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[54] CASELESS SMOKE GRENADE INCLUDING POLYVINYL CHLORIDE BINDER

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[58] **Field of Search** .....149/19, 76, 84, 2; 102/65, 102/90, DIG. 1

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[57] **ABSTRACT**

A caseless smoke generating grenade consists essentially of a cast flexible main charge. The flameless pyrotechnic composition used in the main charge is comprised of substantially equal proportions of zinc oxide and a perchlorate oxidizer distributed throughout a plasticized polymeric resin fuel having a high halogen content. The composition is free of solvent and provides controlled burning coupled with excellent flexibility, cohesive strength and impact resistance.

12 Claims, No Drawings

CASELESS SMOKE GRENADE INCLUDING POLYVINYL CHLORIDE BINDER

BACKGROUND AND SUMMARY OF THE INVENTION

The present invention relates generally to a pyrotechnic smoke producing composition and more particularly concerns a new and improved smoke composition and to caseless grenades made therefrom.

The white smoke formulation used extensively and successively heretofore has contained substantially equal proportions of zinc oxide and hexachlorethane. Upon combustion zinc and ammonium chlorides are produced and are rapidly hydrolized by moisture in the air to yield the desired clouds of white smoke. Frequently a minor amount of metal powder, such as aluminum powder, also is added to control the burning time of the composition. It also has been recognized that the amount and quantity of smoke generated by such compositions can be improved by the addition of perchlorate oxidizers.

These known smoke producing formulations are predominently mixtures of the dry granular components consolidated within a compact mass or charge in order to operate effectively and provide the desired controlled burning rate. Such consolidation required compression or compaction of the mixture under considerable pressure within a suitably strong canister or other container. To resist the pressure loads, costly and bulky containers were used. These generally contained small exhaust ports which frequently and disadvantageously permitted flaming of the composition. Additionally, when the compressed mixture was subjected to shock, it often fractured and exposed large surface areas of the charge, also resulting in open flaming rather than the development of voluminous clouds of white smoke.

The advisability of utilizing plastic binders with such formulations to improve the cohesiveness of the charge and provide a consolidated body has been proposed but never proved feasible. This was due at least in part to the adverse influence of the binder and its solvent on the burning rate of the composition. As a result the binders generally constituted only about 2 – 7 percent of the composition since binder amounts exceeding about 10 percent generally resulted in mixtures which burned too slowly, the excess binder merely acting as a diluent in the composition. Additionally, extra care had to be exercised to remove as much of the solvent as possible.

These compositions also had a tendency to burn at relatively high combustion temperatures, that is at temperatures of about 1,000° C or higher. This high combustion temperature necessarily resulted in destruction of any additional agent being dispersed and consequently smoke formulations incorporating agents such as tear gas or the like exhibited low operating efficiencies. The high combustion temperatures also created a substantial thermal updraft in the area of the smoke canister causing the smoke to rise rapidly and be easily diluted within the atmosphere, thereby resulting in lower efficiency of operation.

These low efficiency, low output rate canisters had the additional inherent disadvantage of becoming quite hot as they discharge their pyrotechnic contents and thus could constitute a safety hazard to the unsuspecting. Further, after all the agent had been dispersed, the spent housing or casing could be used in a manner contrary to its originally intended purpose.

Accordingly, it is a primary object of the present invention to provide a new and improved pyrotechnic smoke composition of the zinc oxide type having a relatively low combustion temperature coupled with high volume smoke output and characterized by flameless combustion at atmospheric pressure.

Another object of the present invention is to provide a new and improved zinc oxide type smoke formulation free of hexachlorethane and exhibiting high efficiency operation and rapid yet controlled dissemination of voluminous clouds of dense smoke. Included in this object is the provision for a charge of the type described which is easily ignitable even in the absence of a special ignition mix.

Still another object of the present invention is to provide a new and improved zinc oxide smoke formulation adapted to being molded, extruded or otherwise formed into caseless smoke producing charges free of the bulky containers heretofore used to confine the pyrotechnic formulation. Included in this object is the provision for a polymeric smoke producing charge exhibiting excellent flexibility and cohesive strength thereby avoiding rupture upon impact with hard surfaces.

