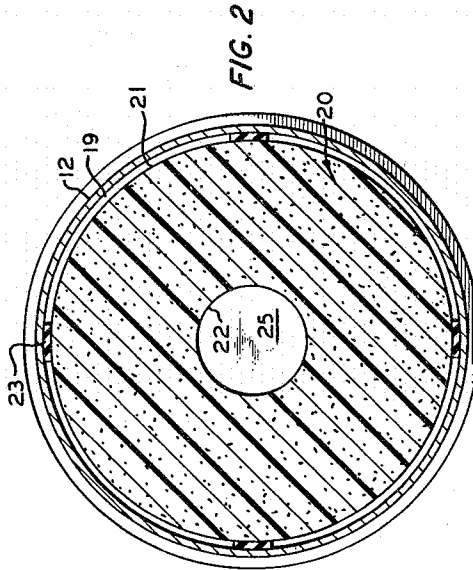
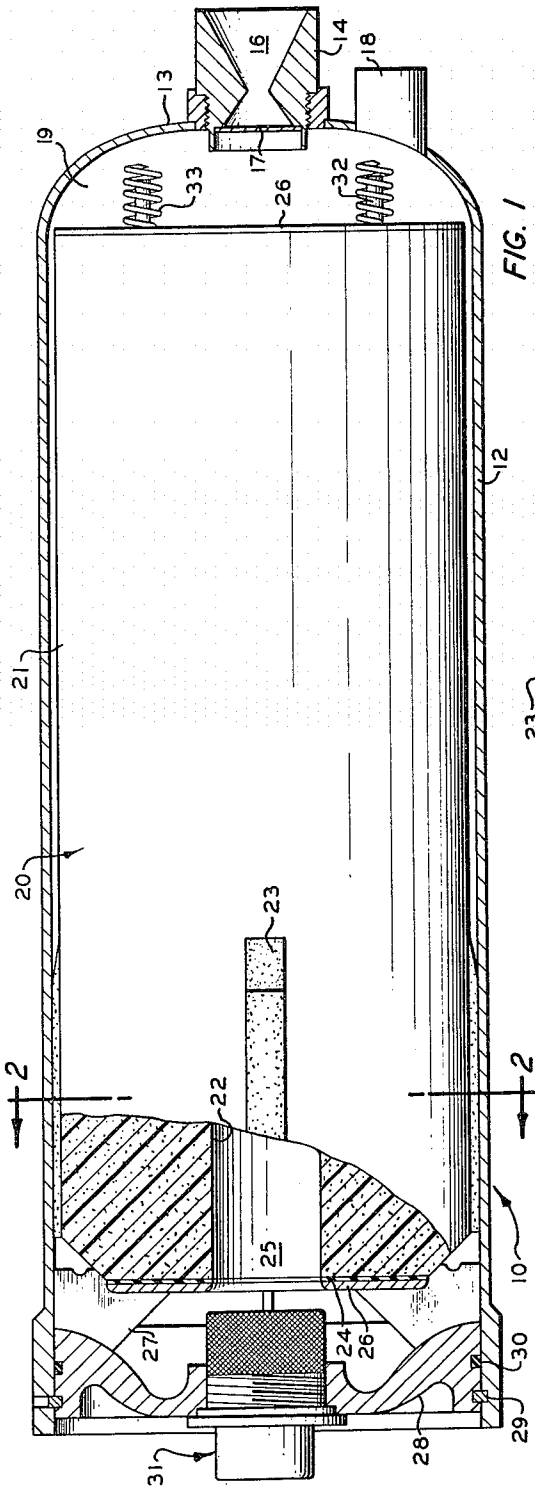


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COMPOSITE PROPELLANTS CONTAINING A CARBON-ALKALI
METAL BURNING RATE CATALYST
Filed Dec. 4, 1958

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COMPOSITE PROPELLANTS CONTAINING A
CARBON-ALKALI METAL BURNING RATE
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6 Claims. (Cl. 149—19)

This invention relates to solid propellant compositions. In another aspect, it relates to novel solid propellant compositions of the composite type having improved burning rates. In a further aspect, it relates to jet propulsion devices, such as missiles, gas generators, rocket motors of the type employed to assist the take-off of aircraft, and the like, the combustion chambers of which devices are loaded with novel solid propellant compositions of the composite type having improved burning rates.

