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PROPELLANT SYSTEM

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This invention relates to solid fuels containing granular aluminum. More particularly, the invention concerns novel solid composite rocket and ramjet propellants containing aluminum or aluminum alloys together with an oxidizing agent.

Solid fuels offer many known advantages over liquids as propellants for rocket and ramjet engines, including such factors as performance, ease of manufacture, and simplicity and reliability of field use. Solid propellants are generally classified into two broad groups: double-base propellants, comprising nitrocellulose or nitroglycerine plasticized with a high energy substance, such as a methacrylate, and composite propellants, comprising discrete particles of fuel and oxidizer in a heterogeneous system. The present invention is concerned with novel composite type propellants.

Among desirable characteristics, those which are of major significance in the development of efficient solid propellants are specific impulse and burning rate. Combustion temperature and molecular weight are factors inherent in the chemical composition of the propellant. Since there are practical limitations on the temperatures (about 3000 degrees Kelvin) which can be contained within the chamber, it becomes of prime importance to obtain a large amount of energy from a small amount of propellant which, upon combustion, will yield products having a low average molecular weight.

Light metals, such as aluminum and magnesium, have been investigated as rocket fuels, both in the form of fine powders, and as finely suspended slurries of such powders in hydrocarbon carriers, since these metals are attractive from the standpoint of high combustion temperature and low cost. Aluminum and magnesium tend to furnish higher thrust than hydrocarbons when used as fuels, owing to their higher burning temperatures, although these metals actually do not contain as much heat energy per pound. The results thus far obtained with aluminum powders have nevertheless been unsatisfactory from the standpoint of safety, since aluminum powder is dangerous to make, handle, and store. Aluminum powders also tend to leave behind an undesirable residue of unburned material.

Although the ratio of propellant cost to missile or rocket cost is relatively low in the military field, because of the great complexity of the devices involved in missile applications, economies in fuel are nevertheless desirable. However, in civilian types of rocket applications, such as, for example, jet-assisted take-off devices used to boost an aircraft up to flight velocity, pounds-seconds of impulse per dollar may be the most important requirement.

In accordance with the present invention, the aluminous metals, including aluminum and its alloys, in the form of granular particles, possessing an oblong or needle-like shape, and produced by casting methods, have been found to possess unique and unexpectedly valuable properties as fuel components of solid composite rocket and ramjet propellants. Aluminum and its alloys having these physical characteristics may be prepared by a process which comprises essentially pouring the molten aluminum or aluminum alloy into a steel cup having the side wall perforated with holes of a predetermined diameter to impart the desired particle size, and rotating the steel cup at fairly high speeds, whereby to expel the molten metal through the holes. In being thus centrifugally projected from the cup over a distance of say 8 or 10 feet, the metal is rapidly cooled and assumes the structural characteristics of cast metal, as well as the oblong or needle-like shape referred to previously.

The novel cast particle structure, and the oblong or needle-like shape of the granular aluminum or aluminum alloy particles utilized in accordance with this invention, results in superior burning characteristics in solid composite propellants into which the novel particles are incorporated. The tendency of the oblong metal particles to form a matted structure provides improved heat conduction between the particles themselves and between the particles and the oxidizer, resulting in greatly improved combustion rates, despite their larger mesh size as compared with propellants made from powdered aluminum in which the particles commonly are much finer.

The granular particles of this invention possess free flowing characteristics, which are indicated by the ability of the particles to pass through the throat of a funnel without any clogging or jamming. Aluminum powders, on the other hand, will clog the throat of a funnel. The granular particles also possess a rather high apparent density, which is of the same order of magnitude as that of powdered aluminum. Thus, the various compositions listed in Table 5 below have apparent densities lying between about 0.75 and 1.02 grams per cubic centimeter, while aluminum powder of less than 325 mesh fineness when measured in the same equipment, showed an apparent density of 0.87 gram per cubic centimeter. The granules permit a good packing effect, allowing ready access of oxygen for combustion, and leaving no unburned residue.

When used as fuel components, the cast aluminum or aluminum alloy particles of this invention are advantageously of an average mesh size of about 20 to 100 mesh. It is advantageous that not less than about 80% by weight of the particles possessing an oblong and irregular shape possess a longest dimension at least five times the average of the other two dimensions. Mixtures of various alloys may also be employed.

