United States Patent

Staudacher et al.

[15] **3,680,483**

[45] **Aug. 1, 1972**

[54] **ANNULAR FLARE GRAINS**

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[22] Filed: **Oct. 6, 1970**

[21] Appl. No.: **78,640**

[52] **U.S. Cl.** **102/37.8,** 149/19, 149/21, 149/38, 149/41, 149/44, 149/112, 149/113, 149/114

[51] **Int. Cl.** **C06d 1/10**

[58] **Field of Search**.....149/19, 20, 21, 38, 41, 44, 149/112–114; 102/99, 37.8

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[57] **ABSTRACT**

Disclosed is an annular grain for use as an illuminating or signaling flare. The grain is prepared by pour casting a composition made up of an oxidizer, particulate magnesium and an epoxy resin-curing agent combination into a desired form and curing it into a coherent grain.

10 Claims, No Drawings

ANNULAR FLARE GRAINS

BACKGROUND OF THE INVENTION

Illuminating flares employing magnesium and an oxidizer as well as a polymeric binder are known. In some cases such flares are fabricated into cylindrical shaped candles. The cylindrical flares are useful as battlefield illumination munitions. For other purposes, such as marking and signaling, star clusters made up of several annular flare pellets are useful. The annular shape provides a center perforation for insertion of the initiator and ignition mixture. The annular pellets have been formed by pressing a dry or damp powdered mixture of ingredients into a die. Pellets prepared in this manner are effective emitters of light; however, they have the disadvantage of burning on all surfaces after ignition at their center. Burning on all surfaces causes the grain to rapidly lose its physical integrity as it burns. The loss of physical integrity results in aerodynamic breakup of the flare pellet into small parts.

It is an object of the present invention to provide an annular flare pellet which, upon center ignition, burns only on the surface of the center perforation.

An additional object is to provide such a pellet which is substantially more resistant to aerodynamic breakup than those presently in use.

An additional object is to provide such a pellet which can be prepared by pour casting a flowable composition into a mold with subsequent curing.

SUMMARY OF THE INVENTION

The invention is a generally annular grain for use as a signaling or illuminating flare. The grain comprises a particulate alkali metal nitrate or perchlorate ranging in size from 10 to 750 μ in the longest dimension as oxidizer. The oxidizer makes up from 21 to 50 percent of the composition. Unless otherwise specified all percentages are intended to represent weight percents of the entire composition. In addition to the oxidizer, the flare comprises from 43 to 70 percent particulate magnesium ranging in size from 25 to 250 μ in the longest dimension. The oxidizer and magnesium are combined with the reaction product of an epoxy resin and an amine terminated polyalkylene oxide; alkylene polyamine; alkyl, aryl or mixed alkyl aryl amine; or a carboxylic acid or anhydrides thereof as binder. As used herein, the amines described also include the nitrate and perchlorate salts thereof. The epoxy resin accounts for from 30 to 70 percent of the binder which is further characterized by containing at least 30 percent chemically combined oxygen and making up from 18 to 24 percent of the composition.

DETAILED DESCRIPTION

In a preferred embodiment of the invention, the flare grain contains from 45 to 55 percent substantially spherical magnesium particles having a mean particle size distribution of from 125 to 250 μ in diameter. Bi- or multi-modal size distribution is preferred for most efficient packing of the magnesium particles. Sodium nitrate particles having mean diameters from 15 to 250 μ are preferred for use as the oxidizer. The amount of oxidizer employed is preferably from 25 to 33 percent of the flare composition.

A number of amine terminated polyalkylene oxide cured epoxy resin binders have been found to be especially effective. Examples of useful epoxy resins are the diglycidyl ether of polypropylene glycol containing 27 percent oxygen, glycerin diglycidyl ether (GDGE) and a glycerin glycidyl ether having an average functionality of between 2 and 3 (GDGE 2/3). The latter two resins have an oxygen content, determined by analysis, of at least 32 percent. Additionally, ethylene glycol diglycidyl ether, polyethylene glycol diglycidyl ethers and the polyglycidyl esters of polyfunctional acids may readily be used.

The epoxy resins are preferably cured with an amine terminated polypropylene oxide having an average molecular weight of 250 or the nitrate or perchlorate salt thereof. The amine terminated polypropylene oxide has an analyzed oxygen content of 23 percent. The nitrate and perchlorate salts of the polypropylene oxide have analyzed oxygen contents of 30 percent and are therefore preferred for use as curing agents. Other amine terminated polyalkylene oxides, e.g. polyethylene oxide or polybutylene oxide, which are curable liquids and contain the requisite high percentages of oxygen, may be used. The epoxy resins may also be cured with an acid anhydride, e.g. maleic, fumaric, succinic, and pyromellitic anhydride to provide a binder having a high oxygen content. Suitable carboxylic acid curing agents include oxalic, citric and formic acid.

