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3,565,706

INCENDIARY COMPOSITION CONTAINING A METALLIC FUEL AND A SOLID FLUOROCARBON POLYMER

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10 Claims

ABSTRACT OF THE DISCLOSURE

Pyrotechnic compositions characterized by long-burning qualities and retentive incandescent ash maximizing effectiveness for incendiary bombs and similar military applications are formed of finely subdivided Groups IIIB, IVB or VB metal or metal hydrides and solid fluorocarbon polymer as oxidizer material in a mol ratio for fuel to oxidizer of between about 2.9 to 15, e.g., depleted uranium as fuel and polyfluoroalkyl acrylate polymer as oxidizer-binder.

BACKGROUND OF THE INVENTION

A wide variety of pyrotechnic compositions are known and are used in vast quantities for a multitude of purposes. For example, some slow burning, low heat output compositions have been devised for heating combustibles at camp sites or the like. By way of contrast, there are the high heat output and short burning compositions which are now used for welding, military incendiary applications and the like, e.g., thermite-type products which are mixtures of powdered aluminum and iron oxide and also other metal-fuel pyrotechnics such as those employing powdered magnesium in conjunction with oxidizers including fluorocarbon materials.

For military applications, a major portion of incendiary compositions utilize hydrocarbon fuels contained in a jellied matrix. However, metal-fuel incendiary compositions including the thermite-type materials, are employed in incendiary bombs and similar military applications.

From the military viewpoint, jellied hydrocarbon fuel and lightweight metal fuel incendiary products, such as those based on aluminum and magnesium, have certain inherent disadvantages. For example, the relatively lightweight of these materials and their low bulk density seriously limit the terminal velocity and penetration ability of devices incorporating such incendiary compositions when air-dropped onto a target. Also, fragment penetration of such incendiary products when explosively disseminated is relatively poor because of their inherent low density. Such relatively low density incendiary products also present difficulties from the military viewpoint since incendiary bombs which contain these products cannot be made to have identical ballistics with explosive bombs and this prevents or inhibits the air-dropping of mixed loads of incendiary and explosive bombs accurately into the same target area.

Although a great bulk of the incendiary compositions utilized for military or industrial applications involve lightweight metals or other light fuels, it is also known to employ heavy metals such as titanium, zirconium and the like as fuel materials in pyrotechnic compositions (see U.S. 3,006,745). Also the utility of halohydrocarbons as oxidizer materials for metals in pyrotechnic compositions has been known for many years (see U.S. 1,318,074). Utilization of this general concept has been applied in the formation of improved pyrotechnic com-

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positions from light metals and liquid fluorocarbons (see U.S. 3,156,595).

The requirements for improved propellants for use in guided missiles, rocket propulsion, underwater propulsion and the like have prompted further research and development with pyrotechnic compositions. This has resulted in the investigation of a wide variety of fluorine-containing materials as oxidizers in conjunction with a multitude of materials as fuel components in pyrotechnic compositions (see U.S. 3,203,171). These investigations have extended to structural shapes and arrangements of the pyrotechnic compositions in addition to their chemical composition (see U.S. 3,163,113). Space limitations in missiles has also prompted research and development to improve energy output to bulk ratio of propellant or other pyrotechnic compositions (see U.S. 3,164,504).

Notwithstanding the vast amount of research and development work which has occurred in the field of pyrotechnic compositions, particularly with the impetus given by a high level of activity in the guided missile and propellant fields, further improvements are needed in pyrotechnics, particularly in provision of long-burning compositions maximizing effectiveness for incendiary bombs and similar military applications.

OBJECTS

A principal object of this invention is provision of new improved pyrotechnic compositions and devices. Further objects include the provision of:

(1) Solid pyrotechnic compositions that are more effective than thermite, magnesium-metal and other existing incendiary materials.

(2) Incendiary compositions which upon initial combustion produce a non-fluid incandescent ash which continues to react with atmospheric oxygen and remains incandescent for an extended period of time.

(3) Methods of altering burning rates in incendiary compositions for control of incendiary effects for various applications, e.g., in connection with particular military targets.