An additional object of the present invention is to provide a caseless grenade of the type described having a pyrotechnic charge that does not require consolidation and can assume a variety of different shapes yet is completely free of solvents that might adversely affect the burning rate of the charge.

A further object of the present invention is to provide a new and improved caseless smoke grenade, that is, a grenade free of the bulky metal or noncombustible containers used heretofore, adapted to incorporate additional vapor producing substances such as tear gas, insecticides, cloud nucleants or the like. This object includes provision for a smoke generating grenade having a relatively low burning temperature, characterized by flameless combustion at atmospheric pressure and facilitating dispersion of tear gas or similar agents in a highly efficient manner without thermal destruction.

Other objects will be in part obvious and in part pointed out more in detail hereinafter.

These and related objects are accomplished in accordance with the present invention by providing a solid caseless charge of flameless smoke producing pyrotechnic material exhibiting excellent flexibility and cohesive strength. The pyrotechnic composition consists essentially of zinc oxide, ammonium perchlorate oxidizer and a solvent-free plasticized polymeric resin having a high halogen content, such as plasticized polyvinyl chloride.

A better understanding of the objects, advantages, features, properties and relationships of the invention will be obtained from the following detailed description which sets forth certain illustrative embodiments and is indicative of the various ways in which the principles of the present invention are employed.

DESCRIPTION OF A PREFERRED EMBODIMENT

As mentioned hereinbefore, the caseless grenade of the present invention consists essentially of a cast, extruded or formed charge of a white smoke formulation

that includes not only the zinc oxide and ammonium perchlorate components used heretofore but also advantageously eliminates the conventional hexachlorethane and replaces it with a plasticized organic thermoplastic resin having a moderate to high halogen content. Unlike prior zinc oxide compositions the resin acts not as just a binder for the reactants but as the fuel for the combustion reaction and as a source of halogen for producing the desired zinc and ammonium chlorides. As mentioned the rapid hydrolysis of these chlorides by the moisture in the air is responsible for the voluminous clouds of white smoke resulting from combustion of the composition. At the same time the composition is free of solvents that adversely affect its burning rate and includes a resin that serves as a control over the combustion temperature of the composition. Although the resultant flameless combustion occurs at relatively low temperatures, that is at a temperature range of about 350°–500° C, the requisite reaction of the zinc oxide is effectively and efficiently carried out to produce the desired smoke output.

Advantageously the organic plasticizer used in conjunction with the halogen containing resin acts as a vehicle for mixing and homogenizing the components of the formulation while obviating solvents in the system. The plasticizer may be of the general purpose type suited for use with halogen containing polymers such as polyvinyl chloride. The preferred plasticizers are generally esters of dibasic acids such as phthalic, adipic, maleic, succinic or the like. For example plasticizers such as dibutyl and dioctyl phthalate, dihexyl sebacate, dilauryl adipate and the like may be used. These liquid plasticizers, being fully compatible with the resin and of low volatility, become an integral part of the plastisol composition that serves as a dispersing medium for the zinc oxide and perchlorate oxidizer as well as a fuel, binder and halogen donor.

The halogenated resins found most suited to functioning both as a combustible organic fuel and as a source of halogen for reaction with the zinc oxide are the high molecular weight polymers and copolymers having a moderate to high halogen content, such as vinyl chloride and copolymers thereof. In this connection the vinyl resins sold by B. F. Goodrich under the trade name Geon, such as "Geon 121," have given good results. These polymers are high molecular weight homopolymers of vinyl chloride having an average molecular weight of about 200,000. The solid particulate resin has a specific gravity of about 1.4 and an inherent viscosity of about 1.2 as measured by test procedure ASTM-D- 1234-60 A. The preferred material also has a chlorine content of about 56 percent; however, other polymers and copolymers of moderate to high halogen content such as vinylidene chloride may be employed.

The polymeric resin as received from the supplier is a fine powder having a bulk density of about 20–25 lbs./cubic foot and a particle size small enough so that 100 percent of the powder easily passes through a 200 mesh screen. The resin is preferably of the "stir-in" type and is preferably plasticized with a general purpose plasticizer of the less volatile type, such as dioctyl phthalate, using substantially equal proportions of the resin and plasticizer. However, frequently it is desired to reduce the relative amount of plasticizer to achieve proper processing conditions.

