United States Patent Office
3,257,801
Patented June 28, 1966

3,257,801
PYROTECHNIC COMPOSITION COMPRISING SOLID OXIDIZER, BORON AND ALUMINUM ADDITIVE AND BINDER

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No Drawing. Filed July 9, 1962, Ser. No. 208,573
6 Claims. (Cl. 60—35.4)

The present invention deals with a new and improved pyrotechnic composition and the use of such composition. More particularly, the invention is directed to a propellant or pyrotechnic composition employing an oxidizer material and a combination of particular metal additives.

Pyrotechnic compositions are used for igniting flares, for ignition purposes in liquid and solid rockets, as solid propellants themselves, as gas generators, and for ramjet fuels. Known compositions generally employ an amount of oxidizer which approaches or exceeds a stoichiometric amount necessary to complete the combustion of the igniter compositions. In general, compositions which have a low amount of oxidizer of the order of less than 50 percent of the calculated stoichiometric ratio are difficult to ignite and once ignited have a low heat output per unit of weight.

An object of this invention is to provide an igniter composition having a high heat output per unit weight.

A further object of this invention is to provide a composition having superior ignition properties.

A still further object of this invention is to provide an ignition composition of generally high density which is of particular importance in space vehicle applications where high weight per unit volume is desired.

An additional object of this invention is to provide a propellant composition with a relatively high strength and stable burning qualities which is simple to prepare and uses readily available ingredients.

The above objects as well as other objects of this invention will be apparent from the accompanying specification.

The objects of this invention are accomplished by a pyrotechnic composition which comprises from 50 to about 80 percent by weight of a mixture of boron powder and aluminum powder, such that from about 27 to 72 percent of the mixture is aluminum, from about 15 to 30 percent by weight of a solid oxidizer, and from about 5 to about 15 percent by weight of a decomposable organic polymeric binder. Stated in terms of the overall composition, the composition of this invention comprises from about 20 to about 30 percent by weight aluminum and from about 35 to 55 percent by weight boron. In addition to the mixture of boron and aluminum powders, the oxidizer, and the binder, the composition of this invention may contain from about 0 to about 5 percent additional miscellaneous additives which are described in detail hereinafter.

Although the elements, aluminum and boron have been used individually in preparing various propellant and pyrotechnic formulations, and although these elements have been used as their metal powders individually, and as compounds in such formulations, it has now been found that the presence of both aluminum powder and boron powder in a specific range of ratios results in a vastly improved composition. Thus, the overall properties of a propellant, igniter, or pyrotechnic composition are such that a highly synergistic effect of greater heat output is produced by the composition of this invention. A unique feature of the composition of this invention is its ready ignitibility. This is a surprising property since the percent of oxidizer is much less than the stoichiometric quantity necessary for the oxidation of the powdered metals. A

typical composition of this invention has a heat of combustion of approximately 11,000 B.t.u. per pound. By comparison, the heats of combustion of most igniter compositions and double-base rocket propellants now in use are about 3,000 B.t.u. per pound and 2,300 B.t.u. per pound, respectively. A typical composite rocket propellant containing ammonium perchlorate has a heat of combustion of approximately 3,300 B.t.u. per pound. Thus, for example, a smaller amount of the composition of the present invention is required to obtain the overall heat necessary for ignition. Furthermore, for the same amount of weight or volume, one will obtain much greater heat output with the improved composition.

The igniter composition of this invention can be used as the fuel or grain in a ramjet engine. This particular application is seen in detail in Figs. 1–2 on page 2 of the book, "Rocket Propulsion Elements," by George P. Sutton, Second Edition, published by John Wiley and Sons, Inc., New York, New York. In this publication a squib which is electrically ignited in turn ignites the grain which is made of the composition of this invention. The burning of this grain creates gaseous products which are ejected from the combustion chamber to produce usable thrust.

As noted above, the present invention is predicated on the presence of certain specific percentages of aluminum powder and boron powder in the igniter or pyrotechnic composition. While, in general, from 50 to 80 percent by weight of the composition is the combination of aluminum and boron, it is preferred to employ from 60 to 70 percent of the mixture of aluminum and boron, since very short ignition delay is experienced in this range of composition.

The decomposable organic polymeric binder material employed in the preparation of the compositions of this invention is an organic polymer, either naturally occurring or synthetically prepared. Thus, thermoplastic, thermosetting, elastomeric, polymeric, and plastic materials of many descriptions may be employed. These materials may be either naturally occurring, modified materials occurring in nature, or synthetically prepared.

