of the same composition, except that the lead styphnate content was replaced by the double salt of this invention. On firing, the shells of series (b) not only produced a much sharper and far louder report than shells of series (a), but also a jet of flame extending several inches beyond the muzzle, in contrast to no visible flame with series (a).

Comparative tests of primer sensitivity and ignition properties consistently confirmed the improved performance of the novel double salt as compared to the performance of the individual lead salt components or of other initiating explosives previously in use. In fact, the sensitivity and propagation are sufficiently better in primers containing the double salt, that the abrasive ingredient such as ground glass, previously necessary in rim-fire primers may be entirely eliminated.

Rim-fire shells of .22 calibre were primed with the following compositions, the processing and handling being the same in all cases.

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PRIMING MIXTURE

	Percent by weight			
	Control	No. 45	No. 40	No. 30
Lead Styphnate.....	45.0			
Double Salt.....		45.0	40.0	30.0
Tetrazene.....	5.0	5.0	5.0	5.0
Barium Nitrate.....	19.7	48.7	53.7	63.7
Lead Peroxide.....	7.0			
Ground Glass.....	22.0			
Gum Arabic.....	1.0	1.0	1.0	1.0
Prussian Blue.....	0.3	0.3	0.3	0.3

Sensitivity tests yield the following results, using a 2 ounce weight and testing 50 shells at each height.

	Inches			
	Control	No. 45	No. 40	No. 30
All fired at.....	10	8	7	8
All misfired at.....	2	3	2	3

The enhanced propagation characteristic of the novel double salt is demonstrated by the performance of rimfire shells primed with mixtures containing a decreased percentage of explosive. In rimfire shells, the priming is spread in a layer of relatively thin cross section, which works against the propagation of flame or explosion from the point in the mass at which initiation is induced by percussion. The phlegmatizing effect of the other components of a priming mixture, such as oxidizers, abrasives, etc., may result in further impediment to propagation. Because of these factors, and to assure an adequate rate of propagation, it has been customary to use a higher percentage of explosive in rimfire priming than is used in centerfire. The usual practice has been to use about 50% explosive (including tetrazene and lead styphnate). The No. 30 mixture described above contains a total of 35% explosive, but exhibits an adequate level of propagation and satisfactory sensitivity. A composition containing 30% lead styphnate instead of double salt, but otherwise identical to the No. 30 mixture was prepared and evaluated in rimfire shells. In the rundown test for sensitivity, the number of misfires decreased as the height of fall of the striker weight was increased, but a height at which no misfires occurred was not attained. Instead, as the height at which usually no misfires are encountered was reached and exceeded, the shells which failed to fire exhibited a blackening of the mixture at the impact point, indicating that an abortive type of initiation had occurred. The data obtained in this test is as follows:

SENSITIVITY TEST CONDUCTED WITH 2 OZ. WEIGHT  
50 SHELLS TESTED AT EACH HEIGHT

	No. 30 (Lead Styphnate)	No. 30
50 at.....	11''—3 misfires*-----	
	10''—3 misfires*-----	
	9''—4 misfires*-----	0 msf.
	8''—3 misfires-----	1 msf.
	7''—6 misfires-----	3 msf.
	6''—35 misfires-----	8 msf.
	5''—48 misfires-----	30 msf.
	4''—50 misfires-----	43 msf.
	3''-----	50 msf.

\*Blackened mixture observed at impact point on the misfire shells.

The novel double salt of this invention is therefore well adapted to enable the formulation of priming mixtures of improved sensitivity by substituting it, in whole or in part, for lead styphnate and other initiating explosives of the prior art. As shown above, a rim-fire primer composition using the double salt can be formulated with-

out ground glass and display greater sensitivity than conventional mixtures containing such abrasive material. Further, the double salt improves the propagation of the explosion without requiring any change in the methods and precautions required in the handling of the primary explosive or of the primer composition. Also, the improved performance enables a reduction in the proportion of primary explosive in primer compositions, thus permitting greater latitude in the formulation, as for example to increase the proportion of oxidizing agent in order to attain more complete combustion.

