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(54) Titre : COMPOSES INFLAMMATEURS EXEMPTS DE PLOMB ET DE BARYUM
(54) Title: LEAD- AND BARIUM-FREE PRIMING CHARGES

(57) Abrégé/Abstract:
The invention concerns lead- and barium-free igniter compounds with initial explosive substances mixed with oxygen-producing substances. The igniter compounds are characterized in that the initial explosive substances are selected from alkali metal salts and/or alkaline earth metal salts of dinitrobenzofuroxanes and the oxygen-producing substances are selected from metallic peroxides, nitrates of ammonium, guanidine, aminoguanidine, triaminoguanidine, dicyandiamidine and the elements sodium, potassium, magnesium, calcium, cerium and/or polyvalent metallic oxides. The igniter compounds according to the invention display higher stability with respect to known pollutant-free igniter compounds.

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(54) Title: LEAD- AND BARIUM-FREE IGNITER COMPOUNDS

(54) Bezeichnung: BLEI- UND BARIUM-FREIE ANZÜNDSÄTZE

(57) Abstract

The invention concerns lead- and barium-free igniter compounds with initial explosive substances mixed with oxygen-producing substances. The igniter compounds are characterized in that the initial explosive substances are selected from alkali metal salts and/or alkaline earth metal salts of dinitrobenzofuroxanes and the oxygen-producing substances are selected from metallic peroxides, nitrates of ammonium, guanidine, aminoguanidine, triaminoguanidine, dicyandiamidine and the elements sodium, potassium, magnesium, calcium, cerium and/or polyvalent metallic oxides. The igniter compounds according to the invention display higher stability with respect to known pollutant-free igniter compounds.

(57) Zusammenfassung

Gegenstand der vorliegenden Erfindung sind Blei- und Barium-freie Anzündsätze mit Initialexplosivstoffen im Gemisch mit Sauerstoff-liefernden Substanzen, die dadurch gekennzeichnet sind, daß die Initialexplosivstoffe aus Alkalimetall- und/oder Erdalkalimetallsalzen von Dinitrobenzofuroxanen und die Sauerstoff-liefernden Substanzen aus Metallperoxiden, Nitraten von Ammonium, Guanidin, Aminoguanidin, Triaminoguanidin, Dicyandiamidin sowie den Elementen Natrium, Kalium, Magnesium, Calcium, Cer und/oder mehrwertigen Metalloxiden ausgewählt sind. Die erfindungsgemäßen Anzündsätze weisen eine erhöhte Stabilität gegenüber bekannten schadstofffreien Anzündsätzen auf.

"Lead- and barium-free priming charges

The invention relates to lead- and barium-free priming charges containing primary explosives mixed with oxygen-supplying substances.

EP-0 031 045 B1 discloses the use of zinc peroxide as the only oxidant or one of the oxidants in explosive-containing or pyrotechnic mixtures.

EP-0 129 081 B1 describes lead- and barium-free priming charges comprising primary explosives mixed with zinc peroxide as oxidant, where the primary explosives are strontium salts of mono- and/or dinitrodihydroxy-diazobenzene in amounts of from 5 to 70% by weight mixed with passivators and in addition tetrazene in amounts of up to 30% by weight and zinc peroxide in amounts of from 10 to 70% by weight, in each case based on the overall mixture.

The primary explosives in known priming charges are compounds, in particular of lead, which are derived from trinitropolyphenols, for example trinitrophenol, trinitroresorcinol and/or hydrazoic acid. In addition, priming charges are known which contain double salts of lead, for example hypophosphite nitrate. During combustion of these priming charges, increased concentrations of lead and its compounds occur in the ambient air, reaching the maximum allowable concentration after only a small number of shots. Solutions have already been proposed which comprise primary explosives containing no

heavy metals. Diazodinitrophenol in particular has become established as such. However, diazodinitrophenol-containing priming charges, for example with zinc peroxide as oxygen-supplying substance, exhibit very strong gas pressure shocks caused by the vigorous reaction of the diazodinitrophenol. This can adversely affect function in the weapon or in the internal and external ballistics. In addition, diazodinitrophenol exhibits increased thermal reactivity.