(4) Methods of altering the density of incendiary materials to control the ballistics of bombs or other devices incorporating the incendiary compositions.

(5) Incendiary bombs that have the identical density of their identical shaped explosive counterparts to provide drop ballistics for both which will be the same enabling mixed loads of incendiary explosive bombs to be dropped accurately within a given target area.

(6) Means for increasing the density of incendiary materials for better penetration of targets by falling incendiaries or explosively disseminated fragments.

(7) Methods of increasing the heat output per unit volume of incendiary compositions.

(8) New information on use of various metals as fuels to control burning time and character of ash in incendiary compositions.

(9) Pyrotechnic compositions with varied hardness and flexibility rendering these materials particularly suitable for various incendiary weapons and devices.

(10) Incendiary compositions which have various Pilling-Bedworth ratios (ratio of slag volume to unburned material volume) by addition of bulk increasing agents to increase the area covered by incandescent ash created by the incendiary composition.

(11) Information on utilization of various binder-oxidizer compositions to control incendiary effects.

(12) Combinations of heavy metal fuel materials with other additives to provide violent reaction with water for

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the purpose of discouraging fire-fighting efforts against incendiary weapons or devices formed from the pyrotechnic compositions.

(13) Incendiary devices which incorporate pyrotechnic compositions with varied fuel-oxidizer ratios to reduce the need for auxiliary ignition compositions in the incendiary device.

(14) New and effective uses of depleted uranium, a nuclear by-product.

Other objects and further scope of applicability of the present invention will become apparent from the detailed description given hereinafter; it should be understood, however, that the detailed description, while indicating preferred embodiments of the invention, is given by way of illustration only, since various changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art from this detailed description. It should also be understood the foregoing abstract of the disclosure is for the purpose of providing a non-legal brief statement to serve as a searching-scanning tool for scientists, engineers and researchers and is not intended to limit the scope of the invention as disclosed herein nor is it intended it should be used in interpreting or in any way limiting the scope or fair meaning of the appended claims.

SUMMARY OF THE INVENTION

These objects are accomplished according to the present invention through the creation of pyrotechnic compositions having a density between about 2.5 and 4.5 capable of burning over an extended period of time with an incendiary ash which comprises:

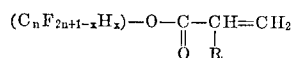
(a) metallic fuel material selected from the group consisting of the metals of Groups IIIB, IVB and VB of the periodic table, the hydrides of such metals and mixtures thereof, said metallic fuel material being of particle size between about 1 and 300 microns, and

(b) oxidizer material composed at least in part of solid fluorocarbon polymer,

(c) the mol ratio of metallic fuel material to oxidizer material being between about 2.9 to 15.

A preferred group of pyrotechnic compositions in the invention employ powdered uranium, zirconium, tantalum, vanadium or mischmetal as the metallic fuel material.

Preferred pyrotechnic compositions of the invention also use as the solid fluorocarbon polymer, copolymer of a major portion of polymerizable unsaturated fluorocarbon and a minor portion of halogen-free unsaturated copolymerizable material. Advantageously, one may use as the fluorocarbon polymer, a solid polymer of unsaturated copolymerizable material. Advantageously, one may use as the fluorocarbon polymer, a solid polymer of unsaturated fluorocarbon of the formula:



wherein

n is an integer between 2 and 20

x is an integer between 0 and n

R is hydrogen or methyl.

Pyrotechnic compositions of the invention which exhibit highly effective qualities of non-fluid incandescent ash and reaction with atmospheric oxygen to produce incandescent ash for an extended period of time have a mol ratio of metallic fuel material to oxidizer material between 3.7 and 6.0.

A preferred technique for preparing the new products of the invention involves first preparing a polymerizable mixture of monomer or monomers containing a polymerization catalyst, incorporating in the polymerizable mixture finely powdered metal or metal hydride as hereinbefore defined and thereafter casting or otherwise shaping the resulting monomer and metallic fuel material

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mixture and subjecting the shaped mass to polymerization or curing conditions to convert the mass into a solid elastic or hard structure. Pyrotechnic compositions formed in this manner may utilize only heavy metals of the type hereinbefore defined or may include as additional fuel material lightweight metals or other elements such as magnesium, aluminum or boron. Various ratios of atomized magnesium or other lightweight material with finely divided depleted uranium or other heavy metal fuel material may be employed, e.g., ratios of lightweight metal to heavy metal between about 10:1 and 1:1000.

