United States Patent Office

3,666,575

Patented May 30, 1972

3,666,575

SOLID PROPELLANT COMPOSITION WITH BURNING RATE CATALYST

Harold M. Fisher, Charlotte, N.C., assignor to the United States of America as represented by the Secretary of the Army

No Drawing. Filed Mar. 10, 1970, Ser. No. 18,321

Int. Cl. C06d 5/06

U.S. Cl. 149—19 8 Claims

ABSTRACT OF THE DISCLOSURE

Free radicals that catalyze the burning rate of propellants. Specifically, the free radical compound, 2,2-diphenylpicrylhydrazyl, increases the burning rate of propellant compositions comprised of the specified free radical compound and other major propellant ingredients consisting of the inorganic oxidizer ammonium perchlorate, polybutadiene binder, optional catalysts (e.g., n-butyl ferrocene or Fe_2O_3), and aluminum metal powder. Processing aids (e.g., lecithin) and curatives may be used in minor amounts in the basic formulation or as an additive to the propellant composition.

BACKGROUND OF THE INVENTION

Much effort has been expended in the area of catalysis and means for promoting burning rates of propellants. Increased burning rates permit the expulsion of a larger amount of energy over a shorter period of time to thereby result in a higher impulse or force to perform a desired function by propulsion means. In many instances the use of a relatively small amount of a catalyst material (e.g., 1–2% by weight) enables one to change a slower burning propellant into a faster burning propellant. Catalyst materials of the prior art include iron oxide, copper, copper chromite, the organoiron compound, ferrocene, and other organometallic compounds. More recently carborane and carborane derivatives have been employed as catalyst materials for propellants.

The present invention deals with a new class of compound and its use as a catalyst material. The new class of compound is classified as a free radical and is non-metallic.

An object of this invention is to employ a free radical material which is a non-metallic material yet a burning rate promoter for solid propellants.

Another object is to provide solid propellant formulations which utilize a free radical material to enhance the propellant burning rate when the free radical is used alone or with other catalyst materials in combination with the major propellant ingredients consisting of the inorganic oxidizer ammonium perchlorate, a polybutadiene binder, and aluminum metal powder.

SUMMARY OF THE INVENTION

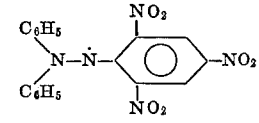
When 2,2-diphenylpicrylhydrazyl is used in a propellant formulation containing ammonium perchlorate, polybutadiene binder, lecithin (processing aid), and aluminum metal powder, the propellant burns at a higher rate as compared to a standard propellant formulation containing all the specified constituents except the free radical, 2,2-diphenylpicrylhydrazyl. The burning rates of a propellant containing other burning rate catalysts (e.g., n-butyl ferrocene or F_2O_3) are also increased when 2,2-diphenylpicrylhydrazyl is used as an additional ingredient.

The amount of the free radical compound, 2,2-diphenylpicrylhydrazyl, may be varied from about 0.5 percent by weight to about 5 percent by weight of the propellant composition.

The burning rate of the propellant increases with increased 2,2-diphenylpicrylhydrazyl content. The amount of the free radical compound may be optimized to achieve a desired burning rate either alone with other propellant ingredients or in combination with other specified burning rate catalysts and other propellant ingredients.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The free radical, 2,2-diphenylpicrylhydrazyl, is used alone or in combination with other catalysts to increase the burning rate of propellants. The free radical, 2,2-diphenylpicrylhydrazyl, is illustrated by the following structural formula:



Propellant formulations are set forth below under Examples I, II, III, IV, and V to illustrate the use of 2,2-diphenylpicrylhydrazyl as a burning rate catalyst. Under Example I, below, control propellant A contains no catalyst; novel propellant A contains 2,2-diphenylpicrylhydrazyl as catalyst.

EXAMPLE I

	Control propellant A	Nove propellant A
Ingredients, percent by weight:		
Carboxy terminated polybutadiene	24.7	21.7
Lecithin	0.3	0.3
Aluminum metal powder	11.6	11.6
Ammonium perchlorate (17μ)	19.0	19.0
Ammonium perchlorate (200μ)	44.4	44.4
2,2-diphenylpicrylhydrazyl		3.0
Totals	100.0	100.0
(Burning rate in./sec. at 500 p.s.i.g.)	.191	.230
(Burning rate in./sec. at 1000 p.s.i.g.)	.283	.312

As evidenced by the above burning rates an average of about 15 percent improvement in burning rate is accomplished when 3 percent by weight of the binder of the uncatalyzed propellant is replaced with 3 percent by weight of 2,2-diphenylpicrylhydrazyl.