The binder may contain, in addition to the epoxy resin and curing agent, from 5 to 85 percent of a plasticizer containing at least 40 percent oxygen. In this embodiment, the binder system makes up from 2 to 30 percent of the composition. The inclusion of an oxygen rich plasticizer in the binder system increases the luminous efficiency of the flare composition. Useful plasticizers are those compositions which contain greater than 40 percent oxygen and either decrease or do not excessively increase the viscosity of the flare composition when added thereto. Examples of such plasticizers are nitroglycerin, diethylene glycol dinitrate (DEGDN), monoethanolamine nitrate, ethylene carbonate, ethylene glycol, ethylene glycol dimethyl ether, glycerin, triethylene glycol dinitrate (TEGDN) and polyglycidyl nitrate. The nitroplasticizer TEGDN has been found to be an excellent plasticizer for castable flare compositions. It is oxygen-rich (56 percent), energetic, safe and compatible with epoxy resins. The amount of plasticizer employed is preferably from 20 to 65 percent of the binder at higher binder levels, i.e. 18 to 30 percent and from 10 to 65 percent at lower binder levels, i.e. 2 to 18 percent. By incorporating the plasticizer into the binder system and selecting the proper ratio of ingredients, a pour castable flare having illuminating efficiency equivalent to the pressed flares presently in use is achieved.

The castable composition is poured into a mold and cured at elevated temperatures, usually for a period of at least 4 hours, in a 60° to 70° C. oven. The size of the annular grain is not critical. Normally, the grain size ranges from one-fourth to three-fourths inches internal diameter, 1 to 3 inches external diameter and one-fourth to 1 ½ inches in thickness.

The invention is further illustrated by the following examples:

EXAMPLE I

A castable composition was prepared from the following ingredients:

Ingredient	Weight % of Composition
Atomized Magnesium	
a) 30/50 mesh	16 ⅓
b) 50/100 mesh	16 ⅓
c) 100/200 mesh	16 ⅓
$NaNO_3$ (400 mesh)	27.0
Triethylene Glycol Dinitrate	9.6
Glycerin Glycidyl Ether having functionality between 2 and 3	8.4
Partial nitrate salt of an amine terminated polyalkylene oxide - ave. mol. wt. of 250 as curing agent	6.0

A preferred method of blending the composition is to combine the glycidyl ether, curing agent, and TEGDN with thorough mixing; add the magnesium with additional mixing and finally blend in the $NaNO_3$.

The composition was pour cast into a cylindrical mold having a 1.43 inch diameter and a one-half inch rod through its center. The rod extended through the mold and was centered at the top and bottom. The interior of the mold had been pretreated with a silicone mold release agent known as SLIPICONE and marketed by the Dow Corning Corporation. The mold was vibrated during the casting with the vibration being continued after filling for an additional 30 minutes. After standing at ambient temperature for about 1 hour, the mold was placed in a recirculating oven at 72° C. for 16 hours. After cooling to ambient temperature, the center rod was removed and the casting manually slipped from the mold.

The casting was cut with a saw into a series of annular grains having diameters of 1.43 inch and thicknesses of 0.585 inch. The center holes were reamed out to 0.585 inch to conform with specifications. Use of a rod having the proper dimensions as mandrel would eliminate the reaming step. Another set of annular grains having thicknesses of 0.383 inch was prepared as above. An additional advantage of the instant composition is that it can be machined to the desired configuration without danger of ignition.

The flare grains were fired in a flare tunnel to determine their luminous efficiency. The light from the flares was sensed by two Weston YYV Selenium Photovoltaic Cells. The signal from one of the cells was amplified and recorded as an analog signal by a Honeywell Model 906 B Visicorder. The signal from the other cell was integrated and recorded digitally by a Dymec Model 2210 Voltage Frequency Converter and a Hewlett Packard Model 523 CR Electronic Counter.

All flare pellet firings were center hole initiated. The center hole was filled with shavings of the flare composition recovered from the sawing operation. Three boron, potassium nitrate igniter pellets were also pressed into the shavings. Igniter cord was then forced into the center hole and ignited remotely with a hot nichrome wire.

When the flare grains were fired standing on edge with the light sensing equipment looking at a flat side the light output was determined to be 31,800 candle seconds/gm. However, when the grain was suspended by two one-fourth inch rods under its flat side, the average efficiency recorded was 51,600 candle seconds/gm.

