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SOLID PROPELLANT AND PROPELLANT BURNING RATE CATALYST SYSTEM

George D. Sammons, Bartlesville, Okla., assignor to Phillips Petroleum Company, a corporation of Delaware

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This invention relates to a burning rate catalyst system for solid propellants. In one aspect, this invention relates to an improved propellant having an increased burning rate. In another aspect, this invention relates to an improved method of developing thrust by employing solid propellants of increased burning rate having an improved burning rate catalyst system incorporated therein.

Solid propellants can be classified with respect to composition as double base type, single base type, and composite type. An example of a double base propellant is "ballistite" which comprises essentially nitroglycerine and nitrocellulose. Examples of single base propellants are nitrocellulose and trinitrotoluene. Composite type propellants are generally composed of an oxidizer, and a binder or fuel. They may contain other materials to improve fabrication or increase ballistic performance such as a burning rate catalyst.

Rocket propellants have achieved considerable commercial importance as well as military importance. Jet propulsion motors of the type in which the propellants of this invention are applicable can be employed to aid a heavily loaded plane in take off. Said motors can also be employed as an auxiliary to the conventional power plant when an extra surge of power is required. Said motors can also be employed to propel projectiles and land vehicles. Said propellants can also be used for uses other than propulsion. For example they can be used as gas generators in starting devices, power units where a fluid is employed as a motive force, and other applications where a comparatively large volume of gas is required in a relatively short period of time.

Solid propellants having relatively slow burning rates are entirely satisfactory for use in "JATO" units, i.e., rocket units employed as jet assist take off units which aid in powering loaded aircraft during take off. However, many of said propellants having relatively slow burning rates are not entirely satisfactory for use where a propellant having a relatively high burning rate is required so that maximum thrust can be developed in minimum time as in booster rocket applications, or in said gas generator systems.

I have discovered that a burning rate catalyst system comprising essentially ammonium dichromate, powdered copper metal or a selected copper compound, and a salt of a trinitrophenolic compound is effective in increasing the burning rate of solid propellants having relatively slow burning rates to the extent that said propellants can be used where propellants having high burning rates are required. The burning rate of propellants containing the three component burning rate catalyst system of my invention is considerably higher than the burning rate of propellants containing any one or any pair of the components of my catalyst system.

An object of this invention is to provide an improved burning rate catalyst system. Another object of this invention is to provide a burning rate catalyst system com-

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prising essentially ammonium dichromate, powdered copper metal or a selected copper compound, and a salt of a trinitrophenolic compound. Another object of this invention is to provide an improved propellant composition comprising a binder component, an oxidizer component, and said burning rate catalyst system. Another object of this invention is to provide an improved gas generation system. Still another object of this invention is to provide an improved method of developing thrust which comprises burning said improved propellant in the combustion chamber of a rocket motor. Other aspects, objects and advantages of the invention will be apparent to those skilled in the art in view of this disclosure.

Thus according to the invention, there is provided a burning rate catalyst system comprising essentially ammonium dichromate, a copper component selected from the group consisting of finely divided copper metal, copper chromite, and copper oxide, and a salt of trinitrophenolic compound selected from the group consisting of 2,4,6-trinitrophenol and 2,4,6-trinitroresorcinol.

Further according to the invention, there is provided an improved solid propellant comprising a binder component, an oxidizer component, and the above described burning rate catalyst system.

Still further according to the invention, there is provided an improved method of developing thrust which comprises burning the improved propellant of the invention in a combustion chamber of a rocket motor.

The amount of the ammonium dichromate component of my catalyst system can vary in the range between 3 and 10 parts by weight based on the total catalyst system. Said ammonium dichromate should be ground as finely as possible, preferably less than 15 microns in size.

The copper component of my catalyst system can be powdered copper metal, copper chromite, or a copper oxide, either cuprous or cupric oxide. Cuprous oxide is presently preferred over cupric oxide. Copper chromite is the presently most preferred copper component. The amount of the copper component of my catalyst system can vary in the range between 0.5 and 7 parts by weight based on the total catalyst system. Said copper component should be ground as fine as possible, preferably to a size of less than 15 microns.

