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HIGH IMPULSE SOLID PROPELLANT COMPOSITION

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This invention relates to high impulse solid propellant compositions containing elemental silicon. In one aspect the invention relates to a solid propellant containing elemental silicon as a high impulse ingredient and also containing elemental aluminum as an ignition aid for the silicon.

High energy fuel components such as aluminum, magnesium, boron, and silicon have been proposed for use as ingredients of solid propellant compositions to improve the specific impulse of such propellant compositions. These high energy fuels can be combined with solid propellant compositions wherein a solid oxidizer, such as ammonium nitrate or ammonium perchlorate, is combined with a binder material which also acts as the fuel component for the propellant composition.

Recently it has been discovered that superior solid propellant compositions are obtained comprising a solid, inorganic, oxidizing salt, such as ammonium nitrate or ammonium perchlorate, and a rubbery binder material, such as natural rubber or a copolymer of butadiene, and a vinyl pyridine or other substituted heterocyclic nitrogen base compound which, after incorporation, is cured by a quaternization reaction for a vulcanization reaction. Solid propellant compositions of this nature and a process for their production are disclosed and claimed in copending application Serial No. 284,447, filed April 25, 1952, by W. B. Reynolds and J. E. Pritchard, now U.S. Patent No. 3,003,861, issued October 10, 1961.

Elemental silicon is considered a superior fuel component for a solid propellant charge because of the great quantity of heat released upon the formation of silicon dioxide; however, attempts to utilize finely divided elemental silicon as a high-energy fuel in solid propellant charges has not been successful and it has been determined that the silicon is usually unchanged after combustion of the propellant charge. Therefore, the silicon provides no thrust to the reaction and the specific impulse of the propellant composition is not improved.

It is an object of this invention to provide a solid propellant composition wherein finely divided elemental silicon is utilized to increase the specific impulse properties of the propellant composition. It is also an object of this invention to provide a solid propellant composition containing finely divided elemental silicon wherein finely divided aluminum is utilized as an ignition aid for the silicon. It is a further object of this invention to provide a method for the ignition of finely divided silicon in a solid propellant composition. Other objects and advantages of the invention will be apparent to one skilled in the art upon study of the present disclosure.

We have discovered that the high impulse characteristics of elemental silicon can be imparted to a solid propellant composition containing silicon by the addition thereto of a sufficient amount of aluminum to insure the ignition of the silicon. Solid propellant compositions, comprising ammonium nitrate as the oxidizer and a rubbery copolymer as the binder materials, have been prepared containing powdered aluminum and the aluminum has ignited with the conventional igniters used for such propellant compositions. We have discovered that in such formulations wherein finely divided or powdered silicon is employed, the silicon can be ignited by incorporating in

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the composition powdered aluminum in an amount of about 1 up to about 60 weight percent of aluminum based on the total of aluminum and silicon. Rapid ignition of the silicon is also facilitated if the igniter employed contains in the ignition charge a substantial amount of powdered aluminum so that the temperature of the burning gases is quickly raised to above the ignition temperature of silicon. When from about 1 to about 4 or 5 weight percent of aluminum is used, with respect to the total of silicon and aluminum, the maximum temperature in the combustion chamber is not attained for several seconds, for example, 2 to 3 seconds, whereas if from about 6 to about 60 weight percent of aluminum is used, with respect to the total of aluminum and silicon, then the temperature rise in the combustion chamber is quite rapid and maximum temperature is achieved almost instantly.

Ammonium nitrate is the preferred oxidizer for the reason that ammonium nitrate contributes more oxygen per unit weight than do other solid oxidizing agents such as ammonium perchlorate. The amount of oxidizer used is that required to convert the aluminum and the silicon to the oxide; the carbon of the binder to carbon monoxide; and the hydrocarbon of the binder to hydrogen and carbon monoxide. While any of the rubbery copolymer binder compositions of the propellant art can be used as the binder and a portion of the fuel of the propellant composition of our invention, the preferred compositions for the binder component, because of superior physical properties and impulse characteristics, are disclosed in copending application Serial No. 730,755, filed April 21, 1958, by F. R. Gessner, Jr.

The following tabulation discloses a typical formulation of a propellant composition containing silicon and aluminum.