The burning was observed to take place only on the surfaces of the internal hole of the annular flare grain. This is in contrast with the burning properties of conventional pressed annular flare grains which burn on all surfaces giving a ball of light. The double jets of luminosity are preferred because of the greater area of luminous flame exposed to the observer, resulting in better recognition. Additionally the manner in which the grain burns renders it more resistant to aerodynamic breakup during combustion.

EXAMPLE II

The 0.585 inch thick pellets were loaded into five star shells and fired to 700 feet altitude with a mortar. During this test, which was conducted in a driving thunderstorm, the flare grains ignited properly and burned for an average of 10.5 seconds without breaking up.

We Claim:

1. A generally annular grain for use as a flare which comprises:
   a. from 21 to 50 percent of a particulate alkali metal nitrate or perchlorate ranging in size from 10 to 750 μ in the longest dimension as oxidizer;
   b. from 43 to 70 percent of particulate magnesium ranging in size from 25 to 250 μ in the longest dimension; and
   c. the reaction product of an epoxy resin and an amine terminated polyalkylene oxide; alkylene polyamine; alkyl, aryl or mixed alkyl-aryl amine; carboxylic acid or acid anhydride curing agent in which the epoxy resin accounts for from 30 to 70 percent of the reaction product as binder, the binder being further characterized by containing at least 30 percent chemically combined oxygen and making up from 18 to 24 percent of the flare composition.

2. The grain of claim 1 which contains from 45 to 55 percent substantially spherical magnesium particles having a mean particle size distribution of from 125 to 250 μ in diameter.

3. The grain of claim 1 which contains from 25 to 33 percent sodium nitrate particles having mean diameters of from 15 to 250 μ.

4. The grain of claim 1 wherein the epoxy resin is a glycerin glycidyl ether having an average functionality of between 2 and 3 and the curing agent is an amine terminated polypropylene oxide having an average molecular weight of 250 or the nitrate or perchlorate salt thereof.

5. A generally annular grain for use as a flare which comprises:
   a. from 21 to 50 percent of a particulate alkali metal nitrate or perchlorate as oxidizer ranging in size from 10 to 750 μ in the longest dimension;
   b. from 43 to 70 percent particulate magnesium ranging in size from 25 to 250 μ in the longest dimension; and
   c. the reaction product of an epoxy resin and an amine terminated polyalkylene oxide; alkylene polyamine; alkyl, aryl or mixed alkyl-aryl amine or acid anhydride curing agent in which the epoxy

resin accounts for from 30 to 70 percent of the reaction product which is further characterized by containing at least 30 percent chemically combined oxygen together with a plasticizer containing at least 40 percent oxygen as binder, said binder making up from 2 to 30 percent of the grain and said plasticizer making up from 5 to 85 percent of the binder.

6. The grain of claim 5 wherein the plasticizer is nitroglycerin, diethylene glycol dinitrate, monoethanolamine nitrate, ethylene carbonate, ethylene glycol, ethylene glycol dimethyl ether, glycerin or polyglycidyl nitrate.

7. The grain of claim 5 wherein the plasticizer is triethylene glycol dinitrate.

8. The annular grain of claim 5 wherein the internal diameter is from one-fourth to three-fourths inch, the external diameter is from 1 to 3 inches and the thickness is from one-fourth to 1 ½ inch.

9. A method for preparing a generally annular grain for use as a flare which comprises:

a. preparing a castable curable composition by mixing:

i. from 21 to 50 percent of a particulate alkali metal nitrate or perchlorate ranging in size from 10 to 750 μ in the longest dimension as oxidizer;

ii. from 43 to 70 percent of particulate magnesium ranging in size from 25 to 250 μ in the longest dimension; and

iii. an epoxy resin and an amine terminated polyalkylene oxide; alkylene polyamine, alkyl, aryl or mixed alkyl-aryl amine or acid anhydride curing agent in which the epoxy resin accounts for from 30 to 70 percent of the mixture, the mixture being further characterized by containing at least 30 percent chemically combined oxygen and making up from 18 to 24 percent of the composition;

b. casting the composition into a generally annular form; and

c. curing the cast composition.

10. The process of claim 9 wherein the castable composition is prepared by mixing:

i. from 21 to 50 percent of a particulate alkali metal nitrate or perchlorate as oxidizer ranging in size from 10 to 750 μ in the longest dimension;

ii. from 43 to 70 percent particulate magnesium ranging in size from 25 to 250 μ in the longest dimension; and

iii. 2 to 30 percent of an epoxy resin and an amine terminated polyalkylene oxide; alkylene polyamine; alkyl, aryl or mixed alkyl-aryl amine or acid anhydride curing agent in which the epoxy resin accounts for from 30 to 70 percent of the mixture which is further characterized by containing at least 30 percent oxygen together with a plasticizer which contains at least 40 percent oxygen.

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