DISCLOSURE OF PREFERRED EMBODIMENTS

The following details of operations in accordance with the invention and reported data illustrate the further principles and practice of the invention to those skilled in the art. In these examples and throughout the remaining specification and claims, all parts and percentages are by weight and all temperatures are in degrees centigrade unless otherwise specified.

Example 1

	Parts
Glycidyl methacrylate	25
2-ethylhexyl acrylate	12.5
1,3-butylene dimethacrylate	0.5
1,1,7-trihydrododecafluoroheptyl methacrylate	62.5
Depleted uranium	300

The mixture was cured to a hard dense casting by catalysis with benzoyl peroxide and an amine activator. Combustion of this mass of material on a one-inch thick horizontal board gave burn-through and ignition of the board in 75 minutes. The density of the composition was 4.08 grams/cc. The mol ratio of fuel to oxidizer was 3.46.

Example 2

	Parts
Glycidyl methacrylate	10.5
2-ethylhexyl acrylate	5.3
1,3-butylene dimethacrylate	0.3
1,1,7-trihydrododecafluoroheptyl methacrylate	27.0
Tantalum	187

The suspension was catalyzed with 1 part of benzoyl and promoted with 0.1 part of N,N -dimethyl- p -toluidine, then polymerized slowly to an elastic solid. The composition burned slowly until the binder was exhausted. After 30 minutes, an exothermic reaction heated the entire mass to incandescence. The mol ratio of fuel to oxidizer was 6.4.

Example 3

	Parts
Glycidyl methacrylate	6.2
2-ethylhexyl acrylate	3.1
1,3-butylene dimethacrylate	0.1
1,1,7-trihydrododecafluoroheptyl methacrylate	25.6
Zirconium	52.0

The composition was catalyzed and promoted, as in Example 2, setting to an elastic solid in several hours. The sample burned vigorously but left a less persistent ash than the other compositions. The density of the product was 2.87 gm./cc. and the mol ratio of fuel to oxidizer was 2.97.

Example 4

	Parts
2-ethylhexyl acrylate	40
1,1,7-trihydrododecafluoroheptyl methacrylate	32
1,3-butylene dimethacrylate	2
Magnesium	108
Uranium	218

The composition was catalyzed and promoted, as in Example 2, for casting to an elastic solid. The composition burned rapidly and left a moderately persistent ash. The mol ratio of fuel to oxidizer was 15.0.

Example 5

	Parts
Glycidyl methacrylate -----	18.7
2-ethylhexyl acrylate -----	9.3
1,3-butylene dimethacrylate -----	0.4
1,1,7-trihydrododecafluoroheptyl methacrylate ---	46.8
Zirconium hydride -----	224.4

The composition was catalyzed and promoted as in Example 2. It polymerized smoothly to a moderately elastic grain. The composition burned slowly with combustion of the polymer in air, but left a retentive ash that burned vertically through a wooden surface, igniting the structure. The density of the product was 3.0 gm./cc. and the mol ratio of fuel to oxidizer was 6.88.

Example 6

	Parts
Glycidyl methacrylate -----	712
2-ethylhexyl acrylate -----	356
1,3-butylene dimethacrylate -----	14.2
Benzoyl peroxide -----	21.3
1,1,7-trihydrododecafluoroheptyl methacrylate ---	1780
Misch metal -----	7120

The composition was cast into a cylindrical mold and polymerized at 20–25° C. for 4 hours. Upon ignition, the resulting pyrotechnic composition exhibited a high heat release rate for two minutes followed by a slow combustion in air for one-half hour. The mol ratio of fuel to oxidizer was 6.39.