The trinitrophenolic salt component of my catalyst system can be any salt of 2,4,6-trinitrophenol (picric acid), or any salt of 2,4,6-trinitroresorcinol (styphnic acid). The amount of trinitrophenolic salt employed in my catalyst system should be at least 2 parts by weight based on the total catalyst system. It is preferred to use not more than 20 parts by weight of the total catalyst system. The particle size of said trinitrophenolic salt is preferably maintained within the range of 10-300 mesh.

The trinitrophenolic salt component also functions as a plasticizer for the propellant compositions of the invention. I have found that the trinitrophenolic salt component plasticizes or softens the propellant composition sufficiently to allow as much as 87 parts of ammonium nitrate per 100 parts of base propellant to be used. This is obviously advantageous because it permits manufacture of extrudable propellants of higher oxidizer content than has been possible heretofore.

Examples of salts of said trinitrophenolic compounds which can be used in my burning rate catalyst system include, among others, the following compounds: sodium styphnate (disodium salt of 2,4,6-trinitroresorcinol), potassium picrate, urea picrate, lead styphnate, calcium picrate, pyridinium styphnate, ammonium styphnate, lithium picrate, silver styphnate, chromium picrate, ammonium picrate, sodium picrate, copper picrate, zinc picrate, cadmium picrate, nickel picrate, aluminum pic-

rate, ferric picrate, tetraethyl ammonium picrate, N-methyl pyridinium picrate, guanidinium styphnate, potassium styphnate, calcium styphnate, guanylurea styphnate, isopropylamine, styphnate, n-heptylamine picrate, barium styphnate, strontium picrate, rubidium styphnate, magnesium styphnate, cesium picrate, and beryllium picrate.

When my burning rate catalyst system is employed in propellant compositions, it is customary to express the amount of catalyst present in the propellant in parts by weight per 100 parts by weight of base propellant. Thus, in propellant compositions when it is desired to express the amount of the components of my catalyst burning rate system based on the base propellant, the same ranges as given above can be employed. Herein base propellant is defined as binder plus oxidizer.

Oxidizers which are applicable in the solid propellant compositions of this invention are those oxygen-containing solids which readily give up oxygen and include, for example, 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 oxidizers for use in the solid propellants of this invention. Other specific oxidizers include sodium nitrate, potassium perchlorate, lithium chlorate, calcium nitrate, barium perchlorate, and strontium chlorate. Mixtures of oxidizers are also applicable. In the preparation of the solid rocket propellant compositions, the oxidizers are ground to a particle size, preferably within the range between 20 and 200 microns average particle size. The most preferred particle size is from 40-60 microns. The amount of solid oxidizer used is usually a major amount of the total composition and is generally in the range between 50 and 85 percent by weight of the total propellant composition. If desired, however, the oxidizer can comprise less than 50 percent by weight of the propellant composition, in some instances. In the case of compression molded propellants, the propellant can contain 90 percent by weight and above of oxidizer based on total composition. Thus, the oxidizer content of the propellant composition usually ranges from 50 to 90 percent by weight.

A class of binder components widely used in solid propellant compositions and which form a presently preferred class of binders for use according to the invention comprises a rubbery copolymer of a conjugated diene and a heterocyclic nitrogen base. These copolymers are prepared by polymerizing a conjugated diene containing from 4 to 8 carbon atoms per molecule such as butadiene, isoprene, piperylene, methylpentadiene, chloroprene, and the like, with a monomer copolymerizable therewith. Preferred copolymerizable monomers are the polymerizable heterocyclic nitrogen compounds such as the vinyl pyridines, vinylquinolines, and the various alkyl-substituted derivatives of these compounds such as 2-methyl-5-vinylpyridine, 2-vinylpyridine, 2-vinyl-5-ethylpyridine, 2-vinylquinoline, and the like. These copolymers can be prepared by any suitable method, as for example, mass or emulsion polymerization. It is often desirable to incorporate carbon black in the copolymer during its preparation, this addition being accomplished by conventional methods, as for example, adding the carbon black to the latex prior to coagulation. The amount of carbon black can be from 0 to 35 parts of black per 100 parts of copolymer. In the preparation of the copolymers, the amount of the conjugated diene will be at least 50 parts by weight per 100 parts of the monomer mixture, while the comonomer will be in the range of 5 to 50 parts. Although, polymerizable heterocyclic nitrogen bases are the preferred comonomers, other comonomers such as styrene are applicable. Further details regarding the preparation of these copolymers can be found in the copending applications Serial No. 284,447, filed April 25, 1952 by W. B. Reynolds et al.; Serial No. 475,000 filed December 13, 1954 by H. G. Cutforth et al.; and Serial No. 470,371, filed November 22, 1954 by R. S.

