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Artz

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[54] RED PHOSPHORUS CASTABLE SMOKE PRODUCING COMPOSITION

[72] Inventor: **Glen D. Artz**, Canoga Park, Calif.

[73] Assignee: **North American Rockwell Corporation**

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[58] **Field of Search** 149/29, 30, 19, 38, 43, 44, 149/61, 62, 88

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Primary Examiner—Carl D. Quarforth

Assistant Examiner—E. A. Miller

Attorney—L. Lee Humphries and Thomas S. MacDonald

[57] **ABSTRACT**

A castable pyrotechnic white smoke composition which comprises red phosphorous, an alkali metal nitrate, magnesium and a suitable castable polymeric binder.

11 Claims, No Drawings

RED PHOSPHORUS CASTABLE SMOKE PRODUCING COMPOSITION

Smoke markers or grenades are very useful in both military and commercial applications. In military applications, smoke markers can be used to identify target sites. Additionally, in both commercial and military applications such smoke markers are used for rescue operations to identify parties being retrieved. In order for a smoke marker to be readily handleable, it should be capable of being placed in a closed can or container which in some instances can actually be a grenade. If the smoke composition is so disposed in an enclosed container, it must be susceptible to generating smoke without the presence of oxygen or air. In other words, the composition should be self-sustaining. Further, smoke composition should be preferably capable of slow dissipation of the smoke over a given period of time, to allow for identification of the area in which the smoke is originating.

Prior to the herein invention, white phosphorous had often been utilized as the main smoke generating ingredient in various compositions. However, white phosphorous has a drawback in that it is spontaneously combustible in air, which makes it extremely dangerous to handle. Further, white phosphorous rapidly dissipates smoke and does not allow for a gradual release thereof.

Little effort had been directed in the past to the use of red phosphorous smoke compositions. When red phosphorous was used it was in the form of pressed powder and was not cast as a grain. This is an expensive, time consuming and sometimes dangerous process. Further, pressed powders do not have the structural integrity of cast grains. The previous pressed red phosphorous compositions additionally need air in order to burn and were not self-sustaining, and thus could not be used in closed containers where air could not reach the material.

Thus an object of this invention is to provide a self-sustaining castable white smoke composition.

Another object of this invention is to provide a self-sustaining castable smoke composition containing red phosphorous.

Still another object of this invention is to provide a castable white smoke composition which has a long and controlled burn time.

The above and other objects of this invention are accomplished by a novel castable white smoke composition of this invention based on red phosphorous which will burn in the absence of atmospheric oxygen. The composition of the invention contains red phosphorous as a primary fuel ingredient to generate the smoke. The composition additionally contains an alkaline metal nitrate as an oxidizer. Additionally, the composition contains a metallic fuel, such as magnesium, in a relatively small amount. Finally, the composition is held together by a castable binder which additionally serves as a fuel. Virtually any polymeric binder which is suitable for solid propellant utilization can be used. It is preferred that the binder have a relatively high oxygen content and that it cure to a rubbery state. A typical example of such a binder is the class of polysulphide rubbers. Additional other materials in small amounts, such as cross-linking agents, plasticizers, fillers and the like can be present in the composition. The ingredients are typically mixed together in a suitable mixer, poured into the containers or hardware for the smoke composition, and cured at suitable curing conditions of temperature and pressure. By varying the composition and including the use of reactive plasticizers, one can subtly control the burning rate of the smoke compositions of this invention.

It is believed that the invention will be better understood from the following detailed description and examples.

The main component of the smoke composition of this invention is red phosphorous. As indicated, prior to this invention, red phosphorous was very seldom used in smoke compositions. For example, in an early patent, U.S. Pat. No. 528,515, red phosphorous was combined with nitrate and pressed in one embodiment to form a composition which would produce a bright flash of light. However, it was not disclosed as a smoke generating composition. Where red phosphorous has been previously used in an attempt to form a smoke generating composition, it additionally was in a pressed form, not cast, and required the presence of air to burn. White phosphorous, on the other hand, has been used mostly in the past in smoke compositions. However, it is spontaneously combustible in air, as indicated, and does not provide a slow controlled dissipation of smoke.

The red phosphorous used in this invention can vary from 31 to 47 weight percent of the smoke composition. Red phosphorous is normally in a fine particle form. It is not readily obtainable in various size particles. Because of this, one cannot readily achieve a high solid loading in a cast composition, and thus the upper limit of 47 weight percent of the material is determined by a solids loading capability for cast compositions.

An alkali metal nitrate is used in the composition of this invention as an oxidizer. Typical nitrates include sodium and potassium nitrates. One of the primary problems in forming a suitable composition is an unwanted reaction between the oxidizer and the phosphorous. Thus, highly reactive materials, such as the chlorates and perchlorates, are not suitable for the compositions of this invention. The nitrate is used in a solid particulate form in amounts varying from 18 to 32 weight percent of the smoke composition.