In the past fifteen years or so, great interest developed in solid propellants for jet propulsion devices, such as missiles, rocket motors, gas generators, and the like. One type of solid propellant which has received particular attention is that of the composite type. A typical composite propellant is one that uses an organic resin as the fuel and binder and uses a solid oxidizer, such as ammonium nitrate. These propellants can also contain a small amount of an additive called a burning rate catalyst which is used to control the velocity at which the solid propellant is burned or consumed during operation.

One of the most important solid propellant parameters is the burning rate of the propellant. The basic solid propellant burning equation for restricted solid propellants, such as the type with which this invention is concerned, is expressed as:

$$r = k(p_c)^n$$

where r is the burning rate in inches per second; p_c is the combustion chamber pressure in pounds per square inch; k is a constant which varies with the ambient grain temperature; and n is a constant known as the burning rate exponent.

Inspection of the above burning equation reveals that the sensitivity of the burning rate of the solid propellant to pressure is represented by the burning rate exponent n . For stable and practical operation, n should lie between 0 and 1, and preferably should be as low as possible since as n approaches 1 the burning rate is very sensitive to changes in combustion chamber pressure, and vice versa. An indication of this sensitivity can be obtained by plotting logarithm r against n (logarithm p_c) + logarithm k . Such a plot, called a burning rate curve, will generally result in a straight line; the closer the slope of this line approaches 0, the less sensitive is the burning rate of the propellant to the combustion chamber pressure. In fabricating any solid rocket propellant of the restricted type, the fabricator is faced with the problem of preparing a propellant having a burning rate which is relatively insensitive to the combustion chamber pressure.

The importance of the burning rate cannot be overestimated since the velocity at which a solid propellant is consumed during operation is determined to a great extent by the burning rate; where high thrusts are required in a relatively short period of time, solid propellants having a fast burning rate are utilized. With the availability of solid propellant compositions having controllable burning rates which are relatively fast and insensitive to combustion chamber pressure, the fabricator of solid propellants has greater latitude in choosing the desired propellant grain design or charge geometry.

Accordingly, an object of this invention is to provide the novel solid propellant composition. Another object is

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to provide a novel solid propellant composition of the composite type having improved burning characteristics. Another object is to provide a jet propulsion device, such as a missile, gas generator, rocket motor, or the like, the combustion chamber of which is loaded with a novel solid propellant composition of the composite type having improved burning characteristics. Another object is to increase the burning rate of a solid propellant composition. Another object is to decrease the sensitivity of the burning rate of a solid propellant composition to combustion chamber pressure. Other objects and advantages of this invention will become apparent to those skilled in the art from the following discussion, appended claims, and accompanying drawing in which:

FIGURE 1 is a side elevational view in partial section of a rocket motor loaded with a solid propellant charge of this invention; and

FIGURE 2 is a cross-sectional view of FIGURE 1 taken along the plane indicated.

The essence of the subject invention resides in the discovery that the burning or consumption of a solid propellant composition, particularly that of the composite type, can be materially improved and controlled by incorporating into the propellant composition a minor but significant amount of a carbon-alkali metal compound or reaction product. Propellant compositions so prepared according to this invention have improved burning rates which not only are relatively fast but are relatively insensitive to combustion chamber pressure. As such, the burning or consumption of the propellant will be controlled and this will afford the propellant grain fabricator a greater latitude in choosing the desired propellant grain design or charge geometry. The propellant compositions of this invention can be formed into a grain having any desired shape or geometry, such as grains of the internal, external, and internal-external burning types. These grains can be molded, or extruded, and can be restricted with any suitable and well-known techniques.

A fuller understanding of this invention will be gained by reference to the accompanying drawing, in which there is illustrated a rocket motor 10, the particular jet propulsion device shown being that employed to assist the take-off of aircraft, which device is known in the art as a JATO unit. The rocket motor 10 comprises a cylindrical casing 12 made of metal or the like, which has a reduced aft portion 13 having an axial opening into which a reaction nozzle 14 is threaded or otherwise secured. The nozzle is formed with internal restrictions so as to define a converging-diverging passage 16 of the De Laval type through which combustion gases pass. A blow-out diaphragm or starter disc 17, which is mounted across the passage 16, is designed so as to be ejected through the nozzle passage when the pressure in the rocket motor reaches a predetermined value, e.g., between 200 and 500 p.s.i. The reduced casing portion 13 is also provided with a safety plug attachment 18 which is adapted to rupture or otherwise function at a predetermined combustion chamber pressure so as to relieve excessive pressures which might otherwise rupture the rocket motor or cause an explosion. The cylindrical casing 12 defines a combustion chamber 19 in which is disposed a charge 20 of the novel solid propellant of this invention. The specific propellant charge illustrated is cylindrical in shape and has an outer diameter smaller than the inner diameter of the casing. The propellant charge 20 is an internal-external burning type by reason of its exposed or unrestricted outer cylindrical surface 21 and its inner exposed cylindrical surface 22 which is defined by an axial perforation 25 extending the length of the propellant. A plurality of resilient retaining pads 23, for example, strips of sponge rubber, are positioned between the head portion of the external burning surface and the adjacent head portion of the casing. The ends of the