Cast aluminum or aluminum particles possessing the foregoing characteristics are readily distinguishable from such fuel components as, for example, fine aluminum powder of a size less than 325 mesh, which is known to be combustible when suspended in air or when mixed with oxygen, and which has been successfully used as a rocket fuel either mixed as a slurry with jet fuel, or when compacted with organic materials and oxidiizing agents to produce a solid fuel. Explosion hazards encountered with fine aluminum powders in fabricating, handling, shipping and storage are totally eliminated by the new product, without sacrificing its functional efficiency.

Explosive compositions are known in which metal wools, such as aluminum or magnesium wool, are admixed with oxygen carriers. In these metal wool acts merely as an adjuvant. Moreover, the aluminum wool is necessarily produced by shearing or cutting forces and thus is not a cast particle, nor does it possess the special characteristics of the cast particles of aluminum or its alloys contemplated by this invention. Such aluminum wool compositions are disclosed, for example, in U.S. Patent 812,195.

Aluminum wool usually has no free flowing properties at all. Its weight-volume ratio is erratic and therefore does not permit the precision required by the narrow limits of volumetric control necessary for rocket fuels. Also the process of producing wool by mechanical comminution causes strain hardening, and hence undesired elasticity which produces springback when it is attempted to compress such wool into a fuel package.

The objective of making pressed rocket fuel with as much aluminum as possible and as little organic binder as possible in order to obtain heat retention, higher thrust, and minimum heat loss in the outgoing gases, cannot be met with wool. The aluminum wool has a space filling quality which prevents it from being brought to an apparent density comparable to that of aluminum granules or powder.

It has further been found, in accordance with this invention, that solid composite rocket and ramjet propellants having desirable specific impulse characteristics may be obtained by employing as the major fuel component granular particles of either aluminum metal itself, or of aluminum alloys. Suitable alloys include alloys of aluminum and magnesium, or of aluminum and zinc, but alloys of aluminum and a minor proportion of magnesium are preferred. In the preparation of, for example, alloys of aluminum and magnesium, there may be employed aluminum of varying degrees of purity, ranging from high purity metal of 99.50% aluminum content, down to wrought aluminum alloys such as 7075 alloy, or scrap, averaging about 87%–88% aluminum content, and including small amounts of magnesium and zinc. Alloys of aluminum with both magnesium and zinc and mixtures of such alloys may also be used as fuel components.

It has been found that aluminum and alloys of aluminum containing at least about 65% aluminum by weight, when in the form of cast particles having an oblong or needle-like shape, as described above, are well suited as fuel components, which are readily ignitable when in contact with suitable oxidizing agents, as in the form of rocket propellants, and which exhibit satisfactory specific impulse and burning rate and uniformity properties. Preferably, an alloy containing from about 15 to about 25 percent of magnesium in the cast product, admixed with a suitable amount of solid oxidant therefor may be employed, for example, an alloy containing 20% magnesium.

It is surprising and unexpected that aluminum and its alloys in the form of such cast particles will ignite readily, since it had been assumed from known data that for solid jet fuels it was necessary to use atomized aluminum powder mixed with magnesium powder, together with sulfur and oxidant to attain suitable ignition and uniform burning.

The cast aluminum and aluminum alloy oblong fuel particles of the present invention are entirely distinct, moreover, from the powdered aluminum-magnesium injection type fuels which have been proposed for steam generation in submarines, such as described for example in U.S. Patent 1,532,930, wherein the alloys contain approximately 50% magnesium and are oxidized with liquid oxidants. The alloys and fuels of the present invention are also wholly different in composition and properties from the actinic aluminum-magnesium alloys used in photoflash lamps, and which are generally in the form of wrought metal such as foil or thin wire containing from about 7% to 13% magnesium, and rely upon gaseous oxygen in the flash bulb for oxidation. Flash bulb alloys are designed to yield maximum actinic ray emission. In the fuel alloys of the present invention, however, the objective is quite different, and hence these fuel alloys are designed to possess physical characteristics which will lead to the maximum development of high energy upon burning within a confined space such as a rocket or ramjet engine.

It has been found that the most satisfactory burning characteristics are obtained when there is used an alloy of aluminum with from about 15 to 35 percent of magnesium. Such an alloy has burning characteristics superior to those of particles of cast aluminum itself, or of cast alloys which contain amounts of magnesium outside the stated range. Thus, an alloy of aluminum and about 10 percent magnesium will burn more slowly in presence of an oxidant than an alloy with 20 to 25 percent magnesium. When the magnesium content rises to about 35 percent, and over, the alloy again burns more slowly, probably due to somewhat more oxidation during the time interval until complete solidification results during the casting.