In order to generate a hot enough flame to sustain burning of the phosphorous, magnesium is added to the composition of the invention. Magnesium reacts with the nitrate present to generate the heat required for continued combustion of the phosphorous without snuffing out. Further, the reaction of the magnesium with the nitrate helps to provide reliable ignition of the smoke composition. It has been found that from 4 to 5 weight percent magnesium in the smoke composition serves to accomplish the aforegoing purposes.

In order to form a suitable castable smoke composition, a polymeric binder is used. Virtually any binder which has been found suitable for solid propellant compositions can be used herein. However, it is not desirable to have the smoke composition too rigid or brittle, since it is subject often to shock loads particularly when it is used as a grenade. In fact it is preferred that the polymer cure to a rubbery state.

Additionally, it has been found desirable to have a high oxygen containing binder because the quantity of solid oxidizer required can be reduced if the binder can supply some of the oxygen required for oxidation of the phosphorous and other fuels present in the composition. As a result, preferred binders include the polysulfide rubbers, polysulfide-epoxy mixtures such as Thiokol LP–3/Dow Epoxy DER 321 and DER 736 and polyesters produced from the reaction of dibasic acids with dihydric alcohols. A typical polyester binder is hydroxy-terminated polyester resin R–18 as supplied by Mobay Chemical Co. formed from adipic acid and diethylene glycol. Additionally, hydroxy and carboxy terminated butadienes are further contemplated. In fact, any of the polymeric binders set forth can be used herein. Together with the polymer material, there is generally utilized a suitable plasticizer and cross-linking agent.

Various suitable plasticizers are contemplated, which are conventional and well known in the art depending upon the binder selected. Typical plasticizers include, for example, triacetin, bis-dinitropropylacrylate-formal (BDNPA–F), and trimethylolethanetrinitrate (TMETN). Various other plasticizers, of course, are contemplated and can be used.

In addition to the plasticizers, the binder composition will have a certain amount of cross-linking material added thereto. Preferred cross-linking material is PAPI which is polymethylene polyphenylisocyanate. Additional cross-linking agents could include, but are not limited to for example, trimethylolpropane, hexanetriol, castor oil, toluene diisocyanate, diphenyl-methane diisocyanate and MAPO which is tris [1-(2-methyl)-aziridinyl] phosphine oxide.

Generally, the binder and plasticizer, if present, will constitute from 25 to 35 weight percent of the smoke composition. The weight ratio of plasticizer to binder can vary from

0:1 to 1.5:1. The cross-linking agent will vary from 10 to 20 weight percent of the active binder material, depending upon the materials used and the state of cure desired in the end product.

Further, it has been found that FEAA, which is ferric acetylacetonate, can be added to the composition of this invention to provide accelerated cure. Generally from 0.001 to 0.01 weight percent of FEAA is added for this purpose. Other accelerators can be used to hasten the cure time. Selection of fuel accelerators will depend on the composition chosen. For example, when TMETN is a plasticizer then trimethylolpropane TMP, is a most suitable accelerator together with FEAA.

It should be pointed out that the aforegoing composition ranges set forth provide a smoke that is underoxidized. In other words, from a stoichiometric standpoint there is not enough oxidizer present to furnish oxygen for the full combustion of the fuel components. This is very important to the herein invention in that it has been found that in fully oxidized or over oxidized compositions the smoke will burn too vigorously in an uncontrollable manner. However, the composition does provide a castable smoke which does burn in the absence of atmospheric oxygen. Prior to the herein invention a castable red phosphorous smoke composition which will burn in the absence of air was not believed to be known.

The formulation of the smoke is simple and straightforward. Generally the magnesium, phosphorous, plasticizer, and binder are first added to a mixer and mixed at a suitable temperature for a period of time to achieve homogeneity. The nitrate is then added and additional mixing under vacuum is accomplished at the mixed temperature. A vacuum is utilized at this stage to remove any air entrapped in the composition so that more dense castings can be made. Finally, after the nitrate has been mixed into the composition the cross-linking agent and other additives such as the FEAA are added and the final mix continued until all the materials have been thoroughly dispersed. It is preferred to vacuum cast the mixture into prepared hardware used, such as cans or grenades or any other suitable containers for the smoke composition. Casting conditions will of course vary depending upon the binder and cross-linking agents utilized. As indicated, the cure should provide a rubbery final composition as compared to a brittle or rigid one.

In order to start or initially ignite the smoke composition an igniter is required. The smoke composition of this invention can be ignited by virtually any ignition technique utilized for solid propellant ignition. These include a boron/potassium nitrate pellet, electric squibs, electric detonators and explosive materials such as Detacord, Primacord, and Pyrocore. Additionally a first fire mix or igniter mix can be coated onto a surface. A typical ignition composition is comprised of silicon, lead oxide and cuprous oxide which would be mixed with nitrocellulose in a suitable solvent to form a lacquer that is spread onto the surface to be ignited. It is believed that the invention will be further understood from the following detailed examples.