Example II below, sets forth control propellant B and novel propellant B to illustrate the use of 2,2-diphenylpicrylhydrazyl in combination with a standard catalyst material, n-butyl ferrocene, to achieve improved burning rates.

EXAMPLE II

	Control propellant B	Novel propellant B
Ingredients, percent by weight:		
Carboxy terminated polybutadiene	21.7	18.7
Lecithin	0.3	0.3
n-Butyl ferrocene	3.0	3.0
Aluminum metal powder	11.6	11.6
Ammonium perchlorate (17μ)	19.0	19.0
Ammonium perchlorate (200μ)	44.4	44.4
2,2-diphenylpicrylhydrazyl		3.0
Totals	100.0	100.0
(Burning rate in./sec. at 500 p.s.i.g.)	.380	.410
(Burning rate in./sec. at 1000 p.s.i.g.)	.495	.520
(Burning rate in./sec. at 1500 p.s.i.g.)	.583	.610

The above burning rates indicate that additional improvement in burning rates is achieved when 3 percent by weight of the binder of the n-butyl ferrocene catalyzed type propellant is replaced with 3 percent by weight of 2,2-diphenylpicrylhydrazyl. The percent increase in burning rate varied from about 10.5% to 5.1% to 4.3% at the pressures of 500, 1000 and 1500 p.s.i.g. respectively.

Example III, below, sets forth control propellant C and novel propellant C to illustrate the use of 2,2-diphenylpicrylhydrazyl in combination with a standard catalyst material, Fe_2O_3, to achieve improved burning rates.

EXAMPLE III

	Control propellant C	Novel propellant C
Ingredients, percent by weight:		
Carboxy terminated polybutadiene	21.7	18.7
Lecithin	0.3	0.3
Fe_2O_3	3.0	3.0
Alluminum metal powder	11.6	11.6
Ammonium perchlorate (17μ)	19.0	19.0
Ammonium perchlorate (200μ)	44.4	44.4
2,2-diphenylpicrylhydrazyl		3.0
Totals	100.0	100.0
(Burning rate in./sec. at 500 p.s.i.g.)	.317	.351
(Burning rate in./sec. at 1000 p.s.i.g.)	.407	.505
(Burning rate in./sec. at 1500 p.s.i.g.)	.483	.573

It is noted that the improvement in burning rates, when 2,2-diphenylpicrylhydrazyl is used in addition to Fe_2O_3, is about 11%, 24%, and 19% at the pressures 500, 1000, and 1500 p.s.i.g. respectively.

Example IV, below, sets forth control propellant D and novel propellant D to illustrate the use of 2,2-diphenylpicrylhydrazyl in combination with a standard catalysts, Fe_2O_3. Smaller particle sized ammonium perchlorate is used in the control propellant D and the novel propellant D. It is noted that the control propellant D burns at a higher rate. It is also noted that additional improvement in burning rate is achieved when 2,2-diphenylpicrylhydrazyl is used in the novel propellant D.

EXAMPLE IV

	Control propellant D	Novel propellant D
Ingredients, percent by weight:		
Carboxy terminated polybutadiene	20.7	17.7
Lecithin	0.3	0.3
Fe_2O_3	3.0	3.0
2,2-diphenylpicrylhydrazyl		3.0
Aluminum metal powder	12.0	12.0
Ammonium perchlorate (4μ)	38.4	38.4
Ammonium perchlorate (17μ)	25.6	25.6
Totals	100.0	100.0
(Burning rate in./sec. at 500 p.s.i.g.)	.715	.815
(Burning rate in./sec. at 1000 p.s.i.g.)	1.030	1.180
(Burning rate in./sec. at 1500 p.s.i.g.)	1.350	1.500

The percent improvement in burning rate of the novel propellant D, containing 3 percent by weight 2,2-diphenylpicrylhydrazyl, is 14%, 15%, and 11% at the respective pressures of 500, 1000, and 1500 p.s.i.g.

Example V, below, sets forth control propellant E and novel propellant E to illustrate the use of 2,2-diphenylpicrylhydrazyl in combination with a standard catalyst, Fe_2O_3. Smaller particle sized ammonium perchlorate is used in the control propellant E and the novel propellant E. Although novel propellant E contains only 1%, 2,2-diphenylpicrylhydrazyl, an improvement burning rate is achieved.