propellant are restricted by means of a layer of restricting material 24 which has a central opening in alignment with the axial perforation 25. Retaining plates 26 having similar openings cover the outside of the restricting material 24. Secured to the head retaining plate are outer-extending prongs or legs 27 which are adapted to register with and are held in place by head closure assembly 28 having retention means for igniter assembly 31. Head closure assembly 28 is held in position in the head end of casing 12 by means of key 29 which fits into appropriate grooves formed in the casing and head closure assembly 28. A sealing ring 30 is positioned in a groove cut into assembly 28 to prevent escape of combustion gases from the head end of the casing. The head end of the cylindrical casing is closed by means of head closure assembly 28 in combination with igniter assembly 31 which is retained in the opening provided in the axial portion of the assembly 28. It is noted that the igniter assembly 31 is provided with a removable cover which extends outwardly from this axial opening. The aft retaining plate has secured to its outer surface a plurality of prongs 32. The prongs are each surrounded by a compression string 33 adapted to come into contact with the reduced portion 13 of the casing. The aft retaining plate is thereby maintained firmly against the restricting material which covers the aft end of the solid propellant charge 20.

It is to be understood that rocket motor 10 is merely illustrative of a preferred type of jet propulsion device which can be loaded with a solid propellant charge fabricated in accordance with this invention. While the rocket motor illustrated is shown loaded with a single grain of solid propellant, it is to be understood that it can be loaded with a plurality of grains of solid propellant assembled in any desired fashion. Any suitable charge support means and igniter can be used other than that shown in the drawing for illustrative purposes.

A suitable igniter which can be employed is that disclosed in copending application, Serial No. 591,340, filed June 14, 1958, now U.S. Patent No. 2,980,021, by B. R. Adelman, which igniter is in the form of a frangible wire container or cup containing suitable ignition material in contact with suitable electro-responsive means, such as squibs, matches, or the like, that are operatively connected to an electrical system connected to a suitable external power source.

In the operation of the rocket motor shown in the drawing, the motor is armed by removing the cover from the igniter assembly 31 and connecting suitable plugs thereof to an electrical circuit, not shown, which includes a source of power. Upon closing of a suitable switch, electric current fires squibs, matches, or the like, embedded in the ignition material within the igniter assembly 31, causing the ignition of the ignition material. The firing of the igniter 31 results in the formation of hot ignition products which are released from the igniter 31 and immediately propagate throughout the combustion chamber 19, heat from the ignition products being transferred to the exposed burning surfaces 21, 22 of the solid propellant charge 20, raising the surface thereof to an ignition temperature. The resulting ignition of the propellant charge 20 and its subsequent burning or consumption results in generating hot combustion gases which raise the pressure and temperature within the combustion chamber. When a predetermined starter disc bursting pressure is reached, for example, 200-500 p.s.i., the starter disc 17 functions, for example, by rupturing, and it is expelled from the rocket motor via the passage 16. The gases are then free to flow at a high velocity from the combustion chamber 19 through the constricted nozzle 16, thereby imparting thrust to the rocket motor.

As mentioned hereinbefore, the propellant compositions of this invention are preferably of the composite type, comprising a major amount of the solid inorganic oxidizing salt, such as ammonium nitrate, a minor amount of a rubbery binder and fuel, such as synthetic rubber, and a

minor but significant amount of a carbon-alkali metal compound or reaction product as a burning rate catalyst.

The carbon-alkali metal compounds, which function as burning rate catalysts, can be prepared by the reaction of vaporized alkali metal with the carbon under conditions suitable to effect the reaction. These compounds or reaction products are pyrophoric and air must be excluded during their preparation and storage. One method for preparing these carbon-alkali metal compounds which has proven satisfactory utilizes a reactor system constructed of glass which is provided with separate compartments for charging the carbon and the alkali metal, separate heating means for each compartment, and a means for evacuating the system while heating the carbon. After evacuating the system to remove all volatile materials and heating the carbon, the reactor is sealed and placed in a vertical position with the compartment containing the carbon below that containing the alkali metal. Upon heating the upper compartment under suitable conditions, the alkali metal is melted and transferred to the lower chamber with the carbon. This chamber is sealed and the reactant heated to effect reaction between the carbon and alkali metal.