The present invention thus relates to improved lead- and barium-free priming charges containing primary explosives mixed with oxygen-supplying substances.

More particularly, the present invention provide a lead-free and barium-free ignition composition that contains at least one initial explosive in a mixture with at least one oxygen-delivering substance, the composition consisting essentially of:

at least one alkali metal and/or at least one alkali earth metal salt of dinitrobenzofuroxan as the sole initial explosive,

tetrazene as a sensitizer,

at least one of metal peroxides; cerium dioxide, tungsten trioxide, nitrates of ammonium, guanidine, aminoguanidine, triaminoguanidine, dicyanodiamidine, the elements sodium, magnesium, calcium and/or cerium as the oxygen-delivering substance, and

a reduction agent selected from the group consisting of carbon, metal powders of boron, cerium, titanium, zirconium and/or silicon, metal alloys, metal sulfides and metal hydrides.

The present invention also provide a lead-free and barium-free ignition composition that contains at least one initial explosive in a mixture with at least one oxygen-delivering substance, the composition consisting essentially of:

alkali metal and/or alkali earth metal salts of dinitrobenzofuroxan as the sole initial explosives,

tetrazene as a sensitizer,

a mixture of multivalent metal oxides and metal peroxides as the oxygen-delivering substance, and

a reduction agent selected from the group consisting of carbon, metal powders of boron, cerium, titanium, zirconium and/or silicon, metal alloys, metal sulfides and metal hydrides.

The novel priming charges have improved stability over the prior art when stored under humid or warm conditions.

For the purposes of the present invention, the primary explosive employed can be, in addition to the

known salts of mono- and/or dinitrodihydroxydiazobenzene, diazodinitrophenol, triazole and tetrazole compounds, for example the salts of nitrotriazolone, the salts of dinitrobenzofuroxan, in particular the potassium salt. As organic compounds containing functional azide groups, mention should be made, in particular, of cyanuric triazide, triazidotrinitrobenzene, styphnyl diazide and 2-picryl-5-nitrotetrazole.

In accordance with the invention, the primary explosives are preferably employed in an amount of from 5 to 70% by weight, in particular from 30 to 60% by weight, based on the overall mixture.

Oxygen-supplying substances which can be employed, besides the metal peroxide, zinc peroxide, known per se from the prior art, are also other oxygen-supplying substances. Examples of other substances which can be employed in this respect in the priming charge are tin dioxide, cerium dioxide, tungsten trioxide and/or nitrates of ammonium, guanidine, aminoguanidine, tri-aminoguanidine, dicyandiamidine and the elements sodium, potassium, magnesium, calcium, cerium, in particular potassium nitrate or basic cerium nitrates. The amount of oxygen-supplying substances in the novel priming charges can vary, for example, between 5 and 70% by weight, based on the overall mixture. For the purposes of the present invention, particular preference is given to an amount of from 8 to 60% by weight of oxygen-supplying substances. The substance can be employed either in the form of fine or coarse particles. Substances in the form of fine

particles having a mean particle size of about 10 μm are preferentially employed if the priming charges are used as compacted charges, while substances in the form of coarse particles having a particle size of about 30 μm are particularly suitable for less-compacted charges, for example in rim-fire rounds.

In accordance with the invention, the priming charges may furthermore contain sensitizers, reducing agents, friction agents, secondary explosives and/or inert substances.

Any sensitizers, preferably tetrazene, may be present in amounts of from 0 to 30% by weight based on the overall mixture.