Among the thermoplastic materials which may be employed as binders are polymers and copolymers of monoolefinic hydrocarbons having at least two carbon atoms. Thus, the polymers and copolymers of ethylene, propylene, various butenes, pentenes, and hexenes, as well as the halogenated counterparts of these olefins may be employed in the practice of this invention. Among the thermosetting polymeric materials which may be employed are those plastics and resins which cure to a solid upon the application of heat with or without a chemical curing agent. Illustrative examples of this class of material include the polyurethane resins, epoxide resins, polyester materials, and di-(thioalkoxy) methylene polymers (polysulfide polymers). In addition, elastomers, such as the natural and synthetic rubbers, may be practicably and profitably employed in the practice of this invention. The synthetic rubbers are ordinary polymers and copolymers of a diolefin (as a major constituent) with other olefin constituents and which are subject to vulcanization with sulfur subsequent to polymerization to cross-link the polymer through any remaining carbon-to-carbon double bonds. In addition to the above, organic polymers derived from naturally occurring non-elastomeric polymeric materials may be employed in the practice of this invention.

In general, carbohydrate condensation-type polymers, amino-acid condensation polymers, synthetic linear condensation polymers including the polyamides and polyesters, linear addition polymers such as hydrocarbon and vinyl-type polymers, and cross-linking polymers may be employed as binders to prepare the products of this invention.

The condensation-type polymers are cellulose, cellulose nitrate, cellulose acetate, cellulose acetate-butyrate, ethylcellulose, and the cellulose ethers such as methyl carboxymethyl, hydroxyethyl, cyanoethyl and benzyl cellulose.

Examples of the amino-acid condensation polymers are regenerated proteins such as casein and vegetable globulins. Synthetic linear condensation polymers which may be employed in the practice of this invention include the polyamides such as nylon, and polyurethane resins, polyesters such as the alkyd and fiber-forming types, polyester and polyesteramide rubbers.

Applicable linear addition polymers include natural and vulcanized rubbers such as gutta-percha, balata, and chicle, cyclized or isomerized rubber, rubber hydrochloride, polybutadiene rubbers including Gr-S and nitrile rubber, polychloroprene and its copolymers, polysulphide rubbers, polyisobutylene and the butyl rubbers, the various polyethylenes including chlorosulphonated polyethylene rubbers, polytetrafluorethylene, polystyrene, polyvinylcarbazole and polyacenaphthylene, indene and coumarone-indene resins, polyvinyl acetate, polyvinyl alcohol, polyvinyl pyrrolidone, polyvinyl formal, polyvinyl acetal, and polyvinyl butyral, polyvinyl chloride, vinyl chloride-vinyl acetate copolymers polyacrylonitrile, vinyl chloride-acrylonitrile copolymers, polyvinylidene chloride and its copolymers, polymethyl methacrylate and related polyacrylates, ketone aldehyde polymers and polyacrylate rubbers.

Cross-linking polymer binders applicable to the present invention include cross-linking type polyester resins, various epoxy resins, polymerized drying oils, aniline formaldehyde resins, sulphonamide-formaldehyde resins, urea-formaldehyde resins, melamine-formaldehyde resins, and the various phenol-formaldehyde condensation resins.

Furthermore, organic polymers containing elements other than carbon, hydrogen, oxygen, and nitrogen may be employed. For example, silicon-containing polymeric materials are advantageously adapted to the practice of this invention. The silicon-containing polymers fall into two general classes; that is, those having direct silicon-to-carbon bonds (the silanes) and those having silicon-bonded to carbon through oxygen (the siloxanes). The silicon-containing materials often have a halogen in the molecule.

It is often advisable to employ plasticizers in the preparation and utilization of the polymeric and pastimeric materials employed in the invention. These plasticizers may be of the general type, inert plasticizers and explosive plasticizers. Examples of inert plasticizers include triacetin, the various phthalates such as diethyl phthalate, dibutyl phthalate, dioctyl phthalate, di-(methoxyethyl) phthalate, methyl phthalyl ethyl glycolate, ethyl phthalyl ethyl glycolate and butyl phthalyl butyl glycolate, sebacates such as dibutyl and dicotyl sebacates, adipates such as dioctyl adipate and di(3,5,5-trimethylhexyl)adipate, glycol esters of higher fatty acids, organic phosphate esters such as tributoxyethyl phosphate, and the like. The explosive plasticizers include nitroglycerin, butane triol trinitrate, diglycol dinitrate, ethylene glycol dinitrate, and the like.

