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Sayles

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[54] **SOLID PROPELLANTS WITH BIRADICAL BURNING RATE CATALYSTS**

[75] Inventor: **David C. Sayles**, Huntsville, Ala.

[73] Assignee: **The United States of America as represented by the Secretary of the Army**, Washington, D.C.

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[51] **Int. Cl.²** **C06D 5/06**

[58] **Field of Search** 149/19, 44, 76, 60, 61, 149/83, 92, 97, 100, 19.8, 19.9

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Primary Examiner—Benjamin R. Padgett
Assistant Examiner—E. A. Miller
Attorney, Agent, or Firm—Nathan Edelberg; Robert P. Gibson; Jack W. Voigt

[57] **ABSTRACT**

Disclosed are p, p'-biphenylene-bis(diphenylmethyl) and p, p'-phenylene-bis(diphenylmethyl) as the means for achieving high burning rates of solid propellant compositions. The disclosed means for achieving high burning rates are compounds which exist in the biradical form and contain two trivalent carbon atoms in each molecule which contains a quinoid structure based on paramagnetic susceptibility measurements. The disclosed biradical compounds may be used to enhance the burning rate of crosslinkable double-base propellants. Representative crosslinkable double-base propellants using the biradical compounds are disclosed. Also, disclosed are representative hydroxyl-terminated polybutadiene (HTPB)-based propellants and carboxyl-terminated polybutadiene (CTPB)-based propellants which employ the biradical compound as catalyst. Processing aids (e.g., lecithin), stabilizers, and curatives may be used in minor amounts in the basic formulation or as additives to the propellant composition.

8 Claims, No Drawings

SOLID PROPELLANTS WITH BIRADICAL BURNING RATE CATALYSTS

BACKGROUND OF THE INVENTION

Catalysis or means for promoting the burning rates of propellants permits the expulsion of a larger amount of energy over a shorter period of time to thereby result in a higher specific 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 oxide, copper chromite, the organoiron compound (ferrocene and its derivatives), and other organometallic compounds. More recently carborane and carborane derivatives have been investigated as catalyst materials for propellants.

Biradical compounds have been studied by Schonberg, Trans. Faraday Soc. 32, 515 (1936).

The present invention deals with earlier studied compounds which exist entirely in the biradical form. More particularly the present invention deals with specific biradical compounds which have been found to be useful as burning rate catalysts for solid propellant compositions.

Therefore, an object of this invention is to provide biradical compounds which are useful as burning rate catalysts for solid propellants.

Another object is to provide solid propellant formulations of the crosslinkable double-base type which utilize a biradical compound which functions as a burning rate catalyst and a ballistic modifier to inhibit resonance burning and combustion instability.

Another object of this invention is to provide hydroxyl-terminated polybutadiene-based propellants which employ a biradical compound as the burning rate catalyst.

Still another object of this invention is to provide carboxl-terminated polybutadiene-based propellants which employ a biradical compound as the burning rate catalyst.

SUMMARY OF THE INVENTION

The catalyst of this invention is selected from the biradical compounds, p, p'-biphenylene-bis(diphenylmethyl) and p, p'-phenylene-bis(diphenylmethyl). The specified biradical compounds serve as catalyst for crosslinkable double-base propellant compositions, hydroxyl-terminated polybutadiene-based propellant compositions, and carboxyl-terminated polybutadiene-based propellant compositions. The amount of the catalyst compound may vary from about 0.5 percent by weight to about 8 percent by weight of the propellant composition.

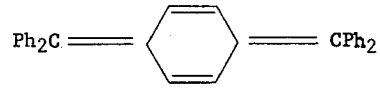
DESCRIPTION OF THE PREFERRED EMBODIMENTS

The biradical compound p, p'-biphenylene-bis(diphenylmethyl) (referred to for simplicity as compound A) is illustrated by the following structural formula:



wherein Ph is the abbreviation for phenyl, C_6H_5—.

The biradical compound p, p'-phenylene-bis(diphenylmethyl) (referred to for simplicity as compound B) is illustrated by the following structural formula:



wherein Ph is the abbreviation for phenyl, C_6H_5 —.

Table I illustrates how the biradical burning rate catalyst of this invention is used in a crosslinkable double-base propellant formulation.

