United States Patent Office

3,370,537

Patented Feb. 27, 1968

3,370,537

CASTABLE PYROTECHNIC COMPOSITION COMPRISING METAL NITRATES OR CHLORATES AND FINELY DIVIDED METAL

Frederick Tepper, Butler, Pa., assignor to Mine Safety Appliances Company, a corporation of Pennsylvania

No Drawing. Filed July 22, 1965, Ser. No. 474,160
12 Claims. (Cl. 102—87)

ABSTRACT OF THE DISCLOSURE

Light emitting pyrotechnic compositions having a metal phase dispersed in a continuous solid oxidizing salt phase, or matrix, are formed by slurrying a finely divided metal in low-melting mixtures of molten salts and cooling the slurry to freeze the molten salts. The dispersed phase may be magnesium, aluminum, titanium, zirconium or alloys and, if desired, also contain tungsten carbide or titanium carbide. The salt mixtures of metal nitrates or metal chlorates contain at least one alkali metal or alkaline earth metal salt.

This invention relates to pyrotechnic compositions for tracer projectiles and more particularly to solid, cast in place pyrotechnic compositions.

Pyrotechnic compositions now used in tracer projectiles, flares and the like are finely divided solid mixtures that are compressed into suitable casings under high pressure, a tedious and expensive procedure. In the case of relatively deep casings of small diameter, a shape frequently dictated by ballistic considerations, the pyrotechnic must be introduced and compressed in several portions.

I have found that certain finely divided metals may be slurried in certain molten oxidizing salts or salt mixtures, and that the slurry can be poured or otherwise injected into casings, which are cooled to solidify the molten salt, forming a pyrotechnic of finely divided metal dispersed in a matrix of solid oxidizing salt that is securely bonded to the casing.

Metals suitable for use in this invention include magnesium, aluminum, titanium, and zirconium, mixtures thereof, or alloys containing a major amount of these metals. The metals are finely divided, or powdered, the selection of particle size depending on the metal used and the desired burning rate. The metals must not be so finely divided that they will react spontaneously when mixed with the molten oxidizing salts. The permissible degree of subdivision varies of course with different metals, but generally any metal powder not pyrophoric in air at a temperature equal to or lower than the molten salt temperature is suitable for use. Powdered metals having an average particle diameter greater than about 10 microns are generally suitable for use with molten salt mixtures melting below about 250° C.; it is generally preferred to use a powdered metal that passes a 270 mesh screen, i.e., a particle diameter of less than 53 microns.

Suitable oxidizing salts for use in this invention include the alkali and alkaline earth metal nitrates and chlorates, such as, for example, lithium nitrate, sodium nitrate, potassium nitrate, calcium nitrate, barium nitrate, strontium nitrate, lithium chlorate, sodium chlorate, potassium chlorate and barium chlorate. Single salts may be used but it is generally preferred to use mixtures of salts having lower melting points, such as binary, ternary or quaternary eutectics or other mixtures, preferably melting below about 250° C. Examples of suitable eutectic mixtures and their melting points include: 68% $LiNO_3$–32% KNO_3 (M.P. 132° C.); 52% KNO_3–17% $NaNO_3$–31% $LiNO_3$ (M.P. 120° C.); 51% $Ca(NO_3)_2$–49% KNO_3 (M.P. 146° C.); 50% KNO_3–50% $NaNO_3$ (M.P. 219° C.); 53.3% $NaNO_3$–46.7% $LiNO_3$ (M.P. 206° C.); 46% $Ca(NO_3)_2$–54% $NaNO_3$ (M.P. 214° C.); 62% $NaNO_3$–38% $KClO_3$ (M.P. 206° C.); and 25% $Sr(NO_3)_2$–75% KNO_3 M.P. 278° C.).

In addition to alkali metal and alkaline earth metal nitrates and chlorates, suitable salt mixtures may include other metal nitrates or chlorates such as $Cd(NO_3)_2$ to lower melting points or impart color to the emitted light on burning, or salts such as alkali metal or alkaline earth metal fluorides for adjusting the viscosity of the molten salt mixtures. Examples of suitable low melting eutectic mixtures include: 14.5% $LiNO_3$–56% $Cd(NO_3)_2$–29.5% $NaNO_3$ (M.P. 110° C.); and 64% $Cd(NO_3)_2$–36% $NaNO_3$ (M.P. 135° C.).

In order to produce a composition with satisfactory burning characteristics the molten salt must be substantially anhydrous. In most cases it is sufficient to use commercial grade anhydrous salts and handle and process them in normal ambient air. Very hygroscopic salts, such as $LiNO_3$, are preferably protected from atmospheric moisture as by handling under inert atmosphere or in a dry room.