The oxidizing agents employed in the composition of this invention can be compounds such as metal perchlorates and metal nitrates. The metal perchlorates employed as oxidizing agents or oxygen carriers in the compositions are anhydrous and have the general formula $M(ClO_4)_x$, wherein M is NH_4 or a metal and x is the valence of M, and ordinarily has a value of 1 or 2. Since the propellant composition is required to withstand high temperature storage, it is preferable that the melting point and the decomposition temperatures of the oxidizer be as high as possible. The perchlorates of the Group I–A, Group I–B, and Group II–A metals are found to have the required high temperature stability and are employed in the preparation of propellant compositions by the process of this invention. Hence, the metal perchlorates used in the preparation of the propellant compositions include lithium perchlorate, sodium perchlorate, potassium perchlorate, rubidium perchlorate, and cesium perchlorate which are the perchlorates of the metals of Group I–A of the Periodic Table of Elements; silver perchlorate which is a perchlorate of the Group I–B metal; and magnesium perchlorate, calcium perchlorate, strontium perchlorate, and barium perchlorate which are the perchlorates of the Group II–A metals. In addition to the metal perchlorates, the compound ammonium perchlorate finds extensive use in propellant compositons. Examples of the nitrates of the Group I–A, and I–B and II–B which are employed in preparing propellant compositions by the process of this invention are compounds such as lithium nitrate, sodium nitrate, potassium nitrate, magnesium nitrate, calcium nitrate, barium nitrate, strontium nitrate, etc. Ammonium nitrate is also used.

The ratio of total solids-to-polymeric binder material in a propellant falls in the range of from about 1:1 to about 9:1 with an optimum ratio of about 8.5:1.5.

Other substances which are employed in the preparation of propellants of this invention include minor amounts of burning catalysts, well known in propellant compositions. These are composed of one or a mixture of two or more metal oxide powders in amounts sufficient to improve the burning rate of the composition. The amounts usually range from about 0.01 to about 3 weight percent, based on the weight of the oxidizer employed. The particle size of the powders can range from about 10 to about 250 microns in diameter. Non-limiting examples of metals that serve as burning catalysts are copper, vanadium, chromium, silver, molybednum, zirconium, antimony, manganese, iron, cobalt, and nickel. Examples of metal oxide burning catalysts are ferric oxide, aluminum oxide, copper oxide, chromic oxide, as well as the oxides of the other metals mentioned above.

Curing catalysts are often added in minor amounts to cure the polymer in the performance of the process of this invention. Non-limiting examples of catalysts used for this purpose are aluminum chloride, tristrimethylsilyl borate, benzoyl peroxide, and other catalysts well known in the curing of plastics, resins, polymers, and rubbers. Examples of various catalysts may be found in text books such as "Synthetic Rubber," by G. S. Whitley, pp. 892–933, 1954 Ed., published by John Wiley and Sons, Inc., New York. The curing catalysts are added in amounts of from 0.1 to about 10 weight percent based on the weight of the polymer, resin or elastomer. The particular catalyst and amount employed depend on the state of cure desired and the nature of the polymeric material employed in the composition.

Example I

A typical pyrotechnic igniter composition of this invention was prepared from aluminum and boron powders, potassium perchlorate as the oxidizing agent, and ethyl cellulose as the binder. In terms of the overall composition, 22 weight percent aluminum powder, 38 weight percent boron powder, 15 weight percent ethyl cellulose, and 25 weight percent potassim perchlorate were added to a mechanical mixer and blended until a uniform composition was obtained. Propellant grains were prepared by compressing portions of the mixture in a die at pressures of 100 lbs. per square inch, 25,000 lbs. per square inch, 2,000 lbs. per square inch and 10,000 lbs. per square inch. The die in which the mixture was placed was heated to 95° C. during the preparation of the grain.

Example II

Another pyrotechnic composition of this invention is prepared by blending 370 parts by weight of boron powder, 155 parts of aluminum powder, 180 parts of a polyurethane liquid monomer, and 250 parts of potassium perchlorate. The mixed fluid ingredients were poured in a mold to form the propellant grain and cured at a temperature of 60° C. for 36 hours.