The resulting condition of the cast granular alloy particles is such that the aluminum-magnesium fuel alloys of this invention as produced under commercial conditions have a burning rate that will increase with increasing magnesium content up to a certain percentage of magnesium, after which point oxidation of the granular commercial product appears to slow down the burning rate. Thus, for example, under similar test conditions, a 9.32 percent magnesium-aluminum alloy exhibited a burning time of 385 seconds, a 22.62 percent magnesium-aluminum alloy had a burning time of 35 seconds, and a 35.40 percent magnesium-aluminum alloy had a burning time of 44 seconds. This oxidation of higher magnesium content alloys can be decreased by special procedures, such as, for example, casting under a blanket of inert gas, such as argon or sulfur vapor or sulfur dioxide vapor, thus permitting inclusion of somewhat more than 35 percent magnesium, but it has been found practicable to limit the magnesium content to about 25 percent as aforesaid.

For the preparation of composite solid propellants, the granular particle aluminum and its alloys may be combined with suitable oxidizers, among which may be mentioned ammonium perchlorate, ammonium nitrate, potassium perchlorate, and potassium nitrate, as well as other conventionally used oxidizers, which generally contain available oxygen ranging from about 20 to 46 percent. Ammonium nitrate is least expensive, but ammonium perchlorate is preferred since it possesses marked advantages in respect to density, attainable combustion enthalpy, and processing characteristics.

The amount of oxidizing agent used in the preparation of fuel mixtures is based upon the stoichiometric requirements for oxidation of the various metallic elements present, as well as that of any organic binder material that is used as a matrix for the fuel charge, such as, for example, Thiokol (organic polysulfide) polymer. However, as a safety factor, it is advantageous to employ an excess of oxidizer of at least 5 percent above the stoichiometric requirements in order to assure efficiency of combustion.

Thus, on the basis of the following oxidation equations:

$$5Al+3NH_4ClO_4 \rightarrow \tfrac{3}{2}N_2+AlCl_3+2Al_2O_3+6H_2O$$

$$C_2H_4S_4+4NH_4ClO_4 \rightarrow 2N_2+SCl_2+2SCl+SO_2+2CO_2+10H_2O$$

it may be computed that, using ammonium perchlorate as an oxidizer, 100 gr. of aluminum will require 263 gr. of NH_4ClO_4, while 100 gr. of Thiokol will require 301 gr. NH_4ClO_4.

In addition to the aluminum or aluminum alloy cast particles and the solid oxidant, rocket and ramjet solid propellants prepared in accordance with this invention may also include suitable organic elastomers as binders, matrices, and auxiliary fuels. Such elastomers may include, for example, natural and synthetic rubbers, such as butadiene-styrene rubbers, acrylonitrile rubbers, Thiokol (polysulfide type rubbers), and the like, and also suitable plastic materials, including phenolic, polystyrene, polyethylene, acrylic, and other types of synthetic resins.

While the present invention contemplates the utilization of the cast granular aluminous particles principally in solid composite propellants, it is also within the scope of this invention to employ these forms of aluminum and its alloys in conjunction with liquid fuels, such as liquid or semiliquid hydrocarbons, either in the form of slurries or suspensions.

The following examples are intended to illustrate the preparation and properties of fuel mixtures produced in accordance with this invention, but the examples are to be considered only as illustrative, and not as limiting.

EXAMPLE 1

10 grams of an aluminum-magnesium alloy granular product having a chemical composition shown in Table 1, and a screen analysis shown in Table 2, was mixed with 28 grams of ammonium perchlorate and placed in a 10" long V-shaped asbestos trough to determine the burning time when ignited with a 1" long Nichrome resistor heated by current supplied from a storage battery. The ignition time was 3 seconds, and the burning time was 66 seconds.

Table 1

CHEMICAL COMPOSITION OF ALUMINUM-MAGNESIUM (22.62%) ALLOY GRANULAR PRODUCT

	Silicon	Iron	Magnesium	Aluminum
Percent	0.15	0.35	22.62	Balance.

Table 2

SCREEN ANALYSIS OF ALUMINUM-MAGNESIUM (22.62%) ALLOY GRANULAR PRODUCT

Mesh	+10	−10+20	−20+40	−40+50	−50+60	−60+70	−70
Percent	0	2	54	30.5	7	3	3.5

EXAMPLE 2

10 grams of a lower purity aluminum-magnesium (20%) alloy granular product, having an average chemical composition shown in Table 3, and a screen analysis shown in Table 4, was mixed with 28 grams of ammonium perchlorate and placed in a 10" long V-shaped asbestos trough similar to the test described previously for the 22.62% magnesium-aluminum alloy and was found to ignite in the same time, 3 seconds, and to burn in 59 seconds. When the same charge was burned inside a 3" diameter extruded aluminum tube the burning time was 33 seconds; this was done to more closely simulate the conditions prevalent inside a rocket.

