United States Patent Office

3,738,878

Patented June 12, 1973

3,738,878

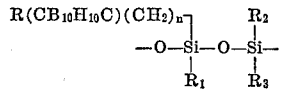
HIGH BURNING RATE SOLID PROPELLANT HAVING A SILICON-CARBORANYL COPOLYMER FUEL BINDER

Joseph Green, East Brunswick, N.J., assignor to Thiokol Chemical Corporation, Bristol, Pa.

No Drawing. Filed Nov. 2, 1967, Ser. No. 681,959
Int. Cl. C06b 11/00
U.S. Cl. 149—19 5 Claims

ABSTRACT OF THE DISCLOSURE

High burning rate solid propellants having fuel-binders based on carboranyl copolymers having the recurring structural units:



wherein R, R_1, R_2 and R_3 are selected from hydrogen, aliphatic, cycloaliphatic and aryl radicals and n is an integer including zero.

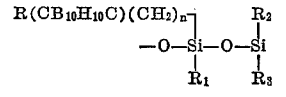
This invention relates to solid propellants adapted to be used as rocket fuels and more particularly to solid propellants comprising fuel-binders containing carboranyl polymers. The propellants of the invention are characterized by exceptionally high burning rates.

Sold propellants commonly comprise a major proportion of particulate inorganic oxidizer, a minor amount of organic fuel-binder and minor amounts of various special purpose additives such as burning rate modifiers, catalysts, plasticizers, pigments and wetting agents. Conventional solid propellants usually have burning rates of the order of 0.2 to 0.4 inch per second. While such burning rates are acceptable for certain applications, there are other applications for which it would be desirable to have a propellant with a substantially higher burning rate.

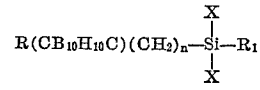
Various materials have heretofore been proposed for incorporation in solid propellants to increase the burning rates thereof. However, in general, such materials have been either relatively ineffective or have produced undesirable side effects, such as adverse effects on the physical properties of the propellant or increases in its impact sensitivity. For example, boron hydrides such as decaborane, because of their high heats of combustion, are capable of increasing the burning rate of a propellant in which they are incorporated. However, propellants containing decaborane have a high impact sensitivity, and if they contain a high concentration of decaborane, have a tendency to detonate upon ignition.

It is accordingly an object of the present invention to provide a solid propellant having a high and stable burning rate. It is another object of the invention to provide a high burning rate solid propellant that can be safely stored and handled. It is still another object of the invention to provide a high burning rate propellant that can be safely used over a wide range of combustion chamber pressures. It is a still further object of the invention to provide a solid propellant having good mechanical properties. Other objects and advantages of the invention will be in part obvious and in part pointed out hereafter.

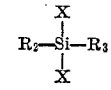
The objects and advantages of the invention are achieved in general by utilizing as the fuel-binder of a solid propellant a carboranyl copolymer having recurrent units of the structure:

(1) 

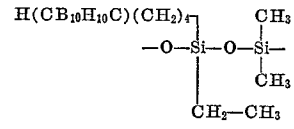
wherein ($CB_{10}H_{10}C$) is the divalent carboranyl radical and may be the ortho, meta or para isomer; R, R_1, R_2 and R_3 are selected from the group consisting of hydrogen, aliphatic, cycloaliphatic and aryl radicals; and n is an integer including zero. Copolymers having recurring units of the above structure may be prepared by copolymerizing a carboranyl compound of the structure:

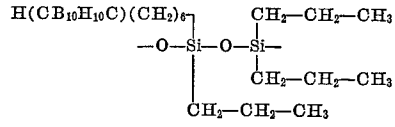
(2) 

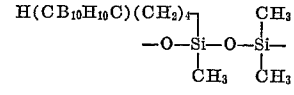
with a silane of the structure:

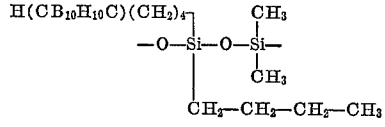
(3) 

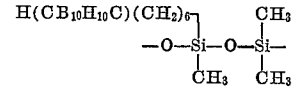
wherein R, R_1, R_2, R_3 and n are defined as above and X is selected from halogen and alkoxy groups. The structures of the recurring units of typical copolymers that can be used as fuel-binders in the present propellants are as follows:

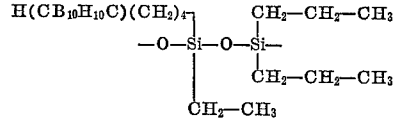
(4) 