Primer compositions containing the novel double salt also effect the improved ignition of propellant powders, as shown by comparative tests of shot shells. Such ammunition presents especially difficult problems with respect to the proper ignition of the propellant, particularly those loaded with a heavy shot charge, for example 12 gauge shotshells having a charge of 1½ ounces of shot. In order to meet the requirements, it has been essential to employ center-fire primers therein containing a primer charge of 0.8 to 0.9 grain of a primer composition having a high content of primary explosive. In lead styphnate primers commercially used in shotshells, the content of this explosive is generally about 40%. However, the novel double salt, used as the sole primary explosive in similar compositions to the extent of only about 20%, has been found to display improved performance as well as stability in center-fire primers for shotshells.

The following results were obtained in comparative ballistic tests of 12 gauge shotshells from the same lot, loaded with 1½ ounces of No. 4 shot over identical wads. The identical primer assembly was loaded in all shells tested, with one series charged with a 20% double salt primer composition and the other series with a commercial 40% normal lead styphnate primer composition. All shells contained propellant of the same lot of powder, using a 38.7 grain charge in the shells primed with the 40% lead styphnate composition and a smaller charge of 37.7 grains in the 20% double salt composition. Measurements of pressure and of velocity of the shot charge three feet beyond the gun muzzle were made on forty shots of each series at room temperature, after storage at -40° F., and after storage at 120° F., with the following results.

Temperature		40% Lead Styphnate Primer	20% Double Salt Primer
70° F.	Velocity:		
	Average.....	1,286 ft./sec.	1,285 ft./sec.
	Extreme Variation.....	49 ft./sec.	16 ft./sec.
	Pressure:		
	Average.....	10,400 p.s.i.	10,700 p.s.i.
120° F.	Velocity:		
	Average.....	1,354 ft./sec.	1,321 ft./sec.
	Extreme Variation.....	37 ft./sec.	40 ft./sec.
	Pressure:		
	Average.....	12,900 p.s.i.	12,300 p.s.i.
-40° F.	Velocity:		
	Average.....	1,178 ft./sec.	1,202 ft./sec.
	Extreme Variation.....	92 ft./sec.	48 ft./sec.
	Pressure:		
	Average.....	7,600 p.s.i.	9,300 p.s.i.
	Maximum.....	8,900 p.s.i.	10,000 p.s.i.
	Minimum.....	5,900 p.s.i.	8,000 p.s.i.

The ammunition provided with the double salt primer in accordance with this invention was thus shown to provide more consistent ballistic properties at ordinary temperature and markedly less variation from such values when fired at higher or lower temperatures.

The above double salt center-fire priming composition had the following preferred composition in percentages by weight, effective results being obtainable within the indicated ranges.

	Preferred	Ranges
Double Salt.....	20	15-35
Tetrazene.....	5	2-6
Barium Nitrate.....	50	15-60
Aluminum.....	10	0-20
Antimony Sulfide.....	15	5-30

The novel double salt successfully withstands the known tests for safety in handling. For example, the moist material, after being freed of adherent water by the use of blotting paper, has been covered with black powder and the latter ignited. On cessation of the flame, the double salt remained somewhat darkened but neither burned nor pitted.

The stability of the novel crystalline product is surprisingly excellent in view of its explosive power and sensitivity to initiation of explosion by impact or thermally. The novel double salt is therefore well qualified by reason of its stability and its explosive, physical and handling properties for use in explosive compositions, such as priming compositions for ammunition and for ignition and initiating compositions in detonators. For such use, it is advantageously employed as the sole initiating explosive, generally in admixture with a small proportion of sensitizer such as tetrazene. It may likewise be used in combination with other known explosive metal salts such as mercury fulminate, normal or basic lead azide, normal or basic lead styphnate, or other explosive nitro compounds or organic nitrates. While barium nitrate is the preferred oxidizing agent, other oxidizing metal compounds, preferable water-insoluble, may be used, such as nitrates, peroxides, chromates, or permanganates. The customary fuel ingredients such as antimony sulfide, lead thiocyanate, calcium silicide, ferrosilicon, or aluminum may likewise be used when desired.

Accordingly, it will be apparent that the novel double salt of this invention is advantageously applicable in a variety of compositions to provide excellent performance arising from its unique combination of properties. It will also be understood that modifications may be made in the above illustrative details within the spirit and scope of the invention.

I claim:

A crystalline double salt of lead nitroaminotetrazole and lead styphnate.

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