United States Patent Office

3,745,074

Patented July 10, 1973

3,745,074

COMPOSITE SOLID PROPELLANT WITH ADDITIVE TO IMPROVE THE MECHANICAL PROPERTIES THEREOF

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No Drawing. Original application July 30, 1969, Ser. No. 851,137. Divided and this application Jan. 12, 1971, Ser. No. 105,938

Int. Cl. C06d 5/06

U.S. Cl. 149—7 5 Claims

ABSTRACT OF THE DISCLOSURE

The reaction products of di- or tri-functional aziridinyl phosphine oxides or their derivatives with polyfunctional carboxylic acids, and the combination of the reaction products with other propellant ingredients such as inorganic oxidizer, binder, plasticizer, metal fuel and etc.

CROSS REFERENCE TO RELATED APPLICATION

This application is a division of application Ser. No. 851,137, filed July 30, 1969.

BACKGROUND OF THE INVENTION

Rocket motors consisting of a solid propellant grain bonded to a rigid metal case are widely used both in military missilery and in non-military applications. The propellant grain usually has an internal perforation parallel to the longest axis of the motor case. Since the propellant and the metal case are bonded together, and since the coefficients of thermal expansion of metal and propellant differ greatly, and since the metal case is rigid, lowering the temperature of the motor induces strain in the propellant proportional to the amount of temperature change. Such strain is usually greatest at the surface of the internal perforation of the propellant grain. If such strain exceeds the strain capability of the propellant, the grain will crack open and thus expose more surface for burning upon ignition. The motor is a hazard in such condition, and must be discarded. Thus it is extremely important that the propellant have ample strain capability to withstand such strains as may be imposed.

Until recently, the relationship between the strain capability of a composite propellant and the extensibility of its binder was not understood. It was known from empirical data that binders with excellent extensibility often made propellants with low strain capability, but the reason for this was unknown. In recent work by the present inventor, it has been discovered that binder-filler physical interactions are a large factor in propellant mechanical properties, and further that a high level of adhesion of binder to filler is necessary to fully utilize the extensibility of a binder in achieving good strain capability in the propellant. Consequently, it is very desirable to use a binder which adheres strongly to the oxidizer and other solid particles of a composite propellant.

Further study of binder-filler interactions have shown that even further improvement in propellant strain capability can be achieved if a thin tear-resistant layer of binder is deposited on the surfaces of the filler particles prior to final binder cure, provided this layer becomes chemically bonded to the rest of the binder during the cure cycle. This layer prevents microscopic voids (which form in the strained cured propellant) from reaching the particle surfaces and causing early separation of binder from the filler.

Therefore, it is an object of this invention to provide a novel reaction product that is produced by reacting di- or tri-functional arizidinyl phosphine oxides or their derivatives with organic molecules which are polyfunctional with respect to carboxyl groups and some of which may contain one or more hydroxyl groups.

Another object of this invention is to provide a novel reaction product that can be used to coat inorganic oxidizer particles such as ammonium perchlorate.

Still another object of this invention is to provide a reaction product that can be used in a propellant composition to increase the strain capability thereof.

A still further object of this invention is to provide a reaction product that can be crosslinked with other binder ingredients to increase the strain capability of the solid propellant composition.

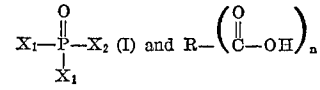
SUMMARY OF THE INVENTION

In accordance with this invention, a binder type reaction product is produced by reacting in the presence of an organic solvent di- or tri-functional aziridinyl phosphine oxides or their derivatives with organic molecules which are polyfunctional with respect to carboxyl groups and which also contain an alkyl structure that may contain one or more hydroxyl groups.

The reaction product is used to coat oxidizer material such as ammonium perchlorate or in a propellant composition that contains ammonium perchlorate. In the propellant composition, the active hydrogen atoms of the reaction product are linked to the rest of the binder ingredients during the cure of the propellant to increase the strain capability of the propellant. The binder cure reactions are usually between hydroxyl groups and isocyanate groups to form a urethane linkage, although other groups may be used in curing without affecting the usefulness of the invention. Examples of such other groups are active hydrogen containing groups such as amine and thiol.

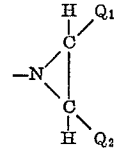
DETAILED DESCRIPTION OF THE INVENTION

The present invention achieves the desired effects described above by causing a high degree of adhesion between binder and ammonium perchlorate oxidizer while simultaneously forming around the particles a tear-resistant layer which contains active hydrogen atoms to chemically bond said layer to the rest of the binder, provided the cure reaction involves groups which react readily with active hydrogen, such as isocyanate groups. This is accomplished through the use of unique chemical properties of the class of compounds according to this invention. This class of compounds consists of the reaction products of di- or tri-functional aziridinyl phosphine oxide or its derivatives with organic molecules which are polyfunctional with respect to carboxyl groups and which may contain one or more hydroxyl groups in their structures. The starting compounds or reactants may be represented as follows:



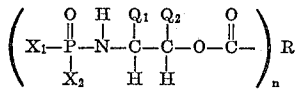
(II)

where X_1 represents an aziridine group of the structure



and Q_1 and Q_2 are either hydrogen or alkyl groups of one to four carbon atoms (Q_1 and Q_2 may be the same or different), X_2 may be the same as X_1 or may be an organic radical such as phenyl, benzyl, methyl, ethyl, etc., R is an alkyl that contains at least one active hydrogen atom or an organic entity of molecules that contain one or more hydroxyl groups, and n is 2, 3, or 4.