Heating of the carbon while the system is being evacuated is generally effected at a temperature in the range between 100 and 600° C. if a glass vessel is used. Higher temperatures can be used with other types of vessels. The time of heating and evacuation will depend upon the temperature. It will generally be in the range between 1 and 40 hours. Obviously, the higher the temperature employed, the shorter the time required for the degassing operation.

The step which involves transfer of the alkali metal to the compartment containing carbon is generally operated at a temperature in the range between 100 and 500° C. The time required for transfer of the alkali metal will depend upon the temperature and will generally be in the range between 10 minutes and 100 hours, preferably between 20 and 50 hours. Temperatures in excess of 200° C. are preferred in this step in order to build up a high vapor pressure of alkali metal and aid its transfer to the compartment containing carbon.

The reaction between the alkali metal and carbon is effected at a temperature generally in the range between 375 and 500° C. and will depend upon the stability of the product.

The term "carbon" as used in this application and in the appended claims is meant to cover that carbon which is reactable with the alkali metals, and representatively includes graphite and amorphous carbons such as channel black, furnace black, soot, and the like. In the graphite crystal lattice, the carbon atoms are arranged in flat layers, each having a honeycomb-like structure. These layers are stacked parallel to each other in such a way that half the atoms in one layer lie normally above half the atoms in the layer beneath, while the other half are normally above the centers of the hexagons of the layer below. Alternate layers lie, atom for atom, normally above each other.

If a piece of carbon, e.g., graphite, is placed in contact with molten potassium in an evacuated tube, a swelling occurs and the alkali metal atoms, or ions, such as potassium, penetrate the hexagon layer-planes of the graphite crystal lattice and increase their spacing. The new lattice in a compound such as C₆K consists of alternate carbon and potassium layer-planes. It is a bronze colored product. The compound, C₁₆K, is a steel blue material. It has a layer of potassium atoms only in every second inter-layer-plane space of the graphite lattice.

The carbon-alkali metal compounds or reaction products (sometimes referred to as alloys) employed as burning rate catalysts in this invention are generally those in which the ratio of carbon atoms to alkali metal atoms is in the range of from 8:1 to 32:1. The particular product formed will depend upon the relative amounts of carbon and alkali metal charged to the reaction system during

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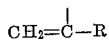
preparation of these compounds. The applicable alkali metals employed in preparing these compounds are sodium, potassium, rubidium, and cesium. The carbon-alkali metal compounds are generally employed in amounts in the range of 2 to 20 weight percent, preferably 5 to 15 weight percent, of the total propellant composition. These compounds are ultrafine in size, e.g., having a surface area on the order of 0.01 to 1000 square meters/grams, as are the carbon and alkali metal reactants.

The inorganic oxidizing salts which are employed as oxidizers in the solid propellant compositions of this invention representatively include the ammonium, alkali metal, and alkaline earth metal salts of nitric, perchloric, and chloric acids. Mixtures of these oxidizing salts can also be used. Ammonium nitrate and ammonium perchlorate are the preferred oxidizers for use in the solid propellant compositions of this invention. Other applicable oxidizers include sodium nitrate, potassium perchlorate, lithium chlorate, calcium nitrate, barium perchlorate, strontium chlorate, and the like. In the preparation of the propellant compositions, the oxidizers are powdered to sizes generally in the range of from 1 to 300 microns average particle size, preferably in the range between 20 and 200 microns. The amount of solid oxidizer employed will usually be a major proportion of the total composition and is generally in the range between 50 and 95 percent by weight of the total mixture. If desired, however, less than 50 percent by weight of the oxidizer can be used.

Although the rubbery binder and fuel utilized in preparing these propellant compositions can be any rubber, either natural or synthetic, I have found that the rubbery binders which are particularly suitable are those rubbery copolymers which are disclosed in copending applications Serial No. 284,447, filed April 25, 1952, and Serial No. 561,943, filed January 27, 1956, both filed by W. B. Reynolds et al. The rubbery copolymers disclosed in said copending applications are prepared by the copolymerization of an open chain conjugated diene and a vinyl heterocyclic nitrogen base compound. It is preferred that these rubbery copolymers have a Mooney value (ML-4 at 212° F.) in the range of 5 to 50. An especially preferred copolymer is a 90/10 copolymer of 1,3-butadiene and 2-methyl-5-vinylpyridine, this copolymer hereinafter abbreviated Bd/MVP.