Reducing agents, which contribute toward the reaction, are suitable in the novel priming charges for improving the ignition capacity and in some cases also increase the mechanical sensitivity. Suitable substances are preferably selected from the group consisting of carbon and/or metal powders, in particular of boron, aluminum, cerium, titanium, zirconium, magnesium and silicon, metal alloys, in particular cerium/magnesium, cerium/silicon, titanium/aluminum, aluminum/magnesium, calcium silicide and metal sulfides, in particular antimony sulfide and molybdenum sulfide, and metal hydrides, for example titanium hydride, in particular in an amount of from 0 to 20% by weight, based on the overall mixture. Some reducing agents may simultaneously also fulfil the function of a friction agent, for example antimony sulfides or calcium silicides. While the propor-

tion of the reducing agents in the priming charge can be from 0 to 20% by weight, friction agents, which do not participate in the reaction during combustion, may be present in the novel priming charges in amounts of up to 45% by weight, based on the overall mixture. Such friction agents are known per se; an example which may be mentioned is glass powder.

Further components which contribute toward the reaction can be, in particular, secondary explosives, for example nitrocellulose or pentaerythritol tetranitrate. Further examples which may be mentioned are octogen and hexogen, and amino compounds of nitrated aromatics, for example of trinitrobenzene, such as mono-, di- or triaminotrinitrobenzene or aminohexanitrobiphenyl, furthermore the acylation products of these compounds, for example hexanitrooxanilide and hexanitrodiphenylurea. These secondary explosives furthermore include, for example, hexanitrostilbene, hexanitrodiphenyl oxide, hexanitrodiphenyl sulfide, hexanitrodiphenyl sulfone and hexanitrodiphenylamine, and tetranitrocarbazole, tetranitroacridone and polyvinylnitrate, and nitrotriazolone and compounds thereof. The proportion of these substances in the priming charge can be from 0 to 30% by weight, based on the overall mixture.

Suitable inert substances in the novel priming charges are substances known per se which are frequently also employed to match the properties of these charges to the particular application. Mention may be made here, in particular, of binders, adhesives, colorants, passivators

and/or agents for odor characterization, which may preferably be present in an amount of from 0 to 20% by weight, based on the overall mixture. Mention may be made here by way of example of calcium carbonate, titanium dioxide and/or white boron nitride.

In order to improve and characterize the odor of the charge fumes, agents for odor characterization which are able to withstand the thermal load during the shot can be added to the charge mixture or binder and the charge cap. In particular, it has been found in this respect that vanillin satisfies these properties.

The novel priming charges are prepared by processes known per se by sieving the dry mixture or compounding the water-moist mixture. Metering of the water-moist composition can be effected by application to the perforated discs or by extrusion.

Examples

Example 1

This example describes a priming charge for an anvil primer cap with a charge weight of 20 mg.

A mixture of 45 parts by weight of potassium dinitrobenzofuroxanate, 5 parts by weight of tetrazene, 30 parts by weight of zinc peroxide, 15 parts by weight of tin dioxide and 5 parts by weight of titanium was homogenized with 22 parts by weight of water and metered by application to perforated discs. After introduction into primer caps, the mixture was dried and compacted.

The novel initiator mixtures exhibited better stability than a conventional diazole-containing priming

charge when stored for 7 days under humid and warm conditions at a temperature of 71°C and an atmospheric humidity level of 90%. Sensitivity investigations showed no evidence of expulsion of the primer cap out of the cases.

Comparative example 1

A water-moist mixture of 40 parts by weight of diazodinitrophenol, 15 parts by weight of tetrazene, 8 parts by weight of zinc peroxide, 35 parts by weight of glass powder (120 to 170 μm) and 2 parts by weight of Adhesin® (adhesive) was spin-filled at a charge weight of 18 mg into .22 (long) caliber rim-fire rifle cartridges.

For reliable full ignition, the priming charge required, as tamping, a coating of 3 to 4 mg of Vinnapas® A50 containing 0.2 mg of vanillin for odor characterization.