EXAMPLE V

	Control propellant E	Novel propellant E
Ingredients, percent by weight:		
Carboxy terminated polybutadiene	20.7	19.7
Lecithin	0.3	0.3
Fe_2O_3	3.0	3.0
2,2-diphenylpicrylhydrazyl		1.0
Aluminum metal powder	12.0	12.0
Ammonium perchlorate (4μ)	38.4	38.4
Ammonium perchlorate (17μ)	25.6	25.6
Totals	100.0	100.0
(Burning rate in./sec. at 500 p.s.i.g.)	0.715	0.775
(Burning rate in./sec. at 1000 p.s.i.g.)	1.030	1.090
(Burning rate in./sec. at 15 0 p.s.i.g.)	1.350	1.400

The percent improvement in burning rate for novel propellant E is about 84%, 5.8%, and 3.7% at the pressures of 500, 1000, and 1500 p.s.i.g. respectively.

No special procedures are required for the mixing of the propellant samples other than standard methods or procedures employed in the art. For example, the polybutadiene, lecithin, catalyst material, and aluminum are blended in a mixer in the order listed after which the inorganic oxidizer is added in increments and throughly mixed until uniform. The curing agents, cross linking agents or other additives are generally added and thoroughly blended with the mix just prior to casting into a suitable mold or rocket motor. Generally, mixing during the last part of the mixing operation and casting operation is accomplished under vacuum to eliminate air entrapment or voids in the propellant. The temperature of the mix is generally maintained in the range of about 140° F.–160° F. A temperature in the range specified serves to maintain a satisfactory viscosity during mixing and casting procedures.

The propellant formulations of this invention using carboxy terminated polybutadiene are cured by the curatives such as diaziridines, triaziridines, diepoxides, triepoxides, and combinations of the same. An amount of curing agent up to about 2 percent by weight of all the combined propellant ingredients is sufficient for curing. The amount of curing agent used is dependent uopn the curing time, the curing temperature, and the final physical properties desired for the propellant.

The free radical compound, 2,2-diphenylpicrylhydrazyl, is not to be limited to its use with carboxy terminated polybutadiene binders. Other binder materials such as hydroxy or epoxy terminated polybutadienes, and the copolymer such as polybutadiene-acrylic acid or the copolymer polybutadiene acrylic acid-acrylonitrile are compatible with the free radical compound, 2,2-diphenylpicrylhydrazyl. Therefore, the improvement in burning rate of a propellant employing ammonium perchlorate oxidizer along with the binder types specified is likewise proportional to the 2,2-diphenylpicrylhydrazyl content as illustrated herein. By proper selection of conventional curing agents for the binder material selected (e.g., polyisocyanates for the hydroxy or epoxy terminated) curing of the propellant is readily accomplished.

The propellant compositions of this invention contain the free radical compound, 2,2-diphenylpicrylhydrazyl, as catalyst, from about 0.5 to about 5 percent by weight of the composition, inorganic oxidizer of ammonium perchlorate from about 50 to about 72 percent by weight of the propellant composition, polybutadiene binder from about 10 to about 24 weight percent by weight of the propellant composition, aluminum metal powder from about 5 to about 15 percent by weight of the propellant composition, and lecithin from about 0.2 to about 0.5 percent by weight of the propellant composition.

Also, the propellant composition may contain an optional catalyst material selected from n-butyl ferrocene and Fe_2O_3 for use with 2,2-diphenylpicrylhydrazyl. The optional catalyst material may be used in amounts up to about 5 percent by weight of the propellant composition. Curatives may be employed as an additional ingredient up to about 2 percent by weight of the combined propellant ingredients.

I claim:

1. A solid propellant composition comprising polybutadiene binder in amounts from about 10 to about 24 percent by weight of said composition, inorganic oxidizer of ammonium perchlorate in amounts from about 50 to about 72 percent by weight of said composition, aluminum metal powder in amounts from about 5 to about 15 percent by weight of said composition, a burning rate catalyst comprising 2,2-diphenylpicrylhydrazyl in amounts from about 0.5 to about 5 percent by weight of said composition, and lecithin in amounts from about 0.2 to about 0.5 percent by weight of said composition.