Hamner et al., wherein propellant compositions and methods of preparation of said propellant and binder components are disclosed and claimed.

The finished binder usually contains various compounding ingredients. Thus, it will be understood that herein and in the claims, unless otherwise specified the term "binder" is employed generically and includes various conventional compounding ingredients. The binder content of the propellant composition will usually range from 10 to 50 percent by weight.

Any of the above described binders can be employed in the practice of my invention. In addition, many plastic, resinous, and other rubbery materials are suitable binder materials for the propellants of my invention. Thus, the invention is not to be limited to any particular binder. Examples of other suitable binders can be grouped as follows: asphalt and pitches including natural asphalts having a 170° F. softening point, air blown asphalts having a 270° F. softening point, mixtures of asphalt and synthetic or natural rubber, pitch having a 240° F. softening point, and mixtures of pitch and rubber; epoxy resins, such as Araldite 502 and Epon 834; liquid polymers such as polybutadiene, polybutene, polyisobutylene, and Thiokol LP-3; polyethylenes; rubbers, both natural and synthetic, such as butyl rubber, ethyl acrylatemethylvinylpyridine copolymers, polybutadiene, and hydrogenated polybutadiene; waxes, both natural and synthetic having a melting point within the range of 150-300° F.; synthetic resins and plastics such as the various acrylic and polyvinyl resins; and nitro polymers such as polynitromethylmethacrylate, nitropolybutadiene and polynitrovinyl alcohols.

The amount of the three-component burning rate catalyst which can be employed in the propellant compositions of this invention can vary widely. The amount of ammonium dichromate can vary in the range between 3 and 10 parts by weight per 100 parts by weight of base propellant, while the copper or copper salt component can vary within the range of 0.5 to 7 on the same basis. The total parts by weight of the said two components per 100 parts by weight of propellant should not exceed 12. The amount of trinitrophenolic salt present should be at least 1.5 parts by weight per 100 parts by weight of base propellant and it is preferred to use not more than 20 parts on the same basis.

A preferred method of formulating the propellant compositions of this invention is to dry-blend the ammonium dichromate and the copper powder of selected copper compound with the oxidizer, incorporate this oxidizer-copper or copper-compound ammonium dichromate mixture into the binder, and thereafter incorporate the trinitrophenolic salt into the resulting mixture. This method is preferred because it assures complete dispersion of the ammonium dichromate and copper or copper compound, and eliminates the possibility of comminuting the trinitrophenolic salt to too fine a particle size. However, if desired, the three components of the catalyst system can be pre-blended with each other and then blended with the oxidizer. Any desirable manner, or order, of incorporating the three components of the catalyst system into the propellant can be employed.

The propellant compositions can be formulated by milling the oxidant, burning rate catalyst, and other compounding ingredients into the binder on a roll mill or in some other suitable type of mixer, as for example, a blade-type mixer. It is sometimes advantageous to mill in the carbon black or other filler at this point rather than to add the carbon black to the latex prior to coagulation. Copolymers having a Mooney value (ML-4) in the range between 15 and 30 are preferred, as it is difficult to incorporate the oxidant, etc., into higher Mooney polymers. Other compounding agents such as vulcanization agents, quaternization agents, vulcanization accelerators, softeners, stabilizers such as antioxidants, surface active agents, etc., can be advantageously added during the milling process.

After formulating the propellant composition, the propellant can be extruded or compression molded into any desired geometric configuration. The three-component burning rate catalyst of this invention is especially useful in propellants which are to be extruded into propellant grains. The extruded grains can then be cured by heating to an elevated temperature for an extended period of time, as for example, 24 hours at 180° F.

A further advantage of the propellants of this invention is that these propellants can be cured without using the usual vulcanization agents, e.g. sulfur and a vulcanization accelerator, or quaternizing agents in the case of binders containing trivalent nitrogen atoms.

A still further advantage of the three-component burning rate catalyst of this invention is that the effective exhaust velocity of rocket motors employing the propellants of this invention is not reduced as would be expected when the percentage of oxidizer in the total propellant mixture is decreased.

The following examples will serve to further illustrate the invention.