Example 2

A priming charge for .22 (long) caliber rim-fire rifle cartridges, charge weight 16 mg, was prepared analogously to Example 1. A mixture of 47 parts by weight of potassium dinitrobenzofuroxanate, 10 parts by weight of tetrazene, 8 parts by weight of zinc peroxide, 34 parts by weight of glass powder (90 to 200 μm) and 1 part by weight of Adhesin® (adhesive) was used analogously to Example 1.

The priming charge ignited without a cover coating as tamping and achieved internal and external

ballistics comparable to that of a commercially available munition.

WHAT IS CLAIMED IS:

1. A lead-free and barium-free ignition composition that contains at least one initial explosive in a mixture with at least one oxygen-delivering substance, the composition consisting essentially of:

at least one alkali metal and/or at least one alkali earth metal salt of dinitrobenzofuroxan as the sole initial explosive,

tetrazine as a sensitizer,

at least one of metal peroxides, cerium dioxide, tungsten trioxide, nitrates of ammonium, guanidine, aminoguanidine, triaminoguanidine, dicyanodiamidine, the elements sodium, magnesium, calcium and/or cerium as the oxygen-delivering substance, and

a reduction agent selected from the group consisting of carbon, metal powders of boron, cerium, titanium, zirconium and/or silicon, metal alloys, metal sulfides and metal hydrides.

2. The lead-free and barium-free ignition composition of claim 1, wherein the at least one initial explosive is contained in the composition in an amount of from 5 to 70% by weight, relative to the entire mixture.

3. The lead-free and barium-free ignition composition of claim 1, wherein the at least one initial explosive is contained in the composition in an amount of from 30 to 60% by weight, relative to the entire mixture.

4. The lead-free and barium-free ignition composition of claim 1, wherein the oxygen-delivering substance is contained in the composition in an amount of from 5 to 70% by weight, relative to the entire mixture.

5. The lead-free and barium-free ignition composition of claim 1, wherein the oxygen delivering substance is contained in the composition in an amount of from 8 to 60% by weight, relative to the entire mixture.

6. The lead-free and barium-free ignition composition of claim 1, wherein the reduction agent is selected from the group consisting of cerium-magnesium, cerium-silicon, titanium-aluminum, aluminum-magnesium, antimony sulphide molybdenum sulphide, titanium hydride and mixtures thereof.

7. The lead-free and barium-free ignition composition of claim 1, wherein the reduction agent is contained in an amount of from greater than 0 to 20% by weight, relative to the entire mixture.

8. The lead-free and barium-free ignition composition of claim 1, wherein the composition further contains at least one friction agents, at least one additional sensitizer, at least one additional secondary explosive and/or at least one inert substance.

9. The lead-free and barium-free ignition composition of claim 1, wherein the composition further contains at least one additional sensitizer and wherein the sensitizers are contained in an amount of from 0 to 30% by weight, relative to the entire mixture.

10. The lead-free and barium-free ignition composition of claim 1, wherein the composition further contains glass powder as a friction agent.

11. The lead-free and barium-free ignition composition of claim 1, wherein the composition further contains at least one friction agent in a amount of from more than 0 to 45% by weight, relative to the entire mixture.

12. The lead-free and barium-free ignition composition of claim 1, wherein the composition further contains at least one secondary explosive selected from the group consisting of hexogen, octogen and amino compounds of nitrated aromatics.

13. The lead-free and barium-free ignition composition of claim 1, wherein the composition further contains at least one secondary explosive in an amount of from more than 0 to 30% by weight, relative to the entire mixture.

14. The lead-free and barium-free ignition composition of claim 1, wherein the composition further contains at least one inert substance selected from the group consisting of a binder, an adhesive, a dye, a retardant and an agent for odor characterization.

15. The lead-free and barium-free ignition composition of claim 14, wherein the inert substances are contained in a proportion from 0 to 20% by weight relative to the entire mixture.