In the preferred practice of this invention, a slurry of metal powder in the fused salt is formed by pouring the metal powder into the molten salt with moderate agitation to insure thorough mixing. Slurries may be safely formed using this procedure even though the procedure of heating a mixture of salt and metal to melt the salt frequently results in spontaneous reaction of the mixture. Aluminum, and to some extent magnesium, are difficult to wet with the molten salts, and somewhat longer mixing times and greater agitation are required than with the easily wetted titanium and zirconium. Wetting of the metals is promoted by the addition of one or more metal fluorides to the molten salt, suitably 1 to 10%, such as, for example, lithium fluoride, sodium fluoride, potassium fluoride and calcium fluoride. The slurry is poured into a casing and permitted to cool to solidify the molten salt, forming a solid pyrotechnic body in the casing. The solidified salt adheres tightly to clean metal, so the solid pyrotechnic body is securely bonded to the casing. Some slurries, with a high proportion of metal or a very viscous salt melt, have a paste consistency not amenable to rapid pouring. Such slurries may be injected into the casing by forcing them through a nozzle into the casing in accordance with conventional paste-loading methods.

Suitable compositions contain up to about 1.5 part by weight of metal for each 3 parts of salt. Compositions richer in metal do not burn smoothly, frequently failing to burn completely; and are not suitable for tracers or other light emission applications where continuous and reliable light emission is required. Preferred compositions contain from about 1 to 1.5 parts of metal for each 3 parts of salt.

The following examples are illustrative of this invention:

Example I

52 parts KNO_3, 17 parts $NaNO_3$, and 31 parts $LiNO_3$ are blended and melted in an open crucible by heating to about 200° C. The temperature of the melt is maintained at about 150° C., 30° C. above the melting point of the eutectic mixture, while 35 parts of powdered magnesium are added to the salt while manually stirring the mixture with a spatula. The powdered magnesium used passed a 200 mesh Tyler sieve and was retained on a 325 mesh Tyler sieve. A 0.75 g. aliquot of the resultant slurry was poured into a stainless steel capsule ¼ inch ID and ¾ inch long having an open end. The filled capsule was permitted to cool to room temperature, to freeze the salt.

The resultant composition of magnesium dispersed in a solid matrix of salt adhered tightly to the stainless steel. When ignited, by a tesla coil discharge, the mixture burned for about two seconds emitting a brilliant white shower of sparks 8 to 10 cm. long.

Example II

Portions of the slurry of Example I were poured into standard 30 caliber casings, the volume of slurry used being equal to the volume occupied in conventional tracers by compacted powder pyrotechnic. After solidfication of the slurry, about 0.1 g. of conventional igniter composition, consisting of 6% magnesium, 9.4% calcium resinate and 84.6% SrO_2, was pressed into the top of the tracer composition and the 30 caliber rounds were finished in the usual manner. When fired, the rounds showed no muzzle burst and gave a brilliant white trace for at least 300 yards that was significantly brighter than the standard NATO 30-caliber round.

Example III

Example I is repeated several times substituting for the magnesium the following powdered metals: titanium, zirconium, aluminum, 50% aluminum–50% magnesium; 50% aluminum–50% titanium, 50% magnesium–50% titanium, and Zircaloy. In each case the pyrotechnic composition adhered tightly to the casing and burned continuously emitting a shower of brilliant white sparks.

Example IV

Examples I and III are repeated several times substituting for the $LiNO_3$–KNO_3–$NaNO_3$ eutectic the following salts or salt mixtures and maintaining the molten salt at the indicated temperature: 50% KNO_3–50% $NaNO_3$ (250° C.); 51% $Ca(NO_3)_2$–49% KNO_3 (170° C.); 56% $Cd(NO_3)_2$–14.5% $LiNO_3$–29.5% $NaNO_3$ (125° C.). In each case the pyrotechnic composition adhered tightly to the casing and burned continuously emitting a shower of brilliant white sparks.

Example V

Example I is repeated several times substituting for the salt mixture from about 0.85 to 0.95 part KNO_3–$NaNO_3$–$LiNO_3$ eutectic mixture and from about 0.05 to 0.15 part $Sr(NO_3)_2$. These molten salt mixtures are more viscous than the ternary eutectic used in Example I and slurries containing more than about 10% $Sr(NO_3)_2$ had a paste consistency. The pyrotechnic compositions case bonded and burned continuously emitting a shower of pink sparks. The compositions of this example ignited more readily than the compositions of Example I

Example VI

Example I is repeated several times substituting for the salt mixture from about 0.85 to 0.95 part KNO_3–$NaNO_3$–$LiNO_3$ eutectic mixture and from about 0.05 to 0.15 part of BaO_2 or $LiNO_3$. In each case the pyrotechnic case bonded and burned continuously emitting a shower of pink sparks.