Excellent results are achieved when substantially equal proportions of the plasticized halogenated resin, perchlorate oxidizer and zinc oxide are utilized. However, variations in the amounts of the respective components are permissible. Accordingly, the plasticized resin or plastisol may broadly vary from about 10 percent by weight up to about 60 percent by weight and the amount of zinc oxide and perchlorate oxidizer may be from about 15 percent to about 40 percent of the pyrotechnic smoke producing composition. Surprisingly, formulations using less than 15 percent of zinc oxide tend to flame while zinc oxide concentrations below 2 percent are completely ineffective. Thus the preferred zinc oxide content is about 18 percent or more. It is also preferred in accordance with the present invention to incorporate into this smoke formulation a minor amount of a supplemental halogen donor, such as ammonium chloride, particularly at medium to low resin concentration levels, the ammonium chloride serving as an additional smoke forming component. Thus, it has been found that the preferred smoke formulation generally falls within the approximate ranges given in Table I.

TABLE I

Component	Parts by Weight Range	Specific
Resin	10–25	18
Plasticizer	10–25	17
Perchlorate Oxidizer	20–35	32
Zinc Oxide	18–40	34
Supplemental Halogen Donor	0–15	9

In preparing the white smoke formulation for fabrication into caseless grenades in accordance with the present invention the various components generally are mixed in a conventional manner so as to obtain full homogeneity thereof. Thus the polyvinyl chloride resin is mixed with an equal amount of the liquid plasticizer to form a fluid dispersion or suspension having a paste-like or gel consistency to which is subsequently added the zinc oxide, ammonium chloride and ammonium perchlorate. The components are blended in a suitable mixing container to provide the requisite homogeneous distribution of the components throughout the composition. For safety considerations it is generally preferred that the perchlorate oxidizer be the last component to be added to the mix. The paste-like mixture is a flammable material having a viscosity of about 200,000 cps. This mixture is then poured into suitable molds and cast into its desired shape or added to an extruder for subsequent fabrication into its final configuration. The suitably configured or extruded pieces or charges of smoke formulation are then slowly heated at moderate temperature, such as temperatures of about 300° F for a period of approximately 2 to 3 hours.

The resultant charges have a density of about 1.5, exhibit excellent structural integrity and strength and are relatively insensitive to impact yet are easily ignited by a cigarette, match or the like even in the absence of an ignition mix. This resiliency, flexibility and impact resistance makes the formulation particularly well suited to caseless grenades. It will be appreciated that frequently it may be desirable to provide a specific grenade structure with a pull wire lighter or other ignition device, or to incorporate a short delay element such as a 5 second delay at the ignition portion of the grenade in order to facilitate its ignition and permit the

user to propel the grenade to its desired location or to otherwise remove himself from the area of the smoke generation prior to the ignition of the main pyrotechnic smoke producing charge.

Where the caseless grenade is to be used for purposes other than merely the production of white smoke, such as where it is to produce tear gas vapors or the like for riot control application, the cured cast or extruded charge may be provided with an elongated cavity along the length thereof and a suitable riot control agent placed therein. Preferably a plurality of such cavities may be provided within the caseless grenade in order to more fully utilize the combustible pyrotechnic composition. The tear gas producing riot control agents frequently employed are the ortho substituted benzal malononitriles, such as the fluoro, chloro, nitro, cyano or hydroxy substituted benzal malononitriles.

It is also within the scope of the present invention to incorporate suitable color producing agents such as organic dyes in the smoke producing composition. These may be incorporated into the mix prior to the casting or extruding operations so long as the dye is not adversely affected by the heating operation. Where the dye pellets are sensitive to temperatures below about 350° F, incorporation of the dye is preferably withheld until after the charge has cooled. As will be appreciated other dispersible agents, such as insecticides or the like, may also be added to the grenade for controlled release upon combustion.

Although varying amounts of the tear gas, dye or other additives may be incorporated into the smoke producing grenade, these additives should generally constitute less than 50 percent of the total weight of the smoke grenade or similar device. In fact, in the preferred formulation wherein the dye is mixed with the composition prior to the casting or extruding operation, the dye constitutes only about 35 percent by weight of the total main charge.