16. The lead-free and barium-free ignition composition of claim 1, wherein the composition further contains vanilla as an agent for odor characterization.

17. A lead-free and barium-free ignition composition consisting of potassium dinitrobenzofuroxan, tetrazene, zinc peroxide, glass powder and an adhesive.

18. A lead-free and barium-free ignition composition that contains at least one initial explosive in a mixture with at least one oxygen-delivering substance, the composition consisting essentially of:

alkali metal and/or alkali earth metal salts of dinitrobenzofuroxan as the sole initial explosives,

tetrazine as a sensitizer,

a mixture of multivalent metal oxides and metal peroxides as the oxygen-delivering substance, and

a reduction agent selected from the group consisting of carbon, metal powders of boron, cerium, titanium, zirconium and/or silicon, metal alloys, metal sulfides and metal hydrides.

19. The lead-free and barium-free ignition composition of claim 18, wherein the oxygen-delivering substance is a metal oxide selected from the group consisting of cerium dioxide, tungsten trioxide, tin dioxide and mixtures thereof.

20. The lead-free and barium-free ignition composition of claim 18, wherein the at least one initial explosive is contained in the composition in an amount of from 5 to 70% by weight, relative to the entire mixture.

21. The lead-free and barium-free ignition composition of claim 18, wherein the at least one initial explosive is contained in the composition in an amount of from 30 to 60% by weight, relative to the entire mixture.

22. The lead-free and barium-free ignition composition of claim 18, wherein the oxygen-delivering substance is contained in the composition in an amount of from 5 to 70% by weight, relative to the entire mixture.

23. The lead-free and barium-free ignition composition of claim 18, wherein the oxygen delivering substance is contained in the composition in an amount of from 8 to 60% by weight, relative to the entire mixture.

24. The lead-free and barium-free ignition composition of claim 18, wherein the reduction agent is selected from the group consisting of cerium-magnesium, cerium-silicon, titanium-aluminum, aluminum-magnesium, antimony sulphide molybdenum sulphide, titanium hydride and mixtures thereof.

25. The lead-free and barium-free ignition composition of claim 18, wherein the reduction agent is contained in an amount of from greater than 0 to 20% by weight, relative to the entire mixture.

26. The lead-free and barium-free ignition composition of claim 18, wherein the composition further contains at least one friction agent, at least one additional sensitizer, at least one additional secondary explosive and/or at least one inert substance.

27. The lead-free and barium-free ignition composition of claim 18, wherein the composition further contains at least one additional sensitizer and wherein the sensitizers are contained in an amount of from 0 to 30% by weight, relative to the entire mixture.

28. The lead-free and barium-free ignition composition of claim 18, wherein the composition further contains glass powder as a friction agent.

29. The lead-free and barium-free ignition composition of claim 18, wherein the composition further contains at least one friction agent in an amount of from more than 0 to 45% by weight, relative to the entire mixture.

30. The lead-free and barium-free ignition composition of claim 18, wherein the composition further contains at least one secondary explosive selected from the group consisting of hexogen, octogen and amino compounds of nitrated aromatics.

31. The lead-free and barium-free ignition composition of claim 18, wherein the composition further contains at least one secondary explosive in an amount of from more than 0 to 30% by weight, relative to the entire mixture.

32. The lead-free and barium-free ignition composition of claim 18, wherein the composition further contains at least one inert substance selected from the group consisting of a binder, an adhesive, a dye, a retardant and an agent for odor characterization.

33. The lead-free and barium-free ignition composition of claim 32, wherein the inert substances are contained in a proportion from 0 to 20% by weight relative to the entire mixture.

34. The lead-free and barium-free ignition composition of claim 18, wherein composition further contains vanilla as an agent for odor characterization.

35. A lead-free and barium-free ignition composition consisting of potassium dinitrobenzofuroxan, tetrazene, zinc peroxide, tin dioxide, and titanium.