EXAMPLE I

Propellants containing various combinations of the three-component burning rate catalyst of the invention were prepared and compared with propellants containing conventional catalysts.

A 1,3-butadiene-2-methyl-5-vinylpyridine rubbery copolymer was prepared by emulsion polymerization at 41° F. according to the following polymerization recipe.

POLYMERIZATION RECIPE

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	0.005

Two and one-half parts by weight per 100 parts of rubber of additional low-abrasion furnace carbon black and 1.25 parts by weight on the same basis of a physical mixture containing 65% of a complex diarylamine-ketone reaction product and 35% of N,N'-diphenyl-p-phenylenediamine were milled into the binder component prepared above. This increased the amount of carbon black present to 22 parts/100 parts of rubber and increased the amount of stabilizer present to 3 parts/100 parts of rubber.

The above described composition was then placed in a roll mill, and 20 parts/100 parts of rubber present of di(3,6-dioxadecyl) formal and 5 parts (on the same basis) of magnesium oxide were milled into the binder. Commercial grade ammonium nitrate, ground to 40 micron average particle size, was then dry-blended with all of the burning rate catalyst system components except the trinitrophenolic salt. This blend was then milled into the binder until a propellant composition containing 83.5 parts by weight ammonium nitrate was obtained. Said propellant composition contains 16.5 parts by weight of rubber binder, which binder comprised rubbery copolymer, substituted formal (plasticizer), carbon black, magnesium oxide, and antioxidant.

The desired amount of trinitrophenolic salt was then milled into the said propellant composition. After the trinitrophenolic salt was intimately dispersed, the propellant composition was extruded into strands approximately $\frac{3}{16}$ " in diameter. The strands were then cured at 180° F. for 24 hours. Said strands were then cut into sections approximately 7" long, and all surfaces, except one end, were restricted to prevent burning except on said end. The strands were then placed in a pressure bomb, and the bomb was pressured to the desired pressure with nitrogen. The bomb was then placed in a temperature bath maintained at 70° F. The strands were then ignited, and the time required for the propellant to burn between two fusible wires spaced 5" apart was recorded. The burning rate was then calculated in inches per second. The results obtained with various burning rate catalysts are given below in Table I.

Table I

Run No.	Burning Rate Catalyst Components (Parts/100 Parts of Base Propellant)								Burning Rate (in./sec.)	
	Milori Blue ¹	Ammonium Dichromate	Copper Chromite	Disodium Styphnate	Copper Oxide	Copper Powder	Urea Picrate	Dipotassium Styphnate	At 600 P.s.i.	At 1,000 P.s.i.
1	2								0.144	0.210
2	2	4							0.222	0.280
3	2			4					0.172	0.221
4			4						0.124	0.182
5		4							0.186	0.246
6		4	4						0.291	0.371
7		4	4						0.277	0.322
8		2	4	4					0.204	0.280
9		4	2	4					0.257	0.338
10		4	8	4					0.267	0.353
11		4	4	2					0.225	0.295
12		4		4	4				0.236	0.307
13		4		4		4			0.240	0.295
14		4					6		0.284	0.352
15		4	4					4	0.281	0.352

¹ Milori Blue is a burning rate catalyst which is widely used in propellants. Said Milori Blue is a pigment similar to Prussian Blue but having a red tint and is prepared by the oxidation of a paste of potassium ferrocyanide and ferrous sulfate.

Tertiary dodecyl mercaptan (modifier)	----	*
Ferrous sulfate heptahydrate	-----	0.2
Potassium pyrophosphate	-----	0.253
Para-menthane hydroperoxide	-----	0.135
Shortstop—potassium dimethyldithiocarbamate	-----	0.15
Stabilizer—phenyl-β-naphthylamine	-----	1.75

* Fifty-five runs were made using the above polymerization recipe. The latex was masterbatched with 19.5 parts of Philblack A (a trademark of Phillips Petroleum Company for a low abrasion furnace carbon black) per 100 parts of rubber. The black masterbatch was then acid coagulated, washed with water, and dried. The average conversion for these 55 runs was 85% in 17.0 hours. The amount of modifier used in each run was in the range of 0.60 to 0.80 part by weight.