The conjugated dienes employed in preparing the rubbery copolymer materials which are utilized as binders are preferably those containing from 4 to 8 carbon atoms per molecule. Representative conjugated dienes which can be employed include 1,3-butadiene, isoprene, 2-methyl-1,3-butadiene, 2,3-dimethyl-1,3-butadiene, piperylene, methylpentadiene, chloroprene, and the like. Various alkoxy derivatives, such as methoxy and ethoxy, and cyano derivatives of these conjugated dienes are also applicable, such as 2,3-dimethyl-1,3-hexadiene, 2-methoxy-3-ethylbutadiene, 2-cyano-1,3-butadiene, and the like. Instead of using a single conjugated diene, a mixture of conjugated dienes can also be employed, such as mixture of 1,3-butadiene and isoprene.

The polymerizable heterocyclic nitrogen bases which are applicable for the production of polymeric binder materials are those having the group

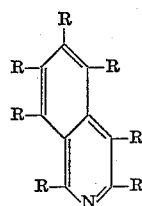
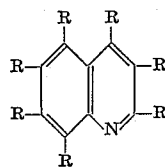
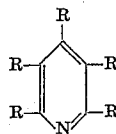


where R is either hydrogen or a methyl group, and are copolymerizable with a conjugated diene. Substituted heterocyclic nitrogen base compounds particularly useful are those selected from the group consisting of pyridine, quinoline, alkyl substituted pyridine and an alkyl substituted quinoline, where the total number of carbon atoms in the nuclear alkyl substituents is not more than 15. Of these, the compounds of the pyridine series are of the greatest commercial interest at present. The preferred, readily available binder employed is a copolymer

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prepared from 90 parts by weight of butadiene and 10 parts by weight of 2-methyl-5-vinylpyridine, hereinafter abbreviated Bd/MVP. This copolymer is polymerized to a Mooney (ML-4 at 212° F.) plasticity value in the range of 10-40, preferably in the range of 15 to 25.

These heterocyclic nitrogen bases can be represented by the following structural formulas:



where R is selected from the group consisting of hydrogen, alkyl, vinyl, alpha-methylvinyl, alkoxy, halo, hydroxy, cyano, aryloxy, aryl, and combinations of these groups such as haloalkyl, alkylaryl, hydroxyaryl, and the like; one and only one of said groups being selected from the group consisting of vinyl and alpha-methylvinyl; and the total number of carbon atoms in the nuclear substituted groups being not greater than 15. Examples of such compounds are 2-vinylpyridine; 2-vinyl-5-ethylpyridine; 2-methyl-5-vinylpyridine; 4-vinylpyridine; 2,3,4-trimethyl-5-vinylpyridine; 3,4,5,6-tetramethyl-2-vinylpyridine; 3-ethyl-5-vinylpyridine; 2,6-diethyl-4-vinylpyridine; 2-isopropyl-4-nonyl-5-vinylpyridine; 2-methyl-5-undecyl-3-vinylpyridine; 2,4-dimethyl-5,6-dipentyl-3-vinylpyridine; 2-decyl-5-(alpha-methylvinyl)pyridine; 2-vinyl-3-methyl-5-ethylpyridine; 2-methoxy-4-chloro-6-vinylpyridine; 3-vinyl-5-ethoxypyridine; 2-vinyl-4,5-dichloropyridine; 2-(alpha-methylvinyl)-4-hydroxy-6-cyanopyridine; 2-vinyl-4-phenoxy-5-methylpyridine; 2-cyano-5-(alpha-methylvinyl)pyridine; 3-vinyl-5-phenylpyridine; 2-(para-methyl-phenyl)-3-vinyl-4-methylpyridine; 3-vinyl-5-(hydroxyphenyl)pyridine; 2-vinyl-4-ethylquinoline; 3-vinyl-6,7-di-n-propylquinoline; 2-methyl-4-nonyl-6-vinylquinoline; 4-(alpha-methylvinyl)-8-dodecylquinoline; 3-vinylisoquinoline; 1,6-dimethyl-3-vinylisoquinoline; 2-vinyl-4-benzylquinoline; 3-vinyl-5-chloroethylquinoline; 3-vinyl-5,6-dichloroisoquinoline; 2-vinyl-6-ethoxy-7-methylquinoline; 3-vinyl-6-hydroxymethylisoquinoline; and the like.