Table I

A Comparison of Crosslinkable Double-Base Propellants With and Without Burning Rate Catalyst

INGREDIENTS/BURNING RATE	PROPELLANT COMPOSITIONS PERCENT BY WEIGHT AND BURNING RATES		
	A	B	C
Casting Powder* (binder)	11.25	11.25	11.25
Triethylene Glycol Dinitrate (TEGDN)	28.75	28.75	28.75
Butanetriol Trinitrate (BTTN)	15.5	15.5	15.5
Cyclotetramethylenetetranitramine (HMX)	40.0	40.0	36.0
Lead Peroxide	4.0	—	4.0
p,p'-Biphenylene-bis(diphenylmethyl)		4.0	4.0
Resorcinol	0.5	0.5	0.5
Toluene Diisocyanate (added)	1.0	1.0	1.0
Burning Rate (ips at 1000 psi)	0.35	0.72	0.85
*Casting powder formulation:	10.1	parts nitrocellulose	
	.95	parts nitroglycerine	
	.20	parts 2-nitrodiphenylamine	
TOTAL	11.25	parts Casting powder	

The biradical catalysts are effective both as burning rate promoters as well as inhibitors for resonance burning and combustion instability as evidenced by comparative tests of propellants A, B, and C of Table I.

In the crosslinkable double-base propellants set forth in Table I, the casting powder serves as the binder, when cured. TEGDN and BTTN serve as plasticizer, HMX serves as the oxidizer, p, p'-biphenylene-bis(diphenylmethyl) serves as catalyst and ballistic modifier, and the other material listed include lead peroxide

(ballistic modifier and catalyst), resorcinol (stabilizer), and toluene diisocyanate (crosslinking agent). Although, compositions A and C of Table I are near smokeless double-base propellants, an improvement in the smokeless properties is gained in composition B where a complete replacement of lead peroxide is made by p, p'-biphenylene-bis(diphenylmethyl).

Table II illustrates how the biradical burning rate catalyst (compound A or B) of this invention is used in a hydroxyl-terminated polybutadiene-based propellant.

Table II

A Comparison of Hydroxyl-Terminated Polybutadiene-Based Propellants With and Without Biradical Burning Rate Catalyst

INGREDIENTS/BURNING RATE	PROPELLANT COMPOSITION PERCENT BY WEIGHT AND BURNING RATES	
	A	B
INGREDIENT		
Hydroxyl-terminated Polybutadiene Prepolymer	9.84	9.84
Dimeryl Diisocyanate	1.92	1.92
Bonding Agent*	0.24	0.24
Ammonium Perchlorate	73.	71.
Aluminum	15.	15.
p,p'-Biphenylene-bis(diphenylmethyl)	—	2.
Burning Rate (ips at 1000 psi)	0.35	0.78

*Bonding agent is formulated of equimolar quantities of tris[1-(2-methyl)aziridinyl]phosphine oxide, tartaric acid, and adipic acid. Bonding agent is used in an amount from about 0.1–0.3 percent by weight of propellant composition.

The propellants of Table II employ a hydroxyl-terminated polybutadiene binder, ammonium perchlorate oxidizer, aluminum metal fuel, the burning rate catalyst p, p'-biphenylene-bis(diphenylmethyl), and materials for additives which include the crosslinking compound dimeryl diisocyanate and a bonding agent to provide desirable physical properties through crosslinking and curing reactions. A marked increase in burning rate is achieved with Propellant B of Table II which contains the burning rate catalyst, p, p'-biphenylene-bis(diphenylmethyl). Propellant A of Table II is the standard propellant. The use of the biradical catalyst to control burning rates of HTPB-based propellants is attractive because of the compatibility of this type compound with HTPB-based propellants.

Table III illustrates how the biradical burning rate catalyst (compound A or B) of this invention is used in a carboxyl-terminated polybutadiene-based propellant.

Table III

A Comparison of a Carboxyl-Terminated Polybutadiene-Based Propellant (CTPB) Using N-Butylferrocene as Burning Rate Catalyst With a CTPB-Based Propellant Using Biradical Burning Rate Catalyst

PROPELLANT INGREDIENTS/BURNING RATE	PROPELLANT PERCENT BY WEIGHT/BURNING RATE	
	COMPOSITION A	COMPOSITION B
Ammonium Perchlorate	66	66
Aluminum	14	14
Normal-Butylferrocene	7	—
p,p'-Biphenylene-bis(diphenylmethyl)	—	7
Carboxyl-terminated Polybutadiene Prepolymer	12.5	12.5
Tris[1-(2-methyl)aziridinyl]phosphine Oxide	0.5	0.5
Tris(oxiranyl)-para-aminophenol (added)	0.1	0.1
Iron Linoleate (added)	0.1	0.1
Burning Rate (ips at 1000 psi)	1.8	2.4

The propellants of Table III employ a carboxyl-terminated polybutadiene binder, ammonium perchlorate oxidizer, aluminum metal fuel, n-butylferrocene catalyst (in standard composition A) and p, p'-biphenylene-bis(diphenylmethyl) (in composition B), and crosslinking agent tris[1-(2-methyl)aziridinyl]-phosphine oxide. Tris(oxiranyl)-para-aminophenol and iron linoleate are curatives each of which are added in trace amounts from about 0.1 to about 0.5 percent by weight of the total weight of all the other combined propellant ingredients.

The ranges of propellant ingredients of the double-base type propellants disclosed herein are (in percent by weight of the propellant composition) as follows: binder from casting powder (formulated of nitrocellulose of about 10.1 parts, of about 0.95 parts nitroglycerine, and of about 0.20 parts 2-nitrodiphenylamine) from about 6 to about 23; TEGDN from about 20 to about 35; BTTN from about 10 to about 20; HMX from about 30 to about 50; biradical catalyst (selected from p, p'-biphenylene-bis(diphenylmethyl) and p, p'-phenylene-bis(diphenylmethyl)) from about 2.0 to about 8.0; lead peroxide from about 2.0 to about 6.0; stabilizers from about 0.5 to about 1.0; and curative additives from about 0.5 to about 2.0.

The ranges of the composite propellant ingredients using HTPB-based binder in the composition are (in percent by weight of the propellant composition) as follows: hydroxyl-terminated polybutadiene prepolymer from about 7 to about 15; ammonium perchlorate from about 65 to about 75; aluminum from about 5 to about 20; biradical catalyst selected from p, p'-biphenylene-bis(diphenylmethyl) and p, p'-phenylene-bis(-diphenylmethyl) from about 2 to about 8; and additives for crosslinking functions, bonding agent functions, curing functions, etc. from about 0.5 to about 2.0.

The ranges of the composite propellant ingredients, using carboxyl-terminated polybutadiene binder in the compositions disclosed herein, are (in percent by weight of the propellant composition) as follows: biradical catalyst selected from p, p'-biphenylene-bis(-diphenylmethyl) and p, p'-phenylene-bis(diphenylmethyl) from about 2.0 to about 8.0; ammonium perchlorate from about 60 to about 70; aluminum metal fuel from about 5 to about 20; carboxyl-terminated polybutadiene prepolymer from about 7 to about 15; crosslinking agent (tris[1-(2-methyl)aziridinyl]phosphine oxide) from about 0.5 to about 2.0; and curatives (tris(oxiranyl)-para-aminophenol) and iron linoleate, each in an amount from about 0.1 to about 0.5 percent by weight of the total weight of all the other propellant ingredients.

Because of the compatibility of the biradical compounds of this invention with both double base-propellant ingredients and composite propellants using hydroxyl-or carboxyl-terminated polybutadiene-based propellant ingredients, a wide variety of propellants having many, varied burning rates can be compounded. The problems associated with propellant mixing using metallic oxide as catalysts, and the problems associated with using liquid iron-containing catalysts are eliminated when the biradical catalysts are used.

The biradical compounds of this invention may be used to replace the boron-containing compounds (e.g. carborane and carborane derivatives) which have been investigated for use in HTPB-based propellants. Although the boron-containing compounds have shown very desirable catalytic properties, a replacement for the boron-containing compounds is desired to offset any unavailability of facilities for the manufacture of the boron-containing catalysts.

No special procedures are required for the mixing of propellants employing the disclosed biradical compounds. The standard methods or procedures employed in the art for propellant mixing of double-base and composite propellants have been proven to be very satisfactory for the propellants of this invention.

I claim:

1. A solid propellant composition comprising a binder, an oxidizer, a burning rate catalyst selected from the biradical compounds consisting of p, p'-biphenylene-bis(diphenylmethyl) and p, p'-phenylene-bis(-diphenylmethyl), and a crosslinking agent.

2. The propellant composition of claim **1** wherein said binder is present in an amount from about 6 to about 23 percent by weight of said propellant composition, said binder being constituted of about 10.1 parts nitrocellulose, about 0.95 parts nitroglycerin, and about 0.20 parts of 2-nitrodiphenylamine; said oxidizer is cyclotetramethylenetetranitramine which is present in an amount from about 30 to about 50 percent by weight of said propellant composition; said catalyst selected is p, p'-biphenylene-bis(diphenylmethyl) which is present in an amount from about 2 to about 8 percent by weight of said propellant composition; said composition includes the plasticizer, triethylene glycol dinitrate in an amount from about 20 to about 35 percent by weight of said propellant composition and the plasticizer, butanetriol trinitrate in an amount from about 10 to about 20 percent by weight of said propellant composition; said propellant composition additionally includes an agent for stabilizing which is resorcinol which is present in an amount from about 0.5 to about 1.0 percent by weight of said propellant composition; and wherein said crosslinking agent is toluene diisocyanate which is added in an amount of about 1.0 percent by weight of the total weight of all the other propellant ingredients.

3. The propellant composition of claim **2** wherein said binder is present in an amount of about 11.25 percent by weight of said propellant composition; said cyclotetramethylenetetranitramine is present in an amount of about 36 to about 40 percent by weight of said propellant composition; said triethylene glycol dinitrate is present in an amount of about 28.75 percent by weight of said propellant composition; said butanetriol trinitrate is present in an amount of about 15.5 percent by weight of said propellant composition; said p, p'-biphenylene-bis(diphenylmethyl) is present in an amount of about 4.0 percent by weight of said propellant composition; and said resorcinol is present in an amount of about 0.5 percent by weight of said propellant composition.

4. The propellant composition of claim **3** wherein said cyclotetramethylenetetranitramine is present in an amount of about 36 percent by weight of said propellant composition; and wherein said composition additionally contains the ballistic modifier, lead peroxide, in an amount of about 4.0 percent by weight of said propellant composition.

5. The propellant composition of claim **1** wherein said binder is hydroxyl-terminated polybutadiene which is present in an amount from about 7 to about 15 percent by weight of said propellant composition; said oxidizer is ammonium perchlorate which is present in an amount from about 65 to about 75 percent by weight of said propellant composition; said catalyst selected is p, p'-biphenylene-bis(diphenylmethyl) which is present in an amount from about 2 to about 8 percent by weight of said propellant composition; said crosslinking agent is dimeryl diisocyanate which is present in an amount from about 0.5 to about 2.0 percent by weight of said propellant composition; said composition contains a bonding agent formulated of equimolar quantities of tris[1-(2-methyl)-aziridinyl]phosphine oxide, tartaric acid, and adipic acid, said bonding agent is present in an amount from about 0.1 to about 0.3 percent by weight of said propellant composition; and wherein said propellant composition additionally contains aluminium metal fuel in an amount from about 5 to about 20 percent by weight of said propellant composition.

6. The propellant composition of claim **5** wherein said binder is present in an amount of about 9.84 percent by weight of said propellant composition; said ammonium perchlorate is present in an amount of about 71 percent by weight of said propellant composition; said p, p'-biphenylene-bis(diphenylmethyl) is present in an amount of about 2 percent by weight of said propellant composition; said dimeryl diisocyanate is present in an amount of about 1.92 percent by weight of

said propellant composition; said bonding agent is present in an amount of about 0.24 percent by weight of said propellant composition; and said aluminium metal fuel is present in an amount of about 15 percent by weight of said propellant composition.

7. The propellant composition of claim 1 wherein said binder is carboxyl-terminated polybutadiene which is present in an amount from about 7 to about 15 percent by weight of said propellant composition; said oxidizer is ammonium perchlorate which is present in an amount from about 60 to about 70 percent by weight of said propellant composition; said catalyst selected is p, p'-biphenylene-bis(diphenylmethyl) which is present in an amount from about 2 to about 8 percent by weight of said propellant composition; said cross-linking agent is tris[1-(2-methyl)aziridinyl]-phosphine oxide which is present in an amount from about 0.5 to about 2.0 percent by weight of said propellant composition; said propellant composition includes aluminum metal fuel in an amount from about 5 to about 15 percent by weight of said propellant composition; and wherein said propellant composition additionally includes the curatives consisting of tris(oxiranyl)-para-aminophenol and iron linoleate which are each added to said propellant composition in an amount from about 0.1 to about 0.5 percent by weight of the total weight of all the other propellant ingredients.

8. The propellant composition of claim 7 wherein said binder is present in an amount of about 12.5 percent by weight of said propellant composition; said ammonium perchlorate is present in an amount of about 66 percent by weight of said perchlorate composition; said p,, p'-biphenylene-bis(diphenylmethyl) is present in an amount of about 7 percent by weight of said propellant composition; said tris[1-(2-methyl)aziridinyl]-phosphine oxide is present in an amount of about 0.5 percent by weight of said propellant composition; said aluminium metal fuel is present in an amount of about 14 percent by weight of said propellant composition; and said tris(oxiranyl)-para-aminophenol and iron linoleate are each present in an amount of about 0.1 percent by weight of all the other propellant ingredients.

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