Table 3

CHEMICAL COMPOSITION OF LOW PURITY ALUMINUM-MAGNESIUM (20%) ALLOY GRANULAR PRODUCT

Si	Fe	Cu	Mn	Mg	Zn	Cr	Ti	Al
.15	.30	1.60	.05	20.00	5.80	.25	.05	Balance.

Table 4

SCREEN ANALYSIS OF LOW PURITY ALUMINUM-MAGNESIUM (20%) ALLOY

Mesh	+10	−10+20	−20+40	−40+50	−50+60	−60+70	−70
Percent	0	1	42	39	7	5	6

EXAMPLE 3

10 grams of a lower purity aluminum-magnesium nesium, in the form of cast particles, and 28 gms. of ammonium perchlorate oxidant were thoroughly mixed and placed inside a 3 inch diameter extruded aluminum tube, to simulate rocket conditions. The mixture was ignited at one end by means of a 1" Nichrome wire. Ignition time was 3 seconds, and burning time 47 seconds, the burning being rapid and intense. In a repetition of this test, the ignition time was less than 2 seconds, and the burning time 22.5 seconds.

The following table summarizes the results of experiments conducted under conditions similar to those of Examples 1 and 2, using aluminum with various percentages of magnesium, and 7075 alloy with 20 and 25 percent magnesium content.

Table 5

Aluminous Metal (gms.)	Percent Magnesium	Amount of NH_4ClO_4, gms.	Ignition Time (sec.)	Burning Time (sec.)	Burning Characteristics
10	10	28	30	385	erratic.
10	20	28	3	35–66	vigorous.
10	30	28	5	144	not vigorous.
10	7075 alloy plus 20% Mg.	28	3	59	good.
10	7075 alloy plus 25% Mg.	28	3	52	Do.

I claim:

1. In a composite solid propellant characterized by an admixture of fuel particles and an oxidant therefor, the improvement which comprises a fuel consisting essentially of cast granular particles having an oblong shape and composed of a metal selected from the group consisting of aluminum and alloys of aluminum having an aluminum content of at least 65 percent by weight, substantially all of said particles being retainable on a 100 mesh sieve.

2. In a composite solid propellant characterized by an admixture of fuel particles and an oxidant therefor, the improvement which comprises a fuel consisting essentially of centrifugally cast particles of a metal selected from the group consisting of aluminum and alloys of aluminum having an aluminum content of at least 65 percent by weight, said particles having an average size between about 20 and 100 mesh.

3. In a composite solid propellant characterized by an admixture of fuel particles and an oxidant therefor, the improvement which comprises a fuel consisting essentially of centrifugally cast particles of a metal selected from the group consisting of aluminum and alloys of aluminum having an aluminum content of at least 65 percent by weight, substantially all of said particles having an oblong shape and not less than about 80 percent of said particles having a longest dimension at least five times the average of the other two dimensions, and substantially all of said particles being retainable on a 100 mesh sieve.

4. A combustible material characterized by safety in handling and high energy release upon combustion, said material consisting essentially of centrifugally cast aluminous metal particles in admixture with an oxidizing agent containing at least sufficient available oxygen for combustion of the metal particles, the aluminous metal being an aluminum alloy containing at least 65 percent aluminum and from 15 to 35 percent magnesium, and substantially all of said particles being retainable on a 100 mesh sieve.

5. In a composite solid propellant which includes fuel particles, an oxidant for said fuel particles, and organic binder materials, the improvement which comprises a fuel consisting essentially of centrifugally cast particles of aluminum-magnesium alloy, said alloy containing about 20 percent magnesium by weight and at least 65 percent aluminum by weight.

6. In a composite solid propellant which includes fuel particles, an oxidant for said fuel particles, and organic binder materials, the improvement which comprises a fuel consisting essentially of centrifugally cast particles of aluminum-magnesium alloy, said alloy containing about 20 percent magnesium by weight and at least 65 percent aluminum by weight, said particles having an oblong shape and an average size between about 20 and 100 mesh.

7. A composite solid propellant material consisting essentially of an alloy of aluminum with from about 15 to 25 percent of magnesium, said alloy being in the form of cast granular particles having an oblong shape and of an average mesh size between about 20 and 100 mesh,

and a solid oxidant therefor selected from the group consisting of ammonium nitrate, ammonium perchlorate, potassium nitrate, and potassium perchlorate.

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