The propellant compositions of this invention can also contain various other conventional compounding ingredients, such as plasticizers, antioxidants, wetting agents, curing agents, metal oxides, reinforcing agents, vulcanization accelerators, and the like. The finished binder usually contains these other compounding ingredients, and the term "binder" as used generically herein is meant to cover the mixture of the rubbery material with these other ingredients.

Suitable plasticizers useful in preparing these propellant grains include TP-90-B (di(3,6-dioxadecyl) formal supplied by Thiokol Corp.); benzophenone and Pentaryl A (monoamylbiphenyl). Suitable silica preparations include a 10-20 micron size range supplied by Davison Chem. Co.; and Hi-Sil 202, a rubber grade material supplied by Columbia-Southern Chem. Corp. A suitable

antioxidant is Flexamine, a physical mixture containing 25 percent of a complex diarylamine-ketone reaction product and 35 percent of N,N'-diphenyl-p-phenylenediamine, supplied by Naugatuck Chem. Corp. A suitable wetting agent is Aerosol OT (dioctyl sodium sulfosuccinate, supplied by American Cyanamid Co.). Satisfactory rubber cure accelerators include Philcure 113 (N,N-dimethyl-tertiary butylsulfenyl dithiocarbamate); Butyl-8 (a dithiocarbamate-type rubber accelerator supplied by R. T. Vanderbilt Co.); and GMF (quinone dioxime, supplied by Naugatuck Chem. Co.). Suitable metal oxides include zinc oxide, magnesium oxide, iron oxide, chromium oxide, or combination of these metal oxides. Reinforcing agents include carbon black, wood flour, lignin, and various reinforcing resins such as styrene-divinylbenzene, methyl acrylate-divinylbenzene, acrylic acid-styrene-divinylbenzene, and methyl acrylate-acrylic acid-divinylbenzene resins. The reinforcing agent is usually used in an amount in the range of 10 to 50 parts by weight per hundred parts by weight of copolymer. The reinforcing agent can be omitted if desired.

Although it is not essential to this invention, various conventional burning rate catalysts can be incorporated into the propellant compositions of this invention, i.e., in addition to the carbon-alkali metal compounds. These conventional burning rate catalysts include ferrocyanides sold under various trade names such as Prussian blue, steel blue, bronze blue, milori blue, Turnbull's blue, Chinese blue, new blue, Antwerp blue, mineral blue, Paris blue, Berlin blue, Erlanger blue, foxglove blue, Hamburg blue, laundry blue, washing blue, Williamson blue, and the like. Other conventional catalysts which can be used are ammonium dichromate and copper chromite.

The following empirical formulas or recipes generally represent the class of propellant compositions preferred for the preparation propellant compositions of this invention:

TABLE I

Ingredient	Parts per 100 parts of rubber	Weight percent
Binder		5-50
Rubbery copolymer (Bd/MVP)	100	
Philblack A (a furnace black)	10-30	
Plasticizer	10-30	
Silica	0-20	
Metal Oxide	0-5	
Antioxidant	0-5	
Wetting Agent	0-2	
Accelerator	0-2	
Sulfur	0-2	
Oxidizer (ammonium nitrate)		50-95
Carbon-alkali metal catalyst		2-20

When preparing the propellant compositions of this invention, the binder ingredients are carbon-alkali metal compound, which is kept under a normally liquid, easily volatilized hydrocarbon to protect it from the air, are added to the rubber and then the oxidant together with any burning rate catalyst which is employed. Mixing is done by any suitable means such as in a sigma-type mixer and the mix is then evacuated to remove the volatile hydrocarbon which was added with the carbon-alkali metal compound. It is convenient to use a solvent mix procedure on account of the pyrophoric nature of the carbon-alkali metal compounds. Such a procedure involves dissolving the rubber in a normally liquid, easily volatilized hydrocarbon, adding the plasticizer and the carbon-alkali metal compound, the latter in said hydrocarbon as hereinbefore stated, and the oxidizer. The materials are blended and the mix then evacuated until the odor of the volatile hydrocarbon can no longer be detected.

In the propellant composition, the rubbery binder forms a matrix or continuous phase in which the solid inorganic oxidizing salt, the carbon-alkali metal burning rate catalyst, and other compounding ingredients, are dispersed as

a discontinuous phase. After preparation of a propellant composition, it can then be formed into grains of suitable size and geometry by compression molding, injection molding, extrusion, or the like. These grains can be restricted by known techniques. The grains of propellant can then be cured according to known techniques so as to form rigid masses, suitable curing temperatures generally being in the range between 70 and 250° F., preferably between 170 and 200° F.