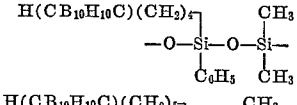
(5) 

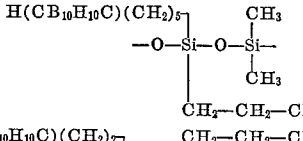
(6) 

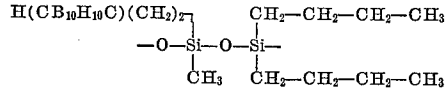
(7) 

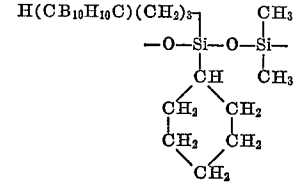
(8) 

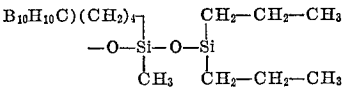
(9) 

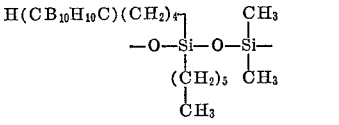
(10) 

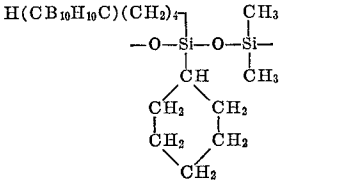
(11) 

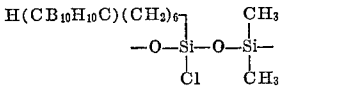
(12) 

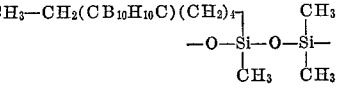
(13) 

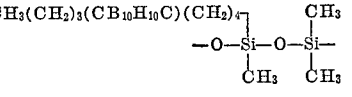
(14) 

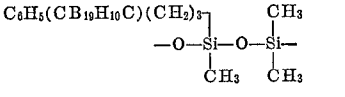
(15) 

(16) 

(17) 

(18) 

(19) 

(20) 

The preferred copolymers for use as a fuel-binder in the present propellant are those having recurrent units of the structure of Formula 1 above and wherein R, R_1, R_2 and R_3 are selected from hydrogen and lower alkyl groups having 1 to 4 carbon atoms and n is 2 to 4 inclusive. Other examples of copolymers having recurring units of the structure of Formula 1 above and details concerning methods of making such copolymers are given in Fein et al. application Ser. No. 400,582 filed Sept. 30, 1964.

It has been found that when copolymers of the type described above are properly formulated with inorganic oxidizers, propellants with exceptionally high burning rates are achieved. In general, the propellant compositions of the invention are formulated by mixing a major amount of inorganic oxidizer with a minor amount of the copolymers, and optionally, various special purpose ingredients conventionally used in solid propellants.

Any of the solid oxidizers known to be useful in solid rocket propellants can be used in the present compositions. However, the preferred oxidizers are ammonium and potassium perchlorates and mixtures thereof.

In some cases it has been found desirable to incorporate a curing agent for the copolymer in the composition. In such instances the curing agent may be, for example, dibutyl tin dilaurate or ferric acetyl acetonate.

It has been further found that both the physical properties and the burning rate of the present compositions can be improved by incorporating therein a plasticizer, preferably isopropyl carborane. While the use of isopropyl carborane is not essential, it has been found generally advantageous. Also other known additives such as aluminum or magnesium powder, burning rate modifiers, catalysts, etc. may be incorporated in the mixture. Upon completion of the mixing operation, the mixture is cast into a desired configuration and cured in situ in known manner to form the solid propellant.

In general, the relative proportions of the several ingredients of the propellant composition used are not particularly critical and may be varied considerably, provided that the oxidizer is used in a major amount and the fuel binder in a minor amount. It is usually desirable to maintain the proportions within the following ranges in parts by weight:

Oxidizer	60–80
Fuel-binder	10–25
Other ingredients if used:	
Plasticizer	5–25
Metal powder	5–25
Additives such as burning rate catalysts, pigments, wetting agents, etc.	0–5

In order to point out more fully the nature of the invention a number of specific examples are given below illustrating the preparation and testing of several propellant compositions embodying the present invention.

EXAMPLE 1

Equimolar quantities (.025 mole) of 1-(methyldiethoxysilyl - 4 - butyl)carborane and dimethyldichlorosilane were refluxed in anhydrous benzene in the presence of a catalytic quantity of anhydrous ferric chloride for a period of about 36 hours. The benzene was stripped off and the residue washed with water and dried. A viscous liquid product having a molecular weight of 2286 was obtained.