Example VII

Example V is repeated substituting $NaClO_3$ for the $Sr(NO_3)_2$. Compositions containing less than about 10% $NaClO_3$ were readily pourable while those containing higher amounts of $NaClO_3$ were quite viscous, reaching a paste consistency at 15% $NaClO_3$. The case bonded pyrotechnic emitted white sparks when ignited.

Example VIII

Example I is repeated two times substituting for the magnesium powder 80% powdered titanium–20% titanium carbide and 80% powdered titanium–20% tungsten carbide. In each instance the case bonded eutectic gave a brighter, more intense light and burned more rapidly than when metals alone were used.

Although the foregoing examples emphasize the use of eutectic compositions, as their low melting points make them particularly convenient, it will be recognized that compositions other than eutectic compositions may be used, if desired.

According to the provisions of the patent statutes, I have explained the principle and mode of practice of my invention and have described what I now consider to represent its best embodiment. However, I desire to have it understood that, within the scope of the appended claims, the invention may be practiced otherwise than as specifically described.

I claim:

1. A combustible composition having a continuous solid phase and a dispersed solid phase, said continuous phase consisting essentially of a mixture of salts melting below about 250° C. and selected from the group consisting of metal nitrates and metal chlorates, at least one of said salts being selected from the group consisting of alkali metal nitrates, alkali metal chlorates, alkaline earth metal nitrates and alkaline earth metal chlorates, and said dispersed phase consisting essentially of a finely divided metal selected from the group consisting of magnesium, aluminum, titanium, zirconium, alloys thereof and mixtures thereof.

2. A composition according to claim 1 in which the continuous phase contains a compound that emits a colored light when burned.

3. A composition according to claim 2 in which the compound is strontium nitrate.

4. A composition according to claim 1 in which the dispersed phase includes a finely divided compound selected from the group consisting of tungsten carbide and titanium carbide.

5. A composition according to claim 1 in which there is between about 1 and 1.5 parts of dispersed phase for each 3 parts of continuous phase.

6. A composition according to claim 1 in which the continuous phase is a eutectic composition.

7. A composition according to claim 1 in which the solid phase is a eutectic composition consisting of about 31% $LiNO_3$, 17% $NaNO_3$ and 52% KNO_3.

8. A composition in accordance with claim 1 in which the continuous phase is a eutectic composition consisting of about 50% $NaNO_3$ and 50% KNO_3.

9. A combustible composition comprising a continuous solid phase consisting essentially of a eutectic mixture of $LiNO_3$, KNO_3 and $NaNO_3$ and a dispersed phase consisting essentially of finely divided magnesium.

10. A tracer projectile comprising a casing and a combustible composition self-bonded to said casing and having a continuous solid phase and dispersed phase, said continuous phase consisting essentially of a mixture of salts melting below about 250° C. and selected from the group consisting of metal nitrates and metal chlorates, at least one of said salts being selected from the group consisting of alkali metal nitrates, alkali metal chlorates, alkaline earth metal nitrates, and alkaline earth metal chlorates, said dispersed phase comprising a finely divided metal selected from the group consisting of magnesium, aluminum, titanium, zirconium, alloys thereof and mixtures thereof.

11. A method of filling a casing with a tracer composition comprising the steps of mixing together to form a slurry a finely divided metal selected from the group consisting of magnesium, aluminum, titanium, zirconium, alloys thereof and mixtures thereof and a molten salt mixture melting below about 250° C. consisting essentially of salts selected from the group consisting of metal nitrates and metal chlorates, at least one of said salts being selected from the group consisting of alkali metal nitrates, alkali metal chlorates, alkaline earth metal nitrates and alkaline earth metal chlorates, introducing said slurry into the casing, and cooling the filled casing to solidify said molten salt.

12. A combustible composition having a continuous

solid phase and a dispersed solid phase, said continuous phase consisting essentially of a mixture of alkali metal nitrates melting below about 250° C. and said dispersed phase consisting essentially of a finely divided metal selected from the group consisting of magnesium, aluminum, titanium, zirconium, alloys thereof and mixtures thereof.

References Cited

UNITED STATES PATENTS

2,425,005	8/1947	Rechel.	
2,970,898	2/1961	Fox	264—3 XR
3,191,535	6/1965	Mulloy.	
3,140,208	7/1964	Adelman	149—42 X
3,275,484	9/1966	Foote et al.	149—42 X

FOREIGN PATENTS

205,914	8/1956	Australia.

L. DEWAYNE RUTLEDGE, *Primary Examiner.*

L. A. SEBASTIAN, *Assistant Examiner.*