It is a further advantageous feature of the present invention that the total burning time and, consequently, the mass consumption rate for each grenade or other device formed from the smoke formulation of the present invention can be easily controlled. The mass consumption rate associated with a particular device is reported in terms of the weight per unit of time and is the product of the linear burning rate of the composition, the density of the composition and the size of the surface area subject to combustion. As will be appreciated, for a single composition, the first two factors may remain constant yet the mass consumption rate can still be varied with the surface area under combustion and will increase or decrease as that area increases or decreases. Thus by simply providing a central aperture or elongated cavity along the length of the device and permitting the composition to burn radially outwardly, the mass consumption rate of a device can be substantially increased over that for a device of identical composition and construction except for the central aperture.

The invention will be further described with reference to the following specific examples which are provided in order that the present invention may be more readily understood. These examples are given by way of illustration only and are not intended to be a limit on the practice of the invention. All amounts are given as parts by weight unless otherwise specified.

EXAMPLE I

A white smoke formulation was prepared by initially mixing equal amounts of polyvinyl chloride (Geon 121 resin) and dioctylphthalate plasticizer until the mix was homogenieous. Thereafter approximately 35 percent zinc oxide and 8 percent ammonium chloride was added and thoroughly blended into the mixture. Next about 27 percent by weight of ammonium perchlorate was added to the composition and the entire mix was blended for about 15 minutes using a wire whip paddle.

The resultant paste-like mixture was then poured into a 4-inch long cardboard mold of generally cylindrical configuration having a diameter of about 1 inch and the filled mold placed in an oven at 300° F for 2 hrs. The composition was cooled and the resultant solid charge removed from the cardboard mold. It exhibited excellent flexibility and upon ignition at one end thereof burned in cigarette fashion at a rate of about 4 inches/minute.

EXAMPLE II

The procedure of Example I was repeated except that the solid cured charge was provided with a central longitudinally extending hole of about one-eighth inch diameter along the entire length thereof. This resulted in a four fold increase in the surface area under combustion and a corresponding increase in the mass consumption rate, the entire charge being consumed in about 15 seconds.

As will be apparent to persons skilled in the art, various modifications, adaptations and variations of the foregoing specific disclosure can be made without departing from the teachings of the present invention.

I claim:

1. A flameless pyrotechnic smoke producing composition comprising from about 15 to about 40 percent by weight zinc oxide, from about 15 to about 40 percent by weight oxidizer and greater than about 10 percent by weight of a plasticized resin fuel comprised of an organic plasticizer and a vinyl polymer resin having a moderate to high chlorine content, said composition exhibiting a combustion temperature well below 1,000° C.

2. The composition of claim 1 wherein the polymeric resin includes polyvinyl chloride and the combustion temperature of the composition is about 500° C and less.

3. The composition of claim 1 including a minor amount of a supplemental halogen donor capable of serving as an additional smoke forming component.

4. The composition of claim 1 wherein the oxidizer is ammonium perchlorate.

5. The composition of claim 1 wherein the plasticized resin fuel constitutes approximately one third the total weight of the pyrotechnic composition.

6. The composition of claim 1 wherein the organic plasticizer and polymeric resin are present in substantially equal proportions by weight.

7. The composition of claim 1 comprising 10–25 percent by weight polymeric resin, 10–25 percent by weight plasticizer, 20–35 percent by weight perchlorate oxidizer and 18–40 percent by weight zinc oxide.

8. A caseless grenade comprised of a solid, flexible, impact resistant charge of a flameless pyrotechnic smoke generating composition comprising from about

15 to about 40 percent by weight zinc oxide, from about 15 to about 40 percent by weight oxidizer and at least 10 percent by weight of a plasticized vinyl polymer resin fuel, said resin having a moderate to high chlorine content, said composition exhibiting a combustion temperature well below 1,000° C.

9. The caseless grenade of claim **8** wherein the charge includes up to about 35 percent by weight based on the weight of the pyrotechnic composition of an auxiliary agent for dispersion with the smoke upon combustion of the pyrotechnic composition.

10. The caseless grenade of claim **9** wherein the auxiliary agent is a tear gas producing agent.

11. The caseless grenade of claim **8** including an ignition mix and delay element for igniting the charge.

12. The caseless grenade of claim **8** wherein the charge includes a color producing agent.

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