The following examples are set forth for illustrative purposes and it should be understood that the specific ingredients, amounts, conditions of preparation, and the like, set forth therein merely represent preferred embodiments of this invention and should not unduly limit the same.

Example I

A dumbbell type of glass vessel having two compartments prepared from 20 mm. tubing, each approximately 6 inches long, connected with a capillary tube 4 mm. in diameter, was provided. A spherical glass bulb or break seal approximately 1 cm. in diameter, which could withstand evacuation but could be broken easily with a sharp instrument, was attached to one end. A side arm for introduction of graphite was attached to the side of the same compartment. An 8 mm. tube leading to a high vacuum system was connected to the opposite dumbbell compartment.

Thirteen grams of graphite was introduced through the side arm into the dumbbell compartment provided with the break seal. The side arm was then sealed. Potassium (5.27 grams), prepared in a special manner as hereinafter described, was introduced into the other dumbbell compartment.

Potassium was prepared in a manner such that it was protected from air oxidation. It was melted under a helium blanket and drawn into small bore glass tubes. The weight of potassium per unit length of tube could be calculated from the total weight. Short lengths of the tube containing potassium were charged to the dumbbell compartment until the desired amount had been introduced.

The glass vessel, containing graphite in one compartment and potassium in the other, was connected to a high vacuum system and, at the same time, the dumbbell compartment containing the graphite was heated to 350° C. This operation was continued for 6 hours. This process expels oxygen and other volatile impurities from the system.

After sealing off the 8 mm. tubing, the glass vessel was placed in a vertical position with the potassium chamber at the top. The potassium chamber and capillary tube were heated at 350° C. for 16 hours during which time the potassium was melted and transferred to the graphite chamber. The capillary tube connector between the chambers was sealed and the chamber containing the reactants was then heated at 450° C. for 24 hours. The material had a coppery-red color characteristic of C₈K and was pyrophoric.

Two propellant compositions were prepared in accordance with the following formulation:

TABLE II

Ingredient	Parts by Weight	
	Composition 1	Composition 2 ^a
Carbon-alkali metal compound (C ₈ K)	10	0
Graphite	0	10
Ammonium nitrate ^b	80	80
Rubbery binder	10	10

^a Control composition.

^b Average particle size of 200 microns.

The binder composition consisted of 100 parts by weight of a 20-Mooney (ML-4) 90/10 butadiene/2-methyl-5-

vinylpyridine copolymer and 20 parts of the plasticizer, di(3,6-dioxadecyl) formal. (This plasticizer is designated as ZP-211 and, after preparation, is topped to remove low boiling materials.) The rubbery copolymer was prepared by emulsion polymerization at 41° F. A satisfactory recipe is as follows:

TABLE III

Ingredient:	Parts by weight
1,3-butadiene -----	90
2-methyl-5-vinylpyridine -----	10
Water -----	200
Potassium Office Synthetic Rubber Soap ----	6
Potassium chloride -----	0.1
Sodium salt of condensed alkylaryl sulfonic acid -----	0.3
Tetrasodium salt of ethylenediaminetetraacetic acid -----	0.005
Tertiary dodecyl mercaptan -----	0.70
Ferrous sulfate heptahydrate -----	0.2
Potassium pyrophosphate -----	2.253
Para-menthane hydroperoxide -----	0.135
Shortstop—Potassium dimethyl dithiocarbamate -----	0.15
Stabilizer—Phenyl-beta-naphthylamine ----	1.75

The propellant compositions were prepared in a one-pint Baker-Perkins mixer using a solvent mix procedure. The butadiene/2-methyl-5-vinylpyridine copolymer was dissolved in methylcyclohexane at the rate of 8 grams/cc. and charged to the mixer. For the composition containing the C₈K, the C₈K was moistened with methylcyclohexane and approximately 40 cc. of additional methylcyclohexane was used per 10 grams of C₈K. This mixture was charged to the mixer together with the plasticizer. The ammonium nitrate was then added and the materials were blended after which evacuation was started. It was continued until the odor of methylcyclohexane could no longer be detected. A similar procedure was followed for the composition containing the graphite.

Each mix was compression molded at 1000 p.s.i. and the specimens were cured 24 hours at 180° F. Samples ¼" x ¼" x 3" were cut from the cured specimens and burning rate tests were made by the Crawford bomb technique. Results were as follows:

TABLE IV

	Composition 1	Composition 2 ^a
Burning rate at 1,000 p.s.i., in./sec.-----	0.205-----	0.205. (1.65 (at 445- 800 p.s.i.).
Slope of burning rate curve, %-----	0.67 (at 700- 1,000 p.s.i.).	0.96 (at 800- 1,590 p.s.i.).

