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PROCESS FOR THE PRODUCTION OF PRIMER COMPOSITIONS FOR PERCUSSION CAPS INCLUDING RIMFIRE CARTRIDGES

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This invention relates to a process for the production of primer compositions for percussion caps including rimfire cartridges.

The function of a primer, for instance of a percussion cap in the cartridge for fire-arms, is to transform the mechanical impulse of the blow of the striker into chemical heat energy in such a short time that the intended maximal pressure is reached in the expected short time.

The percussion caps consist of small cylindrical cups of copper or brass which are closed at one end. They are filled with a priming mixture with a high sensitiveness against percussion. The quantity of the priming mixture depends on the kind and on the size of the cartridges, and amounts to 15–120 milligrams, for small arms to 15–60 milligrams.

The known rimfire cartridges which have no separated percussion caps contain the priming mixture between the two surfaces of the out pressed rim. By the blow of the striker this priming mixture will be crushed so heavily between the two surfaces of the rim that the ignition takes place.

Rimfire cartridges contain a smaller quantity of the priming mixture, usually 10–18 milligrams, but with a higher content of the initial explosive.

These priming mixtures for igniting the powder charge of cartridges consist of an initial high sensitive explosive and of a thermal combination of nitrates, for instance barium nitrate and potassium nitrate, superoxides, for instance lead dioxide and barium superoxide, chromates, for instance lead chromate—and of easy burning substances having a high thermal effect, for instance antimony sulfide, calcium silicide, silicon etc.

For raising the sensitiveness the mixtures contain often gritty substances such as powdered glass are preferably included.

For more than one hundred years mercury fulminate dominated as a sensitizing initial explosive.

Due to certain reasons, from about 1932 on, mercury fulminate was replaced by the guanylnitrosoaminoguanyl-tetrazene-sensitized lead salt of trinitroresorcinol. The use of sensitized lead salt of trinitroresorcinol has proved so advantageous that, since the teaching to use the same, little or no mercury fulminate has been employed in the production of primers.

It is necessary that the lead salt of trinitroresorcinol be sensitized, since the salt per se is not sufficiently sensitive to percussion. The insufficiently sensitive lead salt of trinitroresorcinol has been sensitized only by means of comparatively small quantities of percussion-sensitive guanylnitrosoaminoguanyl-tetrazene, and no other substance which has been tried produced and desired sensitizing of the lead trinitroresorcinol.

The insensitivity to percussion of the lead salt of trinitroresorcinol in primer mixers has been explained by the fact that this salt normally contains one molecule of water of crystallization. The anhydrous lead salt of trinitroresorcinol, produced for example by heating the hydrated salt for several hours to temperatures of about 140° C., possesses not only per se a greater sensitivity to percussion, but also when in combination with the

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other conventional components of priming mixtures.

The use of the dehydrated lead salt of trinitroresorcinol as a primer charge is not satisfactory, because the anhydrous salt is a very hygroscopic and, after only a short time, would have again absorbed the molecule of water of crystallization removed by the dehydration treatment.

As early as 1920, it was found that the lead salt of trinitrophloroglucinol, produced by precipitation of a lead nitrate solution with the solution of a readily soluble salt of trinitrophloroglucinol, was entirely free of water of crystallization and in a most difficultly soluble form. This neutral salt of trinitrophloroglucinol precipitates in the form of a free-flowing powder composed of uniform crystals having a high specific gravity. Due to this specific crystallization structure and high specific gravity, it is very difficult to obtain a uniform and homogeneous mixture with the other necessary components of such priming mixtures.

In consequence of its enhanced combustion temperature (hot flame), its high specific gravity, namely of 3.8, and its freedom from water of crystallization, the lead salt of trinitrophloroglucinol surpasses the lead salt of trinitroresorcinol in satisfying the requirements for a priming charge. However, in spite of these advantages, which would lead one to consider the lead salt of trinitrophloroglucinol as ideal, the fact is that the lead salt of trinitrophloroglucinol is not able, even in view of its greater self-sensitivity, to impart to the mixture with the other primer components a greater sensitiveness to impact than the lead salt of trinitroresorcinol.

Due to this disadvantageous finding, no further attempts have been made to make the lead salt of trinitrophloroglucinol more advantageous for use in the production of percussion (see German Patent No. 377,269). The later attempts to sensitive the lead salt of trinitrophloroglucinol by means of tetrazene does not produce any such decisive advantages that the substitution of the cheaper lead salt of trinitroresorcinol would appear justified.

In accordance with the invention it has now been discovered that a highly suitable substance for use as priming charge in percussion caps and rimfire cartridges is the lead salt of trinitrophloroglucinol, containing one molecule of water of crystallization.

The lead salt of trinitrophloroglucinol containing water of crystallization is prepared by precipitation of a lead nitrate solution with a solution of an easily soluble salt of trinitrophloroglucinol, for instance the magnesium salt, at temperatures between 50–80° C., and by inoculating the precipitation solution with crystals of the lead salt containing water of crystallization.