The above Table I shows the increase in the burning rate which results when the three-component burning rate catalyst systems of this invention are employed. In the above table, Runs 1 through 5 are control runs, while the remainder of the runs, with the exception of Run 8, represent the catalyst systems of the invention. Run 8 was a run in which the amount of ammonium dichromate was below the operating range, and it is easily seen that this smaller amount of ammonium dichromate affected the burning rate adversely.

Runs 1 and 2 in the above Table I represent catalyst systems of the prior art. For many uses these catalysts are regarded by those skilled in the art as superior

catalysts. They give satisfactory or more than satisfactory results, particularly in those instances where moderate burning rates are desired. However, in some instances, such as in booster rockets, exceptionally high burning rates are desired. A comparison of Runs 6, and 9 through 15 (and the data given in Examples IV and V hereinafter) with control Runs 1 to 5 shows the great number of superior catalyst systems afforded by my invention for use when exceptionally high burning rates are desired.

EXAMPLE II

Several of the propellant compositions formulated in Example I were compression molded into propellant grains. These grains were fired in a rocket motor, and the characteristic exhaust velocity was measured. These tests were run to determine if the decrease of ammonium nitrate content in the propellants of this invention would decrease the characteristic exhaust velocity below the velocity normally developed by the conventional binder-oxidizer propellants. A control run (propellant from Run 2 in Table I) using the same binder, but with Milori Blue present as a catalyst was made. The control run, since less catalyst/100 parts of base propellant was used, contained more oxidizer per given amount of finished propellant. The results of these tests are given below in Table II.

Propellant from:	Characteristics exhaust velocity feed/second
Run 2 -----	4000
Run 5 -----	3966*
Additional run having identical composition to Run 6 -----	4009

* Estimated from other firing data.

The above example shows that the decrease in percentage of oxidizer in the finished propellants of this invention, due to increasing the amount of catalyst, does not lower the characteristic exhaust velocity.

EXAMPLE III

A propellant containing 16.5 weight percent of the compounded binder of Example I and 83.5 weight percent of commercial ammonium nitrate which had been ground to 40 micron average particle size was placed in a Baker-Perkins mixer. Four parts/100 parts of pro-

pellant of ammonium dichromate, 4 parts on the same basis of copper chromite, and 4 parts on the same basis of disodium styphnate were then mixed into the propellant. A ribbon of this propellant was then extruded, and this ribbon was placed in an oven maintained at 180° F. for 24 hours. The ribbon was then evaluated for cure by standard tests. The results of these tests are given below in Table III.

It was observed that the ribbon before oven treatment was soft and plastic, while after oven treatment, it was firm and rigid, an evidence of cure. Properties of this cured material are shown below in Table III.

Table III

Property:	Results
Tensile strength -----	p.s.i. 245.7
Elongation -----	percent. 7.3
Modulus (300%) -----	p.s.i. 4422

EXAMPLE IV

Another series of propellants containing various three component burning rate catalyst systems of the invention containing various components were prepared as described in Example I and the burning rates were determined as described in Example I. The burning rates of these additional propellants are given below in Table IV.

Table IV

Run No.	Ammonium Dichromate	Copper Chromate	Binder Used ¹	Trinitrophenol Salt	Parts Trinitrophenol Salt	Burning Rate (inches/sec.)	
						at 600 p.s.i.	at 1,000 p.s.i.
16-----	4.0	4.0	A	Urea styphnate-----	4.0	0.203	0.271
17-----	4.0	4.0	B	Urea picrate-----	8.0	0.303	0.347
18-----	4.0	4.0	A	do-----	6.0	0.225	0.306
19-----	4.0	4.0	A	Potassium styphnate-----	4.0	0.225	0.295
20-----	4.0	4.0	A	Diprylamine-----	6.0	0.362	0.460
21-----	4.0	4.0	C	Sodium picrate-----	10.0	0.326	0.391
				do-----	10.0	0.326	0.391

¹ The following binder formulations were used in the propellant compositions of Table IV:

Compositions (Parts by Weight)	A	B	C
90/10 Bd/MVP copolymer-----	100	100	100
Phlblack "A"-----	22	22	22
Di(3,6-dioxadecyl)formal-----	20	20	30
MgO-----	5	5	None
Antioxidant*-----	3	3	3
Nitrocyclohexane-----	None	10	None

* 1.75 parts of phenyl-β-naphthylamine were put in at the time the rubber was made, and 1.25 additional parts of a physical mixture containing 65% of a complex diarylamine-ketone reaction product and 35% of N,N'-diphenyl-p-phenylenediamine were milled in before the oxidant was milled in.