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Table I

Ingredient:	Weight percent
Butadiene - methylvinylpyridine copolymer	3.00- 6.67
Plasticizer	0.50- 2.00
Silicon and aluminum combined	15.00-32.00
Carbon black	0.50- 1.33
Ammonium nitrate	60.00-81.00

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The various ingredients making up the total composition are thoroughly incorporated by mixing all of the ingredients so that a composition is obtained wherein the binder forms the continuous phase. The silicon and aluminum are utilized as finely divided or powdered materials and can be added separately or mixed together before being added to the composition.

The composition is then formed into the desired shape by a molding or extrusion operation and the propellant composition is cured, for example, for 24 hours at 190° F.

The silicon and the aluminum can be reduced to finely divided form by any of the known methods of pulverization. The aluminum is resistant to pulverization by ordinary methods since it is a soft, tough metal whereas silicon, being extremely brittle, is amenable to ordinary crushing operations and is readily reduced to a finely divided state such as a powder. A preferred method for reducing the aluminum to powdered form is to prepare an alloy of aluminum and silicon in the desired ratio in which case an extremely brittle alloy results which is readily reduced to finely divided form by ordinary crushing methods. In some cases these alloys spontaneously disintegrate to powdered form upon cooling due to stresses set up therein and due to the extremely brittle nature of the alloy.

The rubbery binders of the solid rocket propellant compositions include natural rubber and synthetic rubbers such as butadiene-styrene; polybutadiene; silicon rubber, polysulfide rubber; copolymers of conjugated dienes with

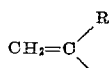
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polymerizable heterocyclic nitrogen bases of the pyridine and quinoline series; and the like.

The conjugated dienes which can be employed are those containing from 4 to 6 carbon atoms per molecule and include 1,3-butadiene, isoprene, 2-methyl-1,3-butadiene, and the like. Various alkoxy, such as methoxy and ethoxy and cyano derivatives of these conjugated dienes, are also applicable. Thus, other dienes, such as phenyl butadiene, 2,3-dimethyl-1,3-hexadiene, 2-methoxy-3-ethylbutadiene, 2-ethoxy-3-ethyl-1,3-hexadiene, 2-cyano-1,3-butadiene, are also applicable in the preparation of the polymeric binders of this invention.

Instead of using a single conjugated diene, a mixture of conjugated dienes can be employed. Thus, a mixture of 1,3-butadiene and isoprene can be employed as the conjugated diene portion of the monomer system.

The polymerizable heterocyclic nitrogen bases which are applicable for the production of the polymeric materials are those of the pyridine, quinoline, and isoquinoline series which are copolymerizable with a conjugated diene and contain one, and only one



substituent wherein R is either hydrogen or a methyl group. That is, the substituent is either a vinyl or an alpha-methylvinyl(isopropenyl) group. Of these, the compounds of the pyridine series are of the greatest interest commercially at present. Various substituted derivatives are also applicable but the total number of carbon atoms in the groups attached to the carbon atoms of the heterocyclic nucleus should not be greater than 15 because the polymerization rate decreases somewhat with increasing size of the alkyl group.

Solid inorganic oxidizing salts which are applicable in the solid rocket fuel compositions of this invention include ammonium, alkali metal, and alkaline earth metal salts of nitric, perchloric, and chloric acids, and mixtures thereof. Ammonium nitrate and ammonium perchlorate are the preferred oxidants for use in the solid rocket fuels of this invention with ammonium nitrate being especially preferred because of the greater amount of oxygen contributed per unit weight by the ammonium nitrate. Other specific oxidants which can be used include sodium nitrate, potassium perchlorate, lithium chlorate, calcium nitrate, barium perchlorate, and strontium chlorate. Mixtures of oxidants are also applicable. In the preparation of the solid rocket fuel compositions, the oxidants are powdered to sizes preferably 10 to 300 microns average particle size. The amount of solid oxidant employed is usually a major amount of the total composition and is generally in the range between 50 and 90 percent by weight of the total mixture of oxidant and binder. If desired, however, less than 50 percent by weight of the oxidant can be used.

Combustion rate catalysts can be used if desired and those applicable in the propellant composition of the invention include ammonium dichromate, metal ferrocyanides and metal ferricyanides. The complex metal cyanides are preferred. Ferric ferrocyanides, such as Prussian, Berlin, Hamburg, Chinese, Paris, and milori blue, soluble ferric ferrocyanide, such as soluble Berlin or Prussian blue which contains potassium ferric ferrocyanide, and ferric ferrocyanide which has been treated with ammonia, are among the materials which can be used. Ferrous ferricyanide, Turnbull's blue, is also applicable. A particularly effective burning rate catalyst is milori blue which is pigment similar to Prussian blue, and is prepared by the oxidation of a paste of potassium ferrocyanide and ferrous sulfate. Other metal compounds such as nickel and copper ferrocyanides can also be employed. The amount of combustion or burning rate catalyst will usually be about 0.25 to about 12 parts by weight per 100

parts of oxidant and binder. The catalyst can be omitted entirely if desired.

Reinforcing agents include carbon black, wood flour, lignin, and various reinforcing resins such as styrene-divinylbenzene, methyl and acrylate-divinylbenzene, acrylic acid-styrene-divinylbenzene, methyl acrylate-acrylic acid-divinylbenzene, and phenyl-formaldehyde resins. The reinforcing agent is usually used in an amount in the range of about 10 to about 50 parts by weight per 100 parts by weight of rubbery material. The reinforcing agent can be omitted if desired.

In general, any rubber plasticizer can be employed in these binder compositions. Material such as Pentaryl A (amyl biphenyl), Parafflux (saturated polymerized hydrocarbon), Circosol 2XH (petroleum hydrocarbon softener having a specific gravity of 0.94 and a Saybolt Universal viscosity at 100° F. of about 2000 seconds), di-(butoxyethoxyethyl)formal, and dioctyl phthalate are suitable plasticizers. Liquid polybutadiene and aromatic hydrocarbon oils resulting from the distillation of petroleum fractions are preferred plasticizers because they are particularly effective in rendering the components of the composition manageable and are entirely consumed as fuel. An aromatic residual oil having an API gravity at 60° F. of about 10 to about 13.5 has been found particularly effective. The amount of plasticizer used will be only that required to render the rubbery material manageable during incorporation of the oxidizer and extrusion of the product, ordinarily, about 0.5 to about 10 weight percent of the total propellant composition.

The various ingredients of the rocket fuel composition can be mixed on a roll mill or in an internal mixer such as a Banbury, or a Baker-Perkins dispersion blade mixer can be employed. The binder forms the continuous phase in the finished propellant composition with the oxidant as the discontinuous phase. The propellant is usually cured as a temperature of about 70 to about 250° F. for about 6 to about 72 hours.

The following specific embodiments of the invention are exemplary and are not to be construed as limiting the invention but are presented to facilitate an understanding of the invention.

EXAMPLE I

The following tabulation discloses one preferred formulation of a propellant composition containing silicon and aluminum with ammonium nitrate as the oxidizer.

Table II

SILICON-CONTAINING SOLID PROPELLANT	
Ingredient:	Weight percent
Butadiene-methylvinylpyridine copolymer	5.50
Furnace carbon black	1.00
Liquid polybutadiene	2.00
Magnesium oxide	0.25
Silicon	25.00
Aluminum	2.25
Ammonium nitrate	64.00

The copolymer, liquid butadiene, carbon black, magnesium oxide are blended together and the silicon and aluminum in the form of a powdered alloy are then added to the blend. The silicon and aluminum, in the proportions indicated in the table, can be alloyed and the resulting alloy crushed to powder form having an average particle size of about 5 microns. The ammonium nitrate is then incorporated into the above blend of materials to form the finished composition which is extruded into the proper grain forms and is cured for 24 hours at 190° F. The specific impulse of the above solid propellant is about 260 to about 270 seconds.

EXAMPLE II

The following tabulation discloses another formulation for a propellant composition.

Table III

SILICON-CONTAINING SOLID PROPELLANT

Ingredient:	Weight percent
Butadiene-methylvinylpyridine copolymer	3.00
Furnace carbon black	0.65
Aromatic residual oil	0.30
Magnesium oxide	0.05
Aluminum	5.00
Silicon	21.00
Ammonium nitrate	70.00

The composition is prepared as hereinbefore disclosed. The specific impulse is about 260 to about 270 seconds.

EXAMPLE III

Another propellant composition is shown in the following tabulation.