DISCUSSION OF DETAILS

The success of the invention discussed herein is, in part, due to the discovery that certain proportions of ingredients in heavy metal-fuel/oxidizer incendiary formulations result in production of pyrotechnic products that undergo an initial combustion at relatively rapid rate forming non-fluid retentive incandescent ash which is of such nature or form that it can continue to combust at least in part with oxygen present in the surrounding atmosphere. As a result, the incendiary material remains incandescent for an extended period, e.g., 15–105 minutes and is capable during the time of supplying heat for useful purpose and/or serve to ignite part of a military target against which it is directed. Pyrotechnic compositions formed in accordance with the invention provide greater total heat output per unit volume and much longer burning time than metal-fuel incendiary compositions that have been previously known.

Another noteworthy feature of the invention is the ability of obtaining a variety of Pilling-Bedworth ratios with a basic combination of metal-fuel and oxidizer through the addition of bulk increasing agents to the incendiary product. This permits area covered by the incandescent ash of the basic combination to be controlled as required by special applications. These bulk increasing agents may be inert materials, e.g., fire clay, alumina, diatomaceous earth, slag, etc., or an active ingredient of lesser density than the principal metal fuel component, e.g., magnesium, aluminum, boron, the hydrides of these, organo-metallic compounds or the like. The exact amount of such additives will be varied depending, in part, upon the specific additive used and, in part, upon the Pilling-Bedworth ratio that is desired. Advantageously, the weight ratio of bulk increasing agent to metallic fuel material as hereinbefore defined will be between 1:2 and 1:1000 and preferred compositions containing uranium or the other preferred metallic fuel materials will involve such ratio between 1:5 and 1:100.

In addition to the preferred metals, i.e., uranium, zirconium, tantalum, and vanadium other metals of Group IIIB, IVB or VB, their hydrides or mixtures of the metals and/or hydrides may be used. Mischmetal, which is a mixture of rare earth metals of the lanthanum series, is an example of another metal fuel which may be advantageously used. A typical mischmetal would comprise Ce,

La, Nd, Pr and Si. Other elements useful as fuel material in the new compositions are Y, La, Ac, Hf, Nb and Ti.

The metal fuel material should be finely subdivided for combination with the oxidizer/binder, advantageously of between about 1 to 300 micron size. Powdered material which will at least pass a standard 50 mesh screen (297 microns) is satisfactory. Material passing a standard 100 mesh screen (149 microns) and retained on 325 mesh screen (44 microns) is particularly useful. Such material can be prepared by any suitable comminution method, e.g., ball milling, rod milling, roller grinding, pug milling, etc., and may be used directly as so obtained or precoated with a thin layer of ignition, primer or other material, washed with monomer or the like. If precoated, 0.1 to 5% of coating material is recommended.

A solid fluorocarbon polymer is an essential ingredient of the new pyrotechnic compositions. Such fluorocarbon polymer may be a homopolymer or a copolymer with another copolymerizable monomer or prepolymer that, itself is a fluorocarbon material or which may be a halogen-free unsaturated material. In the case of the use of such halogen-free copolymer components, weight ratios of fluorocarbon material to halogen-free material will advantageously be between 1:2 and 1:100 and especially 1:2 and 1:10.

A wide variety of fluorocarbons may be used as the oxidizer component of the new pyrotechnics. A preferred class are the polyfluoroalkyl acrylates and methacrylates of the formula hereinbefore prescribed. Specific examples of this class of fluorocarbon include:

1,1,7-trihydrododecafluoroheptyl methacrylate
perfluorobutyl acrylate
perfluoropropyl methacrylate
1,8-dihydrohexadecafluoro octyl acrylate
perfluoro octadecyl acrylate
hexafluoroisopropyl methacrylate

Other useable fluorocarbons include the polymerizable fluorinated alkyl, cycloalkyl, aryl and alkaryl amines, ethers, esters, hydrocarbons and the like. Specific examples of such materials are disclosed in publications relating to pyrotechnics, e.g., U.S. 3,163,113; 3,164,504 and 3,203,171.