EXAMPLE I

A 5,000-gram batch of a smoke composition of this invention was prepared having the following composition expressed in weight percent. In this and the following examples the percent accelerator is added above the entire composition of the smoke.

Compound	Wt. %
Stabilized Red Phosphorous	38.10
Sodium Nitrate	28.30
Magnesium	4.90
Mobay R-18 Polyester Binder	12.70
Triacetin	14.70
PAPI	1.30
FEAA (added)	0.02

A standard 1-gallon Baker-Perkins vertical mixer commonly used for solid propellant mixing was used to mix the ingredients of this invention. The polyester binder, triacetin, magnesium, and phosphorous were all initially added to the mixer and mixed for 15 minutes at 110° F. The mixing was then stopped and the sodium nitrate was then added and mixing continued for an additional 10 minutes under vacuum at 160° F. After completion of this time period the PAPI and FEAA were then finally added and the mixing was continued for an additional 10 minutes at 160° F. under vacuum. At this point, the mixing of the smoke composition was complete and ready for casting. The composition was vacuum cast into polyethylene tubes which were 2⅞ inches long and had a diameter of three-fourths of an inch. The filled tubes were placed in an oven and cured at 160° F. for 16 hours to a rubbery state.

These filled tubes were ignited by an electric squib and the burn times evaluated by visual observation and a stopwatch. Standard solid propellant strand burning rate equipment (Atlantic Research Corp.), which provides automatic recording of burn times, has also been utilized for burn rate evaluation although open air tests are preferable for obvious reasons.

The aforegoing composition was determined to have a burning rate of 0.70 inch per minute. This composition was additionally found to have an autoignition temperature in excess of 500° F. and was insensitive to impact with a 5 pound weight from a height of at least 50 inches. The composition burned with a bright yellow flame and produced voluminous quantities of white smoke.

EXAMPLE II

A slow burning formulation was tested as compared to that described in Example I. The composition of the smoke in this example comprised:

Compound	Wt. %
Red Phosphorous	46.90
Sodium Nitrate	18.30
Magnesium	4.60
Mobay R-18 Polyester Binder	14.00
Triacetin	15.80
PAPI	1.40
FEAA (added)	0.02

The procedures set forth in Example I were followed to formulate the grain using the same size polyethylene tube as a casting vessel and container for the cured material. This formulation had a burning rate of 0.36 inch per minute or approximately half of the burning rate of that in the composition of Example I. This can be attributed to the change in oxidizer to fuel ratio. Once again, this composition produced a bright yellow flame with great quantities of white smoke.

EXAMPLE III

A fast burning formulation in accord with this invention was formulated for this example using the procedures of Example I and the same polyethylene tubes for casting the grain. The composition used in this example comprised:

Compound	Wt. %
Red Phosphorous	31.30
Sodium Nitrate	31.30
Magnesium	4.50
Mobay R-18 Polyester Binder	11.60
PAPI	0.90
TMETN	20.30
TMP (added)	0.10
FEAA (added)	0.02

Because of the presence of the TMETN instead of the triacetin, together with the TMP, burning rates varying from 1.57 to 2.16 inches/minute were obtained from samples tested. This indicates that the burning rate of this composition was from two to three times as great as the composition set forth in Example I. Once again, this composition burned with a bright yellow flame producing large quantities of white smoke.

I claim:

1. A castable smoke producing composition comprising from 31 to 47 weight percent red phosphorous, from 18 to 32 weight percent alkali metal nitrate, from 4 to 5 weight percent magnesium and from 25 to 35 weight percent of a castable polymeric binder.

2. The composition of claim 1 in which said alkali metal nitrate is potassium nitrate or sodium nitrate.

3. The composition of claim 1 in which the castable polymeric binder is a castable polysulphide, polysulphide-epoxy mixture, polyester or polybutadiene.

4. The composition of claim 3 in which the polybutadiene is a hydroxy or carboxy terminated polybutadiene.

5. The composition of claim 3 in which the polyester is prepared by the reaction of a dibasic acid with a dihydric alcohol.

6. The composition of claim 5 in which the dibasic acid is adipic acid and the dihydric alcohol is diethylene glycol.

7. The composition of claim 1 in which the castable polymeric binder includes a suitable plasticizer and cross-linking agent.

8. The composition of claim 7 in which the cross-linking agent is present in an amount of from 10 to 20 weight percent based on a total castable polymeric binder content.

9. The composition of claim 7 in which the plasticizer is trimethylolethanetrinitrate, triacetin, or bis-dinitropropylacrylate-formal.

10. The composition of claim 7 in which the cross-linking agent is polymethylene polyphenylisocyanate.

11. The composition of claim 7 in which the composition includes from 0.001 to 0.01 weight percent of ferric acetylacetonate catalyst.

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