Table IV

SILICON-CONTAINING SOLID PROPELLANT

Ingredient:	Weight percent
Butadiene-vinylpyridine copolymer	6.00
Furnace carbon black	1.35
Polybutadiene	1.90
Magnesium oxide	0.25
Aluminum	15.00
Silicon	11.00
Ammonium nitrate	64.00

The specific impulse of this composition will be lower than those of Examples I and II and will be about 260 seconds.

EXAMPLE IV

Still another propellant composition is shown in the following Table V.

Table V

SILICON-CONTAINING SOLID PROPELLANT

Ingredient:	Weight percent
Butadiene-vinylpyridine copolymer	4.00
Furnace carbon black	0.90
Di-(butoxyethoxyethyl) formal	0.60
Magnesium oxide	0.50
Aluminum	6.00
Silicon	21.50
Ammonium nitrate	66.50

The specific impulse of this composition will be about 260 to 270 seconds.

The combustion temperatures of the above propellants are sufficiently high to prevent plating of solid alumina or silica on the exhaust nozzle surfaces.

The solid propellant compositions of this invention are simple in composition, readily adaptable to present methods of compounding solid propellants, and are characterized by exceptionally high values of specific impulse.

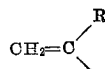
Reasonable variations and modifications are possible within the scope of the present disclosure without departing from the spirit and scope of the invention.

That which is claimed is:

1. A solid propellant composition comprising about 60 to about 81 weight percent of a solid inorganic oxidizing salt; about 4 to about 10 weight percent of a rubber binder material; and about 15 to about 32 weight percent of a mixture of finely divided silicon and finely divided aluminum wherein the aluminum is present in an amount sufficient to raise the temperature of the propellant combustion gases to above the ignition temperature of the silicon and is in the range of about 1 up to about 60 weight percent of the total of aluminum and silicon.

2. A solid propellant composition wherein the herein-after named silicon, aluminum and binder material constitute from 19 to 40 weight percent of the total composition, comprising about 60 to about 81 weight percent ammonium nitrate; about 15 to about 32 weight percent of silicon and aluminum combined wherein the aluminum is present in an amount sufficient to raise the temperature of the propellant combustion gases to above the ignition

temperature of the silicon and is from about 1 to about 60 weight percent of the total of silicon and aluminum; and about 4 to about 10 weight percent of a binder comprising a copolymer of a conjugated diene having from 4 to 6 carbon atoms per molecule and at least one



substituted heterocyclic nitrogen base selected from the group consisting of pyridine, quinoline, an alkyl substituted pyridine and an alkyl substituted quinoline, wherein the total number of carbon atoms in the nuclear alkyl substituents is not more than 15.

3. A propellant composition according to claim 2 wherein the binder comprises about 4 weight percent; the combined silicon and aluminum comprise about 26 weight percent; and the ammonium nitrate comprises about 70 weight percent of the propellant.

4. A propellant according to claim 2 wherein the binder comprises about 9.5 weight percent; the combined aluminum and silicon comprise about 26.5 weight percent and the ammonium nitrate comprises about 64 weight percent of the total propellant.

5. A propellant composition according to claim 2 wherein the binder comprises about 6 weight percent; the combined aluminum and silicon comprise about 27.5 weight percent; and the ammonium nitrate comprises about 66.5 weight percent of the total propellant.

6. A method for producing a solid rocket propellant composition which comprises: intimately admixing about 15 to about 32 parts by weight of a mixture of finely divided silicon and finely divided aluminum wherein the aluminum is about 1 to 60 weight percent of the mixture of silicon and aluminum with about 3 to about 6.67 parts by weight of a rubbery binder comprising a copolymer of a conjugated diene and a polymerizable heterocyclic nitrogen base; incorporating about 60 to about 81 parts by weight of finely divided ammonium nitrate into the resulting mixture; forming the resulting composition into propellant grains; and curing the resulting composition to produce a propellant composition so that the propellant composition contains a sufficient amount of aluminum to raise the temperature of the combustion gases to above the ignition temperature of the silicon.

7. The method of igniting finely divided silicon contained in a solid propellant charge comprising a major proportion of a solid inorganic oxidizing salt and a minor proportion of a rubber binder containing finely divided silicon which method comprises incorporating finely divided aluminum in the binder in an amount sufficient to raise the temperature of the propellant combustion gases to above the ignition temperature of the silicon and in the range of 1 to 60 weight percent of the total of aluminum and silicon.

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