Copolymerizable materials may be included in the fluorocarbon polymers for various purposes, e.g., to make the polymer harder by cross-linking, to render it elastomeric, to modify the burning rate, to increase its adhesion to the fuel material, to increase or decrease polymerization rate or the like. Such copolymerizates may be monofunctional or polyfunctional. Specific examples of monofunctional comonomers include:

2-ethylhexyl acrylate
glycidyl methacrylate
methyl acrylate
vinyl chloride
vinylidene chloride
vinyl acetate
propylene
styrene
vinyl methyl ether
vinyl hexyl ketone
and the like or mixtures thereof.

Specific examples of poly functional comonomers include:

1,3-butylene dimethylacrylate
glycol diacrylate
divinyl benzene
diallyl phthalate
1,3-butylene dichloroacrylate.

Additional useable comonomers are listed in the aforesaid patents.

Advantageously the polyfunctional comonomers are used in minor amount, e.g., between 0.01 to 5% by weight of the total fluorocarbon polymer.

In forming the new pyrotechnics, the finely divided metallic fuel material is preferably homogeneously mixed with the fluorocarbon monomer, monomer mixture or partially polymerized material. Degassing of the powdered fuel material, e.g., in vacuum apparatus, precoating as previously mentioned or any similar treatments known to the polymer art for aid in compounding pigments or powders with polymerizable monomers or prepolymers may be employed in conducting these new operations. Standard catalysts such as peroxides, persulfates, diazo compounds and the like are advantageously used to convert the monomer into the required solid polymer. So-called promoters, e.g., aromatic amines such as N,N-dimethyl-p-toluidine, are useful in effecting the polymerization and curing at low temperatures, e.g., 0–50° C. and especially 10–30° C. High temperatures are naturally to be avoided to mitigate the possibility of premature ignition of the pyrotechnic. Catalysts are preferably used in concentrations of 0.01 to 3% of the total monomer mixture and promoters in like amounts.

The fluorocarbon polymer functions not only as an oxidant for the metallic fuel material but also as a binder matrix in which the fuel material is suspended as a disperse phase. Other oxidizers may be included, e.g., in amounts between about 1 to 50% by weight of the total oxidizer. Such other oxidizers may include ammonium and metal salts of nitrates, perchlorates, percarbonates, perborates, oxides and peroxides of metals or ammonia and similar oxygen containing oxidizers.

The new pyrotechnic compositions may be ignited by heat alone or by chemical igniter agents. When ignited, they burn reliably leaving a coherent incandescent residue or ash. Those compositions that have a fuel material content that is at least 50% or greater heavy metal, e.g., 60–95% uranium and 5–30% magnesium burn to form incandescent residues which maintain heat sufficient to ignite wood, cloth, leaves, etc. for 90 minutes or longer if the combustion residue is left undisturbed. In some instances, e.g., compositions containing tantalum as the major fuel material, the residue or ash reaches incandescence slowly apparently as a result of secondary reaction with air. This phenomena may occur in vigorous fashion as long as 30 minutes after the initial combustion of the oxidizer-binder. The residues of all products of the invention are capable of igniting wood and similar combustibles subsequent to the full initial combustion of the oxidizer-binder.

An additional feature of the invention is the provision of incendiary bombs having a drop ballistic substantially equivalent to those of an identically shaped explosive bomb. This is attained by compounding the incendiary charge using the components as hereinbefore described to have a bulk density substantially identical to the T.N.T. or other explosive charge and metal case used in the explosive bomb. Such bombs may take any desired form known to the art. Incendiary bombs of this type make it possible to air-drop mixed loads of incendiary bombs and explosive bombs with accuracy into the same target area. Furthermore, upon ignition of the incendiary charge of such bombs, retentive incandescent ash or residue will remain in the target area in active combustible igniting condition for extended periods, e.g., 30–90 minutes.

The embodiments of the invention in which an exclusive property or right is claimed are defined as follows:

1. An incendiary composition which upon initial combustion produces a non-fluid incandescent ash which continues to react with atmospheric oxygen and remains incandescent for an extended period of time which comprises:

- (a) metallic fuel material selected from the group consisting of metals of Groups III-B, I-VB and V-B of the Periodic Table, the hydrides of such metals and mixtures thereof, said metallic fuel material being

of particle size between about 1 and 300 microns, and

- (b) oxidizer material at least 50% of which consists of solid fluorocarbon polymer,

- (c) the mol ratio of said metallic fuel material to said oxidizer material being between about 2.9 to 15.