Table II

Propellant from:	Characteristics exhaust velocity feed/second
Run 2 -----	4000
Run 5 -----	3966*
Additional run having identical composition to Run 6 -----	4009

* Estimated from other firing data.

The above example shows that the decrease in percentage of oxidizer in the finished propellants of this invention, due to increasing the amount of catalyst, does not lower the characteristic exhaust velocity.

EXAMPLE III

A propellant containing 16.5 weight percent of the compounded binder of Example I and 83.5 weight percent of commercial ammonium nitrate which had been ground to 40 micron average particle size was placed in a Baker-Perkins mixer. Four parts/100 parts of pro-

In the runs listed in Table IV, the same Bd/MVP copolymer described in Example I was used. In Runs 16-20, the ratio of binder component to oxidizer component in parts by weight was 16.5 to 83.5. In Run 21, said ratio was 15 to 85. The increased amount of oxidizer component used in Run 21 illustrated the previously described plasticization advantage realized when the trinitrophenolic salt of the burning rate catalyst system is used.

EXAMPLE V

An amount of the butadiene-2-methyl-5-vinylpyridine copolymer of Example I, containing 22 parts of low-abrasion furnace carbon black per 100 parts rubber and 3 parts per 100 parts of rubber of a physical mixture containing 65% by weight of a complex diarylamine-ketone reaction product and 35% by weight of N,N'-diphenyl-p-phenylenediamine, was placed in a roll mill, and 20 parts per 100 parts of rubber of di-(3,6-dioxadecyl)formal and 5 parts per 100 parts of rubber of magnesium oxide were milled into the rubber.

Five propellants were made in which the binder, prepared as described above was used. These propellants were made up according to the following recipes.

RECIPES

	Composition in Parts by Weight—Propellant Number				
	1	2	3	4	5
Binder.....	16.5	16.5	16.5	16.5	16.5
Oxidant (NH ₄ NO ₃ —Avg. particle size—40 microns).....	83.5	83.5	83.5	83.5	83.5
Ammonium Dichromate (particle size—approx. 15 microns).....	0	4.0	0	0	4.0
Copper Chromite (particle size—approx. 3-4 microns).....	0	0	4.0	0	4.0
Sodium Picrate (particle size—approx. 65-100 mesh).....	0	0	0	10.0	10.0

In propellant #1, the proper amount of oxidant was milled into the binder by adding the oxidant in portions to the binder while the mill was running. The total milling time was 3.5 minutes. Propellants 2 and 3 were made by dry blending the proper amount of ammonium dichromate (#2) or copper chromite (#3) with the oxidant and then adding the blend portionwise to the binder on the mill. Total milling time was the same as for propellant #1. Propellant #4 was prepared by milling oxidant into the binder as in #1 (3.5 minutes mill time) and thereafter milling in the sodium picrate with the minimum amount of milling to insure intimate dispersion. Propellant #5 was made by dry blending the ammonium dichromate and copper chromite with ammonium nitrate and thereafter milling this blend into the binder (mill time 3.5 minutes). The sodium picrate was then milled into the resulting material as in propellant #4.

The propellants, prepared as described, were then extruded into strands approximately $\frac{3}{16}$ " in diameter. The strands were then cured at 200° F. for 24 hours. The cured strands were then cut into sections approximately 7" long, and all surfaces, except one end, were restricted to prevent burning except on said end. The strands were then burned in a bomb as described in Example I to determine their burning rate.

The results of these burning rate tests are given below in Table V.

Table V

Propellant Number	Burning Rate at 600 p.s.i. (inches/sec.)	Increase in Rate (ΔR) Over Control Propellant (#1)	Burning Rate at 1000 p.s.i. (inches/sec.)	Increase in Rate (ΔR) Over Control Propellant (#1)
1 (control).....	0.069	-----	0.107	-----
2.....	0.192	0.123	0.252	0.145
3.....	0.124	0.055	0.192	0.075
4.....	0.125	0.056	0.169	0.092
5.....	0.350	0.281	0.442	0.335

It can be seen by examining the above burning rate data that the three-component catalyst system of the present invention produces an unexpectedly high burning rate. This can be seen if the rate increases ($\Delta R'$) for propellants 2, 3, and 4 are summed up and compared to ΔR for propellant 5. At 600 p.s.i., the sum of the ΔR 's for 2, 3, and 4 is 0.234, while the ΔR for #5 is 0.281. This represents an unexpected increase of 20.1%. Similarly, at 1000 p.s.i., an unexpected increase of 18.8% is obtained.

EXAMPLE VI

An amount of the binder of Example I, containing 100 parts by weight of the butadiene-vinylpyridine rubber of Example I, 22 parts by weight per 100 parts of rubber of low-abrasion furnace carbon black, 3 parts by weight per 100 parts of rubber of a physical mixture containing 65% by weight of a complex diarylamine-ketone

reaction product and 35% by weight of N,N'-diphenyl-p-phenylenediamine, 20 parts by weight per 100 parts of rubber of di-(3,6-dioxadecyl)formal and 5 parts by weight per 100 parts of rubber of magnesium oxide was placed in a 0.7 gallon Baker-Perkins mixer. An amount of ammonium nitrate, having an average particle size of 40 microns, was then milled into the binder (nitrate added in increments) until a composition containing 16.5 weight percent binder and 83.5 weight percent ammonium nitrate was reached. This material, labeled base propellant, was then removed from the mixer and split into five portions. The first portion was placed in a roll mill and milled for 3 minutes without adding any other components. This portion, base propellant, was labeled Run 1. The second portion, labeled Run 2, was placed in a roll mill and the desired amount of ammonium dichromate was milled in, using a milling time of 3 minutes. Run 3 was carried out in the same manner as Run 2, copper chromite being the added component instead of ammonium dichromate. The fourth portion, labeled Run 4, was placed in a roll mill and milled for 3 minutes, after which the desired amount of sodium picrate was milled in, using a milling time of the shortest possible duration to insure intimate dispersion (approximately 20 seconds). The fifth portion (Run 5) was placed in a roll mill and the proper amounts of copper chromite and ammonium dichromate were milled into the base propellant using a total milling time of 3 minutes. The proper amount of sodium picrate was then milled into the mixture, using the very short mill time (20 seconds) as was used in Run 4.

The above-described propellants were then extruded into strands, cured, restricted, and burned in a bomb as described in Example V. The compositions and results of the burning rate tests are given below in Table VI.

Table VI

Component ¹	Composition in Parts by Weight—Propellant Number				
	1	2	3	4	5
Binder.....	16.5	16.5	16.5	16.5	16.5
Oxidant (NH ₄ NO ₃).....	83.5	83.5	83.5	83.5	83.5
Ammonium Dichromate.....	0	4	0	0	4
Copper Chromite.....	0	0	4	0	4
Sodium Picrate.....	0	0	0	10	10

¹ NH₄NO₃—particle size approx. 40 microns. Ammonium dichromate—particle size approx. 15 microns. Copper chromite—particle size approx. 3-4 microns. Sodium picrate—particle size approx. 65-100 mesh.

Propellant No.	Burning Rate Data (inches/sec.)	
	at 600 p.s.i.	Increase over Base Propellant (ΔR)
1 (control).....	0.074	-----
2.....	0.179	0.105
3.....	0.132	0.058
4.....	0.133	0.057
5.....	0.321	0.247

It can be seen from the above data that the 3-component burning rate catalyst system of the present invention produces an unexpectedly fast burning rate. Summing the ΔR 's (as in Example V) for propellants 2, 3, and 4, the additive increase at 600 p.s.i. over the control propellant is 0.220. The ΔR for propellant 5 over the control propellant is 0.247, an unexpected increase of 12.3 percent.

The two examples, Examples V and VI, clearly demonstrate the synergism of the catalyst system of the present invention. Example V represents a preferred method of incorporating the catalyst system of the present in-

vention into a propellant material. Example VI, which illustrates a less preferred method of incorporating the catalyst system into a propellant, likewise illustrates the synergistic properties of the catalyst system of this invention.

As will be evident to those skilled in the art various modifications of the invention can be made, or followed, in the light of the above disclosure without departing from the spirit or scope of said invention.

I claim:

1. A propellant burning rate catalyst system consisting essentially of, in parts by weight based on said system: from 3 to 10 parts of ammonium dichromate; from 0.5 to 7 parts of a copper component selected from the group consisting of finely divided copper metal, copper chromite, and copper oxides; and from 2 to 20 parts of a salt of the trinitrophenolic compounds selected from the group consisting of 2,4,6-trinitrophenol and 2,4,6-trinitroresorcinol.

2. A propellant burning rate catalyst system according to claim 1 wherein said salt is sodium picrate.

3. A propellant burning rate catalyst system according to claim 1 wherein said salt is sodium styphnate.

4. A propellant burning rate catalyst system according to claim 1 wherein said salt is urea picrate.

5. A propellant burning rate catalyst system according to claim 1 wherein said salt is urea styphnate.

6. A propellant burning rate catalyst system according to claim 1 wherein said salt is potassium styphnate.

7. A propellant burning rate catalyst system according to claim 2 wherein said copper component is copper chromite.

8. A propellant burning rate catalyst system according to claim 3 wherein said copper component is copper chromite.

9. A propellant burning rate catalyst system according to claim 4 wherein said copper component is copper chromite.

10. A propellant burning rate catalyst system according to claim 5 wherein said copper component is copper chromite.

11. A propellant burning rate catalyst system according to claim 6 wherein said copper component is copper chromite.

12. A propellant burning rate catalyst system consisting essentially of in parts by weight, equal parts of: ammonium dichromate; copper chromite; and sodium styphnate.

13. An improved solid composite type propellant composition comprising: as a base propellant, a solid inorganic oxidizing salt as an oxidizer component and a suitable binder component; and a burning rate catalyst system consisting essentially of from 3 to 10 parts by weight per 100 parts by weight of said base propellant of ammonium dichromate, from 0.5 to 7 parts by weight per 100 parts by weight of said base propellant of a copper component selected from the group consisting of finely divided copper metal, copper chromite, and copper oxides, and from 2 to 20 parts by weight per 100 parts by weight of said base propellant of a salt of a trinitrophenolic compound selected from the group consisting of 2,4,6-trinitrophenol and 2,4,6-trinitroresorcinol.

14. An improved solid propellant composition according to claim 13 wherein: said ammonium dichromate is

present in an amount of 4 parts by weight per 100 parts by weight of said base propellant; said copper component is copper chromite and is present in an amount of 4 parts by weight per 100 parts by weight of said base propellant; and said salt of a trinitrophenolic compound is sodium styphnate and is present in an amount of 4 parts by weight per 100 parts by weight of said base propellant.

15. An improved solid propellant according to claim 13 wherein said salt is sodium picrate.

16. An improved solid propellant according to claim 13 wherein said salt is sodium styphnate.

17. An improved solid propellant according to claim 13 wherein said salt is urea picrate.

18. An improved solid propellant according to claim 13 wherein said salt is urea styphnate.

19. An improved solid propellant according to claim 13 wherein said salt is potassium styphnate.

20. An improved solid propellant according to claim 15 wherein said copper component is copper chromite.

21. An improved solid propellant according to claim 16 wherein said copper component is copper chromite.

22. An improved solid propellant according to claim 17 wherein said copper component is copper chromite.

23. An improved solid propellant according to claim 18 wherein said copper component is copper chromite.

24. An improved solid propellant according to claim 19 wherein said copper component is copper chromite.

25. In the method of developing thrust wherein a solid propellant charge contained in a combustion chamber of a rocket motor is ignited and then burned with the evolution of combustion gases which are exhausted from said combustion chamber, the step which comprises burning in said combustion chamber a propellant charge comprising: as a base propellant, a solid inorganic oxidizing salt as an oxidizer component and a suitable binder component; and a burning rate catalyst system consisting essentially of from 3 to 10 parts by weight per 100 parts by weight of said base propellant of ammonium dichromate, from 0.5 to 7 parts by weight per 100 parts by weight of said base propellant of a copper component selected from the group consisting of finely divided copper metal, copper chromite, and copper oxides, and from 2 to 20 parts by weight per 100 parts by weight of said base propellant of a salt of a trinitrophenolic compound selected from the group consisting of 2,4,6-trinitrophenol and 2,4,6-trinitroresorcinol.

26. A propellant burning rate catalyst system consisting essentially of equal parts by weight of: ammonium dichromate; a copper component selected from the group consisting of finely divided copper metal, copper chromite, and copper oxides; and a salt of a trinitrophenolic compound selected from the group consisting of 2,4,6-trinitrophenol and 2,4,6-trinitroresorcinol.

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