^a Control.

As shown in Table IV, the propellant composition 1, containing the carbon-alkali metal burning rate catalyst, exhibited a faster burning rate and was less sensitive to pressure than that of the control composition 2.

Example II

The preparation of C₈K was effected in the manner described in Example I except that a high surface area furnace black (236 sq. m./gram) was used instead of graphite. Thirteen grams of carbon black and 5.35 grams of potassium were introduced into the dumbbell-type glass vessel. The carbon black compartment was heated to 200° C. and evacuated for approximately 6 hours. The potassium chamber was heated at 350° C. for 16 hours after which the capillary tube connector was sealed and the reactants, now in the carbon black compartment, were heated at 450° C. for 72 hours. The material had a coppery-red color characteristic of C₈K and was pyrophoric.

Two propellant compositions were prepared in the same manner described in Example I using the same quantities of materials except that furnace black was substituted for graphite. Results of burning rate tests were as follows:

TABLE V

	Composition 1	Composition 2 ^a
Burning rate at 1,000 p.s.i., in./sec.-----	0.153-----	0.090.
Slope of burning rate curve, %-----	0.63 (at 300- 1,600 p.s.i.).	0.82 (at 300- 1,600 p.s.i.).

^a Control.

As shown in Table V, the propellant composition 1, containing the carbon-alkali metal burning rate catalyst, exhibited a faster burning rate and was less sensitive to pressure than that of the control composition.

Various modifications and alterations of this invention will become apparent to those skilled in the art from the foregoing discussion and examples which set forth illustrative and preferred embodiments of this invention which are not to unduly limit the same.

I claim:

1. A solid propellant composition of the composite type consisting essentially of (1) a major amount of a mixture of 50 to 95 weight percent of a solid inorganic oxidizing salt and 5 to 50 weight percent of a rubber binder, the sum of said amounts of said salt and said binder totaling 100 weight percent of said mixture, and (2) a minor but significant amount of a reaction product of carbon and an alkali metal, the amount of said reaction product being sufficient to increase the burning rate of said propellant composition, said reaction product being prepared by contacting vaporized alkali metal and carbon in the absence of oxygen and at elevated temperature in the range between 375° and 500° C.

2. A solid propellant composition of the composite type consisting essentially of (1) a major amount of a mixture of 50 to 95 weight percent of a solid inorganic oxidizing salt selected from the group consisting of ammonium, alkali metal, and alkaline earth metal salts of nitric, perchloric and chloric acids and 5 to 50 weight percent of a rubber binder, the sum of said amounts of said salt and said binder totaling 100 weight percent of said mixture, and (2) a minor amount of a reaction product of carbon and an alkali metal, said reaction product functioning as a burning rate catalyst and being present in an amount sufficient to increase the burning rate of said propellant composition, said reaction product being prepared by contacting vaporized alkali metal and carbon in the absence of oxygen and at elevated temperature in the range between 375° and 500° C.

3. The solid propellant composition of claim 2 wherein said binder comprises a rubbery copolymer of a conjugated diene and a vinyl-substituted heterocyclic nitrogen base compound, and wherein said inorganic oxidizing salt is ammonium nitrate.

4. The solid propellant composition of claim 2 wherein said binder comprises a rubbery copolymer of a conjugated diene and a vinyl-substituted heterocyclic nitrogen base compound, and wherein said inorganic oxidizing salt is ammonium perchlorate.

5. A solid propellant composition of the composite type consisting essentially of (1) a mixture of 50 to 95 weight percent of an inorganic oxidizing salt selected from the group consisting of the ammonium, alkali metal, and alkaline earth metal salts of nitric, perchloric, and chloric acids, and 5 to 50 weight percent of a binder comprising a copolymer of a conjugated diene and a vinyl-substituted heterocyclic nitrogen base compound, the sum of said amounts of said salt and said binder totaling 100 weight percent of said mixture, and (2) from 2 to 20 weight percent based on said propellant composition of

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a reaction product of carbon and an alkali metal, said reaction product functioning as a burning rate catalyst and being prepared by contacting vaporized alkali metal and carbon in the absence of oxygen and at elevated temperature in the range between 375° and 500° C.

6. The propellant composition according to claim 5 wherein said inorganic oxidizing salt is ammonium nitrate, said copolymer is a copolymer of 1,3-butadiene and

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2-methyl-5-vinylpyridine, and said burning rate catalyst is the reaction product of graphite and potassium.

References Cited in the file of this patent

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