EXAMPLE FOR THE PRECIPITATION OF THE LEAD SALT OF TRINITROPHLOROGLUCINOL CONTAINING WATER OF CRYSTALLIZATION*First Precipitation Solution*

56 gm. of trinitrophloroglucinol are dissolved in 500 ml. distilled warm water together with 16 gm. of technical magnesium oxide.

The addition of the magnesium oxide must be done very carefully to avoid a foaming of the liquid. After boiling for 3–4 minutes the dark red solution is filtered off from the excess of magnesium oxide.

Second Precipitation Solution

110 gm. of lead nitrate are dissolved in 600 ml. of distilled warm water and the possible impurities filtered off. This solution is introduced into a precipitation vessel of about 3 liters and acidified with 2.8 gm. of free trinitrophloroglucinol.

Method of Precipitation

The lead nitrate solution is heated in the waterbath to 50–80° C. and inoculated with several milligrams of pre-formed crystals of lead salt of trinitrophloroglucinol containing water of crystallization.

The time for adding the second solution shall be 10–12 minutes. The temperature shall neither fall below 50° C. nor rise above 80° C. Good stirring is necessary.

After having finished the addition of the second solution stirring is continued for about 1 minute and the solution diluted with 1 liter of cold water.

After separation of the precipitated lead salt by suction the salt is washed several times with warm and cold water and dried at a temperature of 60–80° C.

The lead salt of trinitrophloroglucinol containing one molecule of water of crystallization is obtained in the form of small orange-colored, comparatively voluminous needles in contrast to the dark-red free-flowing crystals having a high specific gravity of the anhydrous lead salt of trinitrophloroglucinol. The explanation for the differences in appearance and properties is that the anhydrous lead salt forms crystals classified with the isometric or regular system, while the hydrated lead salt precipitates as crystals classified with the monoclinic or prismatic system.

The sensitivity to percussion of the hydrated lead salt is somewhat less than that of the anhydrous lead salt of trinitrophloroglucinol. Nevertheless, it has been found, in accordance with the invention, that the lead salt of trinitrophloroglucinol containing water of crystallization imparts to the priming mixtures produced therewith an essentially higher sensitivity to percussion than the denser anhydrous salt of more compact crystalline structure.

My explanation for this is that the fine, needle-form crystals of the salt containing water of crystallization have an effect similar to the loose, needle-form, soft "tetrazene"-sensitizer, imparting to the priming mixtures, in spite of their own lack of sensitivity, through the bound water of crystallization a higher sensitivity than the very uniform, dense and coarser crystals of the anhydrous salt.

The increase in sensitivity to percussion is extremely pronounced in the primer compositions produced with the lead salt of trinitrophloroglucinol containing water of crystallization. Merely by suitably varying the proportions of the components of the mixture employed, even the degree of sensitivity of primer charges of the lead salt of trinitroresorcinol sensitized with tetrazene is surpassed.

The sensitivity of the new primer charges lies in the substitution of the hydrated lead salt of trinitrophloroglucinol for the lead salt of trinitroresorcinol, as well as in the elimination of the "tetrazene" employed as sensitizing agent.

As is well known, the lead salt of trinitroresorcinol is also objectionable when considered from a safety viewpoint. The lead salt of trinitroresorcinol very quickly takes on an electrostatic charge so that, unless sufficient precautions are taken, a risk of building up a charge of sufficient magnitude to produce a spark, which may unintentionally initiate an explosion, is always involved. This necessarily increase the risk in drying, handling, in mixing and charging.

In contrast to the lead salt of trinitroresorcinol, the electrical self-excitation in the lead salts of trinitrophloroglucinol is only about one fifth as great as that of the lead salt of trinitroresorcinol. The amount of electrical charge accumulated by the lead salt of trinitrophloroglucinol, despite its higher ignition sensitivity, never attains the dangerous values observed in the case of the lead salt of trinitroresorcinol.

Thus, in the case of the lead salts of the trinitrophloroglucinol, ignition through a self-produced electric spark is eliminated, and therewith accidental explosion. Therefore, the composition in accordance with the invention has the additional advantage that it is safer to handle in

both the mixing and charging operations, as well as in storage and transportation, etc., due to its physical properties.

The explanation for the ability of the lead salts of trinitrophloroglucinol to accumulate less static electricity is to be traced back to the higher metal content of the lead salt of trinitrophloroglucinol, as compared to the lead salt of trinitroresorcinol. This phenomenon is observed for both the anhydrous and hydrated forms of the salt. The theoretical lead content of the hydrated salt amounts to 52.95%, and that of the anhydrous lead salt of trinitrophloroglucinol to 54.63%.

In accordance with the invention, no sensitizer for the hydrated lead salt of trinitrophloroglucinol is required. The elimination of the need for guanyl-nitrous-amino-guanyltetrazene as sensitizer is highly desirable, in that this easily hydrolyzable substance is extremely sensitive to heat, detonating at about 140° C., which has frequently resulted in serious accidents.