2. An incendiary composition as claimed in claim 1 wherein said metallic fuel material is selected from the group consisting of uranium, zirconium, tantalum, vanadium and mischmetal and mixtures thereof.

3. An incendiary bomb having a drop ballistic substantially equivalent to an identically-shaped explosive bomb permitting mixed loads of such incendiary bombs to be dropped with such explosive counterpart in the same target area, said incendiary bomb upon detonation yielding incendiary material which upon initial combustion produces a non-fluid incandescent ash which continues to react with atmospheric oxygen and remains incandescent for at least 15 minutes, said bomb comprising shaped means of incendiary composition having a density between about 2.5 and 4.5 consisting essentially of:

- (a) nuclear by-product depleted uranium, and

- (b) solid fluorocarbon polymer,

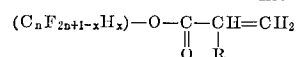
- (c) the mol ratio of said uranium to said polymer being between about 2.9 and 1.5.

4. An incendiary pyrotechnic composition as claimed in claim 1 wherein said solid fluorocarbon polymer is a copolymer of a major portion of polymerizable unsaturated fluorocarbon and a minor portion of halogen-free unsaturated copolymerizable material.

5. An incendiary pyrotechnic composition as claimed in claim 4 wherein the unsaturated fluorocarbon is polyfluoroalkyl methacrylate and the copolymerizable material is a mixture of alkyl methacrylate and alkylene polymethacrylate.

6. An incendiary pyrotechnic composition as claimed in claim 1 wherein said metallic fuel material is homogeneous disperse phase in a solid matrix of said oxidizer material.

7. An incendiary pyrotechnic composition as claimed in claim 1 wherein the metallic fuel material is uranium existing as a disperse phase in a solid matrix of polymer of unsaturated fluorocarbon of the formula:



wherein

n is an integer between 2 and 20

x is an integer between 0 and n

R is hydrogen or methyl.

8. An incendiary pyrotechnic composition as claimed in claim 1 wherein said ratio is between 3.7 and 6.0, said metallic fuel material is nuclear by-product depleted uranium and said oxidizer material consists essentially of solid polymer of polyfluoroalkyl methacrylate.

9. A pyrotechnic composition as claimed in claim 1 which comprises powdered boron, magnesium or aluminum.

10. An incendiary bomb having a drop ballistic substantially equivalent to an identically-shaped explosive bomb permitting mixed loads of such incendiary bombs to be dropped with such explosive counterpart in the same target area, said incendiary bomb upon detonation yielding a long-burning incendiary material characterized by retentive incandescent ash, said bomb comprising:

a pyrotechnic composition having a density between about 2.5 and 4.5 capable of burning over an extended period of time with an incendiary ash which comprises:

- (a) metallic fuel material selected from the group consisting of the metals of Groups III-B, IV-B and V-B of the Periodic Table, the hydrides of such metals and mixtures thereof, said metallic fuel material being of particle size between about 1 and 300 microns, and

(b) oxidizer material composed at least 50% of solid fluorocarbon polymer,	3,198,678	8/1965	Zeman et al.	149—44
(c) the mol ratio of metallic fuel material to oxidizer material being between about 2.9 to 15.	3,203,843	8/1965	Jackson	149—87X
	3,275,484	9/1966	Foote et al.	149—44X
	3,291,665	12/1966	Jackson	149—44X

References Cited

⁵ BENJAMIN R. PADGETT, Primary Examiner
S. J. LECHERT Jr., Assistant Examiner

UNITED STATES PATENTS

2,986,456	5/1961	Toulmin	149—87	
3,122,462	2/1964	Kaufman	149—87X	
3,152,935	10/1964	Cadwallader	149—87X	10 102—6; 149—19, 20, 22, 37, 44, 114

U.S. Cl. X.R.

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,565,706 Dated February 23, 1971

Inventor(s) HAL R. WAITE

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Claim 3, penultimate line, change "radio" to --ratio--
 , last line, change "1.5" to --15--.

Signed and sealed this 18th day of April 1972.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents