United States Patent Office 3,811,966
Patented May 21, 1974



3,811,966

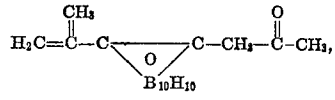
# COMPOSITE MODIFIED DOUBLE-BASE PROPELLANTS WITH VERY HIGH BURNING RATES

William E. Hill and Lew R. Beason, Huntsville, Ala., assignors to the United States of America as represented by the Secretary of the Army

No Drawing. Filed June 24, 1969, Ser. No. 836,177
Int. Cl. C06d 5/06
U.S. Cl. 149—19.2 5 Claims

## ABSTRACT OF THE DISCLOSURE

Composite modified double-base propellants with very high burning rates result when 11-isopropenyl, 12-prop-(2-one)-yl-carborane



(IPCA), a liquid ketone derivative of isopropenylcarborane, is employed as the burning rate catalyst for the propellant composition.

## BACKGROUND OF THE INVENTION

This invention relates to solid double-base propellant compositions which generally include the ingredients: nitrocellulose, an inorganic oxidizing salts, plasticizers, stabilizer, burning rate modifier or catalyst, curing agent, processing aid, and generally, metal as a fuel.

Dicarbaclovododecaborane (carborane) and derivatives of carborane belong to a class of compounds which are known to be effective ballistic modifiers for obtaining high burning rates; however, most derivatives of carborane are not compatible with the nitrocellulose used as binders in composite modified double-base propellants.

The problem resulting from using most derivatives of carborane with nitrocellulose is failure of the nitrocellulose to swell to form a homogeneous rubbery matrix which is essential for a solid propellant grain. As known in the art, nitrocellulose must be swollen by nitrate ester plasticizers such as Triethyleneglycoldinitrate (TEGDN) in order to form a homogeneous, rubbery matrix in which the solid components of the propellant (e.g., ammonium perchlorate and aluminum) are evenly dispersed.

A need exists for non-fiber composite modified double-base propellants with high burning rates. In order to use carborane derivatives as ballistic modifiers to produce a high burning rate propellant without sacrificing the mechanical properties of the propellant, the carborane derivative must not interfere with the swelling process of nitrocellulose caused by the reaction of the plasticizer and the nitrocellulose.

A need exists for carborane derivative which will not interfere with the swelling reaction of nitrocellulose. Thus, a carborane derivative which provides ballistic modifier action by causing a very high burning rate when used with double-base formulations containing nitrocellulose is greatly desired.

Therefore, the present invention has, as its principal object to provide a very high burning composite modified double-base propellant utilizing a derivative of carborane as the burning rate catalyst.

Another object is to provide a derivative of carborane which does not interfere with the swelling process of nitrocellulose caused by plasticizer reaction in the propellant processing.

Another object is to provide derivative of carborane which is compatible with the other propellant ingredients of the formulation wherein used.



Another object is to provide a derivative of carborane which can be used in propellants which are relatively easy to produce by standard techniques known to those familiar with the art.

A further object is to provide propellant formulations which represent an improvement over prior art propellant formulations which require the use of metal fibers and special mixing and casting techniques to obtain fast burning rates for composite modified double-base propellants.

## SUMMARY OF THE INVENTION

The objects of this invention are achieved by means of a derivative of carborane employed in composite modified double-base propellant compositions. 11-isopropenyl, 12-prop-(2-one)-yl-carborane, a derivative of carborane and referred to as IPCA, serves to increase the burning rate of double-base propellants wherein used. The double-base propellants of this invention are comprised of IPCA of about 5 to about 25 weight percent, nitrocellulose of about 5 to about 20 weight percent, plasticizer of about 10 to about 30 weight percent, inorganic oxidizer of about 35 to about 52 weight percent, metal fuel of about 5 to about 20 weight percent, stabilizer of about 0.5 to about 2 weight percent, cross-linking agent selected from suitable plasticizer type compounds of about 3 to about 10 weight percent, and processing aid (e.g. lecithin).

Suitable plasticizers of this invention include nitroglycerin, triacetin, adiponitrile, di-n-propyl adipate, and TEGDN (triethyleneglycoldinitrate). Useful inorganic oxidizing salts of this invention include the ammonium, alkali metal and alkaline earth metal salts of nitric, perchloric, and chloric acids, and mixtures thereof. Metal fuels such as the powdered metals, of aluminum, magnesium, titanium, zirconium and borons are useful in this invention (aluminum is the preferred metal). Stabilizers such as resorcinol and 2-nitro-diphenylamine are used in the compositions of this invention. Plasticizer compounds of the type which perform functions of curing propellant by assisting in cross-linking, chain extending, and chain branching reactions which directly result in imparting desirable physical properties to the propellant are used. Suitable plasticizer type compounds for the described function are adiponitrile, di-n-propyl adipate, triacetin, and the like.

Various other ingredients in trace amounts can also be added for specific purposes without departing from the scope of the invention. For example, lecithin can be added to improve the castability of the uncured propellant. Certain polymerization modifiers such as t-butyl catecol or cobalt 2-ethyl hexanoate may be employed to obtain certain curing conditions and finished product. Modifiers of this type do not interfere with the catalytic values imparted by IPCA to the combustion processes when the propellant is used.

## DESCRIPTION OF THE PREFERRED EMBODIMENT

A fast burning double-base propellant with qualitatively attractive mechanical properties is produced by incorporating IPCA, a liquid ketone derivative of isopropenyl-carborane, into the propellant mixture as a ballistic modifier. The burning rates and composition of the propellant mixture are compared to a control propellant with no ballistic modifier as indicated in Table I.

The propellants are made by weighing the ingredients into a jacketed vertical mixer kept at 60° F. by cooling water. Mixing is accomplished with an air motor driven paddle stirrer for two hours. The propellant mixture is kept under vacuum during mixing at 60° F. When the propellants are well mixed they are cast into small motors at atmospheric pressure. After casting, vacuum is applied to the motors, and they are vibrated for about

45 minutes. This procedure results in motors with void free propellant which are cured over night by placing the motors in an oven held at 60° C. The burning rates of the propellant are then determined by firing the motors fitted with appropriate nozzles to produce various pressures during firing. The burning rates obtained for the propellant with IPCA as the ballistic modifier are about double the rates for the control without modifier at all three pressures listed in Table I.

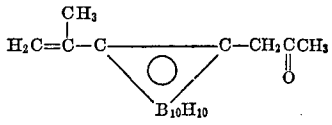
TABLE I

Burning rates of double-base propellants (IPCA modifier)

| | Control, percent | IPCA, percen |
|---|---|---|
| Component: | | |
| Nitrocellulose | 12.0 | 12.0 |
| TEGDN | 35.0 | 20.0 |
| Aluminum | 2.0 | 2.0 |
| Ammonium perchlorate: | | |
| 8 micron | 40.0 | 40.0 |
| 15 micron | 8.0 | 8.0 |
| Adiponitrile | | 3.0 |
| IPCA | | 12.0 |
| Resorcinol | 1.0 | 1.0 |
| Burning rate (in./sec.): | | |
| 2,000 p.s.i. | 2.00 | 4.00 |
| 1,000 p.s.i. | 1.30 | 2.50 |
| 500 p.s.i. | 0.83 | 1.60 |

The burning rate at 2000 p.s.i. for the composite modified double-base propellant containing IPCA shown in Table I is increased to 6.5 in./sec. by substituting ultrafine ammonium perchlorate (2.5 microns particle size) for the ammonium perchlorate blend shown in Table I. The calculated burning rate (maximum possible) for propellant without IPCA as a ballistic modifier but with ultrafine ammonium perchlorate as oxidizer is 3.0 in/sec. at 2000 p.s.i. Preparative procedures for IPCA which provides the ballistic modifier action for the propellant formulations of this invention are as follows: after flushing the reaction flask and accessory equipment, with dry nitrogen, 50 grams of isopropenylcarborane and 300 milliliters of anhydrous ethyl ether are combined in a three necked flask equipped with two addition funnels, cooling and heating accessory equipment, and accessory equipment for reflux procedure. Butyl lithium (171 milliliters of 1.60 molar) is placed into one addition funnel, and 40 milliliters of propylene oxide is placed in the other one. The flask is cooled to 0° C., and the butyl lithium is added dropwise. After the butyl lithium is added, the flask is heated to reflux and the propylene oxide is added dropwise. After the addition is complete the flask is refluxed for an additional 1½ hours. Contents of the flask are then poured into a separatory funnel and washed with an equal portion of water. The water layer is drained off and discarded and the ether layer is washed with two 200-ml. portions of 10% HCl in water. The acid layers are discarded and the ether layer dried over magnesium sulfate. The ether is removed on a rotary evaporator. The remaining oil is washed into another 3-neck flask with 100-ml. of ether and treated dropwise with a chromic acid solution of 95.6 grams $K_2Cr_2O_7$, 42.6 ml. conc. $H_2SO_4$, and 120 ml. water after the flask is cooled to 0° C. Throughout the addition the ice bath should remain around the flask as heat is generated in this reaction. After the addition of the chromic acid, the ice bath is removed and the reaction stirred at room temperature over night.

The reaction mixture is poured into a separatory funnel and washed with water. The water layer is discarded. The ether layer is then washed twice with saturated sodium bicarbonate-water solutions. The water layer is discarded and the ether layer dried over magnesium sulfate. The ether is removed on an evaporator and the remaining oil distilled to give IPCA (1), bp 140° C. at ~0.025 mm., 35 grams yield.



(1)

The NMR spectrum consists of four absorptions centered at 1.95, 2.18, 3.07 and 5.57 p.p.m. The 5.57 p.p.m. absorption, due to the vinylic protons, has the gross appearance of a quartet (J=~1 c.p.s.) and a singlet superimposed on one another. The 3.07 and 2.18 p.p.m. absorptions, due to the $CH_2$ and $CH_3$ of the acetone group, are singlets while the 195 ppm peak assigned to isopropenyl $CH_3$ group has the appearance of a doublet (J=~1 c.p.s.).

The examples set forth hereinabove demonstrate that non-fiber double-base propellants with fast burning rates can be produced when certain compatible derivatives of carborane are used as ballistic modifiers The propellants are relatively easy to produce by standard techniques known to those familiar with the art and represent an improvement over prior art which requires the use of metal fibers and special mixing and casting techniques to obtain fast burning rates for composite modified double-base propellants.

We claim:

1. In a double-base solid propellant composition having a rubbery matrix binder formed by swollen nitrocellulose, the improvement in burning rate of said composition achieved by including in said composition a derivative of carborane that is compatible with the swelling process whereby nitrocellulose is swollen by a reaction between the nitrocellulose and plasticizers contained in said composition, said derivative of carborane being 11-isopropenyl, 12-prop-(2-one)-yl-carborane; said double-base solid propellant composition comprising an inorganic oxidizing salt, plasticizers, metal fuel, nitrocellulose, and said 11-isopropenyl, 12-prop-(2-one)-yl-carborane.

2. The propellant composition of claim 1 and wherein said inorganic oxidizing salt is selected from ammonium, alkali metal, and alkaline earth metal salts of nitric, perchloric, and chloric acids, and mixtures thereof in an amount from about 35 to about 52 weight percent; said plasticizers are selected from nitroglycerin, triacetin, adiponitrile, and triethyleneglycoldinitrate in an amount from about 10 to about 30 weight percent; said metal fuel is selected from aluminum, magnesium, titanium, zirconium, and boron in amount from about 5 to about 20 weight percent; said nitrocellulose is present in amount from about 5 to about 20 weight percent; and wherein said 11-isopropenyl, 12-prop-(2-one)-yl-carborane is present in amount from about 5 to about 25 weight percent.

3. The propellant composition of claim 2 and also comprising a stabilizer selected from resorcinol and 2-nitrodiphenylamine in amounts from about 0.5 to about 2 weight percent.

4. The propellant composition of claim 3 and wherein said inorganic oxidizing salt is ammonium perchlorate, blended of about 5 parts ammonium perchlorate having particle size of about 8 microns and 1 part of ammonium perchlorate having particle size of about 16 microns; said blended perchlorate present in an amount of about 48.0 weight percent; said nitrocellulose is present in an amount of about 12.0 weight percent; said plasticizer comprised of triethyleneglycoldinitrate of about 20.0 weight percent of the propellant composition and adiponitrile of about 3.0 weight percent of the propellant composition; said 11-isopropenyl, 12-prop-(2-one)-yl-carborane is present in an amount of about 12.0 weight percent; and said stabilizer is resorcinol present in an amount of about 1.0 weight percent.

5. The propellant composition of claim 3 and wherein said inorganic oxidizing salt is ammonium perchlorate

having particle size of about 2.5 microns, said perchlorate being present in an amount of about 48.0 weight percent; said nitrocellulose being present in an amount of about 12.0 weight percent; said plasticizer comprised of triethyleneglycoldinitrate of about 20.0 weight percent of the propellant composition and adiponitrile of about 3.0 weight percent of the propellant composition; said 11-isopropenyl, 12-prop-(2-one)-yl-carborane being present in an amount of about 12.0 weight percent; and said stabilizer is resorcinol present in an amount of about 1.0 weight percent.


**References Cited**

UNITED STATES PATENTS

| | | | |
|---|---|---|---|
| 3,107,187 | 10/1963 | Rumbel et al. | 149—22 |
| 3,130,097 | 4/1964 | Drummond | 149—22 |
| 3,306,790 | 2/1967 | Crescenzo et al. | 149—93 |
| 3,307,985 | 5/1967 | Jago | 149—18 |
| 3,375,148 | 3/1968 | Finnegan et al. | 149—18 |
| 3,378,416 | 4/1968 | Perry et al. | 149—22 |
| 3,406,203 | 10/1968 | Morrow et al. | 260—583 |
| 3,419,445 | 12/1968 | Markels | 149—19 |
| 3,489,623 | 1/1970 | Griffith et al. | 149—20 |

OTHER REFERENCES

Zakharkin et al: "Journal of General Chemistry of the USSR," 37, p. 1301 (June 1967).





CARL D. QUARFORTH, Primary Examiner

E. A. MILLER, Assistant Examiner

U.S. Cl. X.R.

149—22, 38, 76, 97, 98