The percussion caps and rimfire cartridges, in connection with which the invention is employed, are and may be of any suitable and usual construction well-known to those skilled in the art. The active components of the priming composition are admixed in the same manner as in the case of the conventional compositions, employing the lead salt of trinitroresorcinol. However, due to the greater effectiveness of the lead salt of trinitrophloroglucinol containing water of crystallization, the proportion of this substance in the explosive mixture can be, if necessary, somewhat reduced to about 28–35% of the total mixture. The percentage of the lead salt in the mixtures depends on the desired effect in priming the powder charge of the cartridges.

The other components of the mixture are similar to those employed in connection with the mixtures containing the lead salt of trinitroresorcinol. As oxygen carriers, there may be utilized barium nitrate and potassium nitrate, lead dioxide, red lead, lead nitrate or lead chromate, etc.

As thermally acting materials, antimony sulfide, calcium silicide, ferro-silicon and lead thiocyanate may be employed. According to the most recent observations and experiences, finely distributed silicon and elementary boron may also be used. The two last-named substances are, on account of the peculiar affinity of these elements for lead compounds, particularly effective in priming mixtures which contain as the explosive agent a lead compound. Further, they contribute to the sensitization of the compositions.

EXAMPLE ILLUSTRATING THE POSSIBLE COMPOSITIONS OF THE PRIMING MIXTURES

(1) Percussion Caps

	Percent
Lead salt of trinitrophloroglucinol containing 1 molecule of water of crystallization	25–50
Barium nitrate	20–35
Lead dioxide	5–8
Antimony sulfide	4–9
Calcium silicide	6–12
Boron	1–8

(2) Rimfire Cartridges

	Percent
Lead salt of trinitrophloroglucinol containing 1 molecule of water of crystallization	40–80
Barium nitrate or lead nitrate	20–30
Lead dioxide	3–7
Antimony sulfide	4–7
Boron or finely divided silicon	1–8
Powdered glass	2–6

As has already been mentioned, the specific gravity of the lead salt of trinitrophloroglucinol containing water of crystallization is lower than that of the anhydrous salt, namely 3.0 to 3.4. If for any reason a priming com-

position of higher specific gravity, and being more brisant, is desired, a part of the hydrated salt may be replaced by the anhydrous lead salt of trinitrophloroglucinol. However, the amount of the hydrated salt in the composition must amount to at least about 10% of the total composition, in order to impart to the same the necessary sensitivity to percussion. The hydrated lead salt of trinitrophloroglucinol in such mixtures assumes the roll of the sensitizer similar to that played by tetrazene.

It will, therefore, be seen that the invention accomplishes its objects. A method for preparing a priming composition is provided in which ignition by percussion is ensured. A priming charge consisting of at least 10% of the hydrated lead salt of trinitrophloroglucinol is superior to the regular charge containing the tetrazene-sensitized lead salt of trinitroresorcinol. It is safer to handle in both the mixing and charging operations, due to its physical properties. Furthermore, while certain proportions of the components of the priming charge have been indicated as preferable, these proportions may be varied within limits. It is further obvious that various changes may be made in details without departing from the spirit of this invention. It is, therefore, to be understood that this invention is not to be limited to the details described.

I claim:

1. A primer composition for percussion caps consisting essentially of

25-50% by weight of the lead salt of trinitrophloroglucinol containing 1 molecule of water of crystallization,

20-35% by weight of barium nitrate,

5-8% by weight of lead dioxide,

4-9% by weight of antimony sulfide,

6-12% by weight of calcium silicide, and

1-8% by weight of finely divided elementary boron.

2. Primer composition for rimfire cartridges consisting essentially of

40-80% by weight of the lead salt of trinitrophloroglucinol containing 1 molecule of water of crystallization,

20-30% by weight of a member selected from the group consisting of barium nitrate and lead nitrate,

3-7% by weight of lead dioxide,

4-7% by weight of antimony sulfide,

5 1-8% by weight of finely divided elementary boron, and

2-6% by weight of powdered glass.

3. A primer composition for percussion caps and rimfire cartridges comprising a mixture of at least one oxygen carrier, at least one thermally acting material, at least one additional member selected from the group consisting of finely distributed silicon, elementary boron, and gritty inert material, and from 10-80% by weight of the total composition of a lead salt of trinitrophloroglucinol containing water of crystallization.

15 4. A primer composition according to claim 3 wherein at least a portion of the lead salt of trinitrophloroglucinol containing water of crystallization in excess of 10% by weight is replaced by an anhydrous lead salt of trinitrophloroglucinol.

20 5. A primer composition for percussion caps and rimfire cartridges consisting essentially of 10-80% by weight of the lead salt of trinitrophloroglucinol containing one molecule of water of crystallization, 20-35% by weight of a member selected from the group consisting of barium nitrate and lead nitrate, 3-8% by weight of lead dioxide, 4-9% by weight of antimony sulfide, 0-12% by weight of calcium silicide, 1-8% by weight of finely divided elementary boron, and 0-6% by weight of powdered glass.

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