The copolymer as thus obtained was heated to 50° C. to lower its viscosity and formulated into a propellant in a conventional mixer according to the following recipe in parts by weight:

Ammonium perchlorate (300 to 800 micron particle size)	68.6
Copolymer	9.5
Isopropylcarborane	9.5
Aluminum powder (about 40 micron particle size)	11.0
Lecithin	1.0
Kosmos carbon black	0.4

The resulting propellant was tested to determine its burning rate at 500 p.s.i. and 1000 p.s.i. pressures. Also the exponent n of the burning rate equation for the propellant was determined. The value of the pressure exponent n of a solid propellant is indicative of the stability of the propellant. Solid propellants having pressure exponents that approach unity tend to have unstable burning characteristics.

The solid propellant of this example was found to have a burning rate of 1.75 inch/sec. at 500 p.s.i. and 3.19 inch/sec. at 1000 p.s.i. Its pressure exponent n was found to be 0.86 in the 600 to 1600 p.s.i. range. Certain other properties of the propellant such as tensile strength, storability and resistance to cracking when subjected to temperature cycling were determined and found to be comparable to those of a conventional propellant. The measured burning rates of the propellant of this example were of the order of 3 to 10 times as great as those of a conventional prior art propellant.

EXAMPLE 2

Another propellant composition was prepared using the copolymer of Example 1 and a somewhat modified recipe as follows:

Potassium perchlorate	68.6
Copolymer	9.5
Isopropylcarborane	9.5
Aluminum powder	11.0
Ammonium dichlromate	2.0
Lecithin	1.0
Kosmos carbon black	0.4

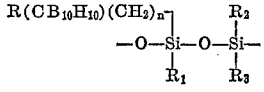
The burning rate of this propellant was measured and found to be 5.0 inches/sec. at 500 p.s.i. and 9.95 inches/sec. at 1000 p.s.i. The burning rate of this propellant was of the order of 30 times that of conventional prior art propellants. The exponent n of the burning rate equation of this propellant was found to be .130 in the 1000 to 2000 p.s.i. range.

From the foregoing examples it should be apparent that solid propellants embodying the present invention have exceptionally high burning rates, in some cases as much as 10 to 30 times as great as those of conventional propellants. Moreover, they have relatively low pressure exponents, and physical properties that permit them to be used in rocket motors having a variety of grain designs and under a variety of operating conditions.

It is of course to be understood that the foregoing examples are intended to be illustrative, and that numerous changes can be made in the ingredients, proportions and conditions set forth therein without departing from the spirit of the invention as defined in the appended claims.

I claim:

1. In a solid propellant of the type which comprises a major amount of finely divided inorganic oxidizer and a minor amount of a fuel binder the improvement which comprises using as a fuel binder a polymer consisting essentially of recurring units of the structure:



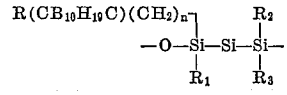
wherein R, R_1, R_2 and R_3 are selected from the group consisting of hydrogen, aliphatic, cycloaliphatic and aryl radicals and n is an integer including 0.

2. A solid propellant according to claim 1 containing a minor amount of a plasticizer which is isopropyl carborane.

3. A solid propellant according to claim 1 containing a minor amount of aluminum powder.

4. A solid propellant according to claim 1 and wherein said oxidizer is selected from ammonium perchlorate, potassium perchlorate and mixtures thereof.

5. In a solid propellant of the type which comprises a major amount of finely divided inorganic oxidizer and a minor amount of a fuel binder the improvement which comprises using from 60 to 80 parts by weight of said oxidizer and from 10 to 25 parts by weight of a polymeric fuel binder having recurring units of the structure:



wherin R, R_1, R_2 and R_3 are selected from hydrogen and alkyl groups of 1 to 4 carbon atoms and n is 2 to 4, 5 to 25 parts by weight of isopropyl carborane and 5 to 15 parts by weight of aluminum powder.

References Cited

UNITED STATES PATENTS

3,219,498	11/1965	Nitzsche et al.	149—22
3,137,719	6/1964	Papetti	149—22 X

STEPHEN J. LECHERT, JR., Primary Examiner

U.S. Cl. X.R.

149—20, 22, 40, 42, 44, 76, 83, 85