The aluminum powder employed should generally have a particle size of from 200 mesh to 325 mesh; preferably

99.5 percent of the aluminum should be smaller than 200 mesh size. However, depending on the application of any particle sizes less than 100 mesh can be used. Likewise, the boron powder should have an average particle diameter of less than 1.0 micron when tested on a Fisher subsieve sizer or alternate method of equal precision.

Other examples of compositions of this invention are shown in the accompanying table, wherein each of the percentages given is in terms of weight percent.

TABLE I

Run	Oxidizer	Weight Percent	Binder	Weight Percent	Al Weight Percent	B Weight Percent	Other Weight Percent
2	NH_4ClO_4	15	Polyurethane Resin [1]	8	32	44	1
3	$KClO_4$	15	Polyester Resin [2]	15	43	25	2
4	NH_4NO_3	25	Ethyl Cellulose	8	18	48	1
5	$KClO_4$	25	do	10	32	32	1
6	$KClO_4$	25	do	15	27	28	5

[1] "Adiprene" L-100 made by E. I. du Pont de Nemours and Co.
[2] "Laminac" made by American Cyanamid Co.

The overall composition comprises from about 15 to 30 percent solid oxidizer, 20 to 30 weight percent aluminum powder, 35 to 55 weight percent boron powder, and 5 to 15 percent plastic or elastomeric binder. Other additives of from 0 to 5 percent, discussed above, may also be employed to control the particular physical properties of the resultant composition.

The igniter composition of this invention may be used in igniting either solid or liquid propellants. In the case of solid propellants, the igniter material will ordinarily be in grain form adjacent to the solid propellant to be ignited. A suitable electrically actuated squib is provided in juxtaposed position in order to set off the igniter material which when ignited ejects its combustion products into direct contact with the particular solid propellant. In the case of liquid propellant rockets a conventional ignitor having the composition of this invention therein is ignited by a conventionally operated squib and the combustion products of the igniter composition distributed over the face of an injector plate from which issues, under pressure, streams of liquid oxidizer and fuel which are ignited by the gaseous products being ejected from the igniter composition. It can likewise be seen that the composition of this invention has applicability as a propellant composition itself wherein the propellant composition is burned in a conventional combustion chamber and the gaseous products from the reaction or combustion are ejected downstream from the combustion chamber through a nozzle to develop usable thrust.

Although this invention has been described and illustrated in detail, it is to be understood that the same is by way of illustration and example only and is not to be taken by way of limitation, the spirit and scope of this invention being governed by the terms of the appended claims.

We claim:

1. A pyrotechnic composition comprising a solid oxidizer, 50 to 80 weight percent of metal additive consisting of boron and aluminum, approximately 27 percent to 72 weight percent of said additive being aluminum, the remainder of said additive being boron, and a binder for binding said oxidizer and metal additive together.

2. A pyrotechnic composition comprising from about 15 to 25 weight percent of solid oxidizer, 8 to 15 weight percent of a binder, and 50 to 80 weight percent of a metal additive consisting of boron and aluminum, approximately 27 to 72 weight percent of said additive being aluminum, the remainder of said additive being boron.

3. The method of igniting solid and liquid propellants comprising ejecting into contact with said propellants the combustion products of a compound comprising a solid oxidizer, a binder, and 50 to 80 weight percent of a metal additive of aluminum and boron, said aluminum being in the amount of 27 to 72 weight percent of said metal additive, the remainder of said metal additive being boron.

4. A readily ignitible composition comprising potassium perchlorate, 50 weight percent to 80 weight percent of metal additive consisting of boron and aluminum, approximately 27 weight percent to 72 weight percent of said additive being aluminum, the remainder of said additive being boron, and an ethyl cellulose binder.

5. The invention as set out in claim 4 in which said potassium perchlorate is in the amount of 15 to 30 weight percent of the overall composition and in which the binder material is in the amount of 5 to 15 weight percent of the overall composition.

6. The method of developing thrust comprising ejecting from a combustion chamber the gaseous reaction products produced by the combustion of a solid oxidizer, 50 to 80 weight percent of metal additive consisting of boron and aluminum, approximately 27 to 72 weight percent of said additive being aluminum, the remainder of said additive being boron, and a binder material in the amount of 5 to 15 percent of the total composition.

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