2. The propellant composition of claim 1 and wherein said polybutadiene binder is carboxy terminated and is used in an amount of about 21.7 percent by weight of

said composition, said lecithin is used in an amount of about 0.3 percent by weight of said composition, said inorganic oxidizer of ammonium perchlorate is used in an amount of about 63.4 percent by weight of said composition; said 63.4 percent being comprised of about 19.0 percent by weight of 17 micron particle sized ammonium perchlorate and of about 44.4 percent by weight of 200 micron particle sized ammonium perchlorate, said burning rate catalyst 2,2-diphenylpicrylhydrazyl is used in an amount of about 3.0 percent by weight of said composition, said aluminum metal powder is used in an amount of about 11.6 percent by weight of said composition and wherein said composition is cured by curatives selected from diaziridines, triaziridines, diepoxides, triepoxides, and combinations of the same, said curatives being used in amounts up to about 2 percent by weight of all the combined propellant ingredients.

3. The propellant composition of claim **1** wherein said composition contains an additional catalyst material selected from n-butyl ferrocene and Fe_2O_3, said additional catalyst material being used in amounts up to about 5 percent by weight of said composition.

4. The propellant composition of claim **3** and wherein said polybutadiene binder is used in an amount of about 18.7 percent by weight of said composition, said lecithin is used in an amount of about 0.3 percent by weight of said composition, said additional catalyst material is n-butyl ferrocene which is used in an amount of about 3.0 percent by weight of said composition, said aluminum metal powder is used in an amount of about 11.6 percent by weight of said composition, said inorganic oxidizer of ammonium perchlorate is used in an amount of about 63.4 percent by weight of said composition; said 63.4 percent being comprised of about 19.0 percent by weight of 17 micron particle sized ammonium perchlorate and of about 44.4 percent by weight of 200 micron particle sized ammonium perchlorate, and said burning rate catalyst 2,2-diphenylpicrylhydrazyl is used in an amount of about 3.0 percent by weight of said composition.

5. The propellant composition of claim **4** and wherein said polybutadiene binder is used in an amount of about 18.7 percent by weight of said composition, said lecithin is used in an amount of about 0.3 percent by weight of said composition, said additional catalyst material is Fe_2O_3 which is used in an amount of about 3.0 percent by weight of said composition, said aluminum metal powder is used in an amount of about 11.6 percent by weight of said composition, said inorganic oxidizer of ammonium perchlorate is used in an amount of about 63.4 percent by weight of said composition; said 63.4 percent being comprised of about 19.0 percent by weight of 17 micron particle sized ammonium perchlorate and of about 44.4 percent by weight of 200 micron particle sized ammonium perchlorate, and said burning rate catalyst 2,2-diphenylpicrylhydrazyl is used in an amount of about 3.0 percent by weight of said composition.

6. The propellant composition of claim **4** and wherein said polybutadiene binder is used in an amount of about 17.7 percent by weight of said composition, said lecithin is used in an amount of about 0.3 percent by weight of said composition, said additional catalyst material is Fe_2O_3 which is used in an amount of about 3.0 percent by weight of said composition, said aluminum metal powder is used in an amount of about 12.0 percent by weight of said composition, said inorganic oxidizer of ammonium perchlorate is used in an amount of about 64 percent by weight of said composition; said 64 percent being comprised of about 38.4 percent by weight of 4 micron particle sized ammonium perchlorate and of about 25.6 percent by weight of 17 micron particle sized ammonium perchlorate, and said burning rate catalyst 2,2-diphenylpicrylhydrazyl is used in an amount of about 3.0 percent by weight of said composition.

7. The propellant composition of claim **4** and wherein said polybutadiene binder is used in an amount of about 19.7 percent by weight of said composition, said lecithin is used in an amount of about 0.3 percent by weight of said composition, said additional catalyst material is Fe_2O_3 which is used in an amount of about 3.0 percent by weight of said composition, said aluminum metal powder is used in an amount of about 12.0 percent by weight of said composition, said inorganic oxidizer of ammonium perchlorate is used in an amount of about 64 percent by weight of said composition; said 64 percent being comprised of about 38.4 percent by weight of 4 micron particle sized ammonium perchlorate and said burning rate catalyst 2,2-diphenylpicrylhydrazyl is used in an amount of about 1.0 percent by weight of said composition.

8. The propellant composition of claim **4** cured by curatives selected from diaziridines, triaziridines, diepoxides, triepoxides, and combinations of the same, said curatives being used in amounts up to about 2 percent by weight of all the combined propellant ingredients.

References Cited

UNITED STATES PATENTS

3,297,747 1/1967 Thornton ---------- 149—36 X

BENJAMIN R. PADGETT, Primary Examiner

U.S. Cl. X.R.

149—20, 36