Since both reactants are polyfunctional, the reaction product must necessarily be a mixture of compounds. However, the nominal structure may be represented by the following general formula:



(III)

where X_1, X_2, Q_1, Q_2, R and n are as already defined.

The optimum amounts of reactants are such that essentially all carboxyl groups in (II) are reacted and nominally one aziridine group in (I) is reacted. Thus one mole of (I) is required for each carboxyl equivalent of (II). The use of less than one mole of (I) per carboxyl equivalent of (II) will result in a polymeric form of (III), while the use of more than one mole of (I) per carboxyl equivalent of (II) will result in essentially (III) plus unreacted (I). Such variations from the optimum ratio of (I) to (II) can be tolerated to a certain extent without seriously affecting the effectiveness of the invention. Further, if it is desired to increase the ratio of aziridine groups to hydroxyl groups in (III), a second acid (IV) may be used of the same general formula as (II) except that no hydroxyl groups are contained in its structure. Thus (II) and (IV) can be mixed in any desired proportion prior to reacting with (I), with the optimum amount of reactants being one mole of (I) per the sum of the carboxyl equivalents of (II) and (IV).

The reaction product is produced by dissolving the reactants in a suitable inert solvent such as methanol, ethanol, methylene chloride, tetrahydrofuran, diethyl ether, or mixtures of these. It has been found to be perferable that methanol or ethanol comprise at least a part of the solvent. Reaction temperature is not critical, and may range from 70° F. to 200° F. for such time as is needed for essentially all carboxyl groups in (II) [and (IV) if used] to be reacted. The solvent is then removed by any suitable means, such as evaporation under vacuum at elevated temperatures. The residue is the reaction product which is usually straw-colored and quite viscous.

In propellants in which ammonium perchlorate is the principal oxidizer, addition of 0.05% to 1.0% of the reaction product greatly enhances the strain capability of the cured propellant. In preparing such a propellant, it is common practice to first place in a suitable mechanical mixer the liquid polymer, plasticizer, antioxidant and any other binder ingredient except the curing agent. The reaction product may also be added at this time. Metal powder, if used, is added next and mixed into the binder ingredients. Then the oxidizer being principally ammonium perchlorate is added and mixed in after the oxidizer has been thoroughly incorporated by mixing, the curing agent is added to initiate the reaction which in time changes the liquid propellant slurry into a flexible solid propellant. The rate of the cure reaction must be slow enough to allow time for casting the propellant into motors or other receptacles before the viscosity of the liquid slurry becomes unmanageable.

It is postulated that the manner in which the reaction product enhances the mechanical properties of a propellant is as follows: The compound of the reaction product has a polar character due to the P=O groups, and this polarity causes it to migrate preferentially to the polar surface of the ammonium perchlorate oxidizer, thus coating it with a film of the reaction product. The ammonium perchlorate catalyzes the homopolymerization of the remaining aziridine rings in the reaction product, thus linking the molecules together in a highly cross-linked network structure. Thus the film of the reaction product on the AP surfaces becomes a hard, tear-resistant layer which adheres strongly to the surface, and which can react chemically with the curative through the active hydrogen atoms which are contained in the

structure of the reaction product. Such a propellant, when stressed after cure, must fail in large part by tearing the binder rather than by separation of the binder from the filler particles. As stated earlier, this is very desirable, and imparts greatly increased strain capability and tensile strength to the propellant, thus the invention accomplishes the desired objectives. Specific examples of the invention are given below:

Example I

21.5 grams (0.10 mole of tris-1-(2-methyl aziridinyl) phosphine oxide and 7.5 grams (0.10 equivalent) of tartaric acid were dissolved in 200 ml. of methanol. The solution was kept at room temperature (about 75° F.) for three days, at which time essentially all carboxyl groups in the tartaric acid were reacted, as evidenced by infrared spectra and titration. The methanol was removed under 0.1 mm. vacuum at 70° C. to a constant weight. This reaction product (A) was added in the amount of 0.3% by weight of the total to a propellant mix consisting of 68% by weight ammonium perchlorate of which half was 17 micron nominal diameter, and half was 200 micron nominal diameter, 16% by weight of a powdered metal fuel (aluminum), and 16% by weight of binder ingredients of which the additive (A) was part. The remaining binder ingredients were a hydroxy-terminated liquid polybutadiene, toluene diisocyanate, and a plasticizer (dioctyl adipate). After cure, the propellant exhibited much improved mechanical properties as compared to a similar propellant without (A), as tabulated below:

	Strain at break, percent		Tensile strength, p.s.i.	
Additive	77° F.	−40° F.	77° F.	−40° F.
None	31.6	30.7	72	164
0.3% of (A)	33.0	51.6	104	226

Example II

21.5 grams (0.10 mole) of tris-1-(2-methyl aziridinyl) phosphine oxide, 2.25 grams (0.03 equivalent) of tartaric acid and 5.11 grams (0.07 equivalent) of adipic acid were dissolved in 200 ml. of ethanol. The solution was warmed to about 120° F. for 24 hours, at which time essentially all the carboxyl groups in the tartaric and adipic acids were reacted. The ethanol was removed under heat and vacuum to a constant weight. This reaction product (B) was added in the amount of 0.5% of the total to a propellant mix as described in Example I. The cured propellant had greatly improved strain capability and resistance to separation of the binder from the filler as compared to a similar propellant without additive. More specifically, the propellant containing 0.5% of (B) exhibited 73% strain at failure at −40° F. whereas the similar propellant without additive exhibited 13% strain at failure at −40° F.

Example III

0.10 mole of bis-1-(2-methyl aziridinyl) phenyl phosphine oxide, 0.05 equivalent of malic acid and 0.05 equivalent of succinic acid were reacted 4 hours at reflux in a mixture of 100 ml. of methanol and 100 ml. of methylene chloride. The solvents were removed under heat and vacuum to a constant weight. The product (C) was added to a propellant mix as described in Example I in the amount of 0.25% by weight of the total. The propellant exhibited markedly improved mechanical properties as compared to a similar propellant without additive.

Example IV

0.10 mole of tris-1-(2-methyl aziridinyl) phosphine oxide, 0.04 equivalent of citric acid and 0.06 equivalent of sebacic acid were reacted as in Example I. The reaction product (D) was added to a propellant mix as in Example I in the amount of 0.75% by weight of the

total. The strain capability of the resulting propellant was greatly improved as compared to a similar propellant without additive.

Example V

Reaction product (B) from Example II was added in the amount of 0.15% of the total to a propellant of the following composition: 18% powdered aluminum, 21% 17 micron nominal diameter ammonium perchlorate 49% 200 micron nominal diameter ammonium perchlorate, and 12% binder which was made up of a mixture of hydroxy-terminated liquid polybutadiene, light hydrocarbon oil as plasticizer, antioxidant, and hexamethylene di-isocyanate. When cured, this propellant exhibited greatly improved strain capability and tensile strength as compared to a comparable propellant without additive. The exact data are as follows:

	Strain at break, percent		Tensile strength, p.s.i.	
Additive	77° F.	−40° F.	77° F.	−40° F.
None	19.7	25.5	54	120
0.15% (B)	24 2.	39.7	152	270

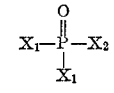
This and other data show that the effectiveness of the invention is not affected by the solids concentration or plasticizer type.

Example VI

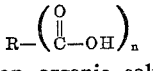
21.5 grams (0.10 mole) of tris-1-(2-methyl aziridinyl) phosphine oxide and 7.3 grams (0.10 equivalent) of adipic acid were reacted in 200 ml. of methanol at reflux for four hours. The methanol was then removed under vacuum to constant weight, and the reaction product (E) was added in the amount of 0.20% to a propellant as described in Example 1. The strain capability and tensile strength of the resulting propellant was greatly improved as compared to a similar propellant without additive, but the improvement was not as much as when a hydroxyl-containing polyacid, such as tartaric acid, comprised part of the reaction product.

I claim:

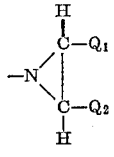
1. The reaction product formed by reacting phosphine oxides of the general formula



with organic molecules of the general formula

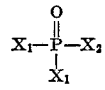


in the presence of an organic solvent, and where X_1 represents an aziridine group of the structure

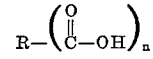


and Q_1 and Q_2 are selected from the group consisting of hydrogen or alkyl groups of one to four carbon atoms, X_2 is an organic radical, R is selected from the group consisting of an alkyl containing an active hydrogen atom and an organic entity of molecules some of which contain at least one hydroxyl group, and n is a whole number between 1 and 5, said phosphine oxides and said organic molecules being reacted in a ratio of one mole of the phosphine oxide to one carboxyl equivalent of the organic molecules, said organic solvent being selected from the group consisting of methanol, ethanol, methylene chloride, tetrahydrofuran, diethyl ether, and mixtures thereof, and said reaction product being mixed with ammonium perchlorate to form a coating on the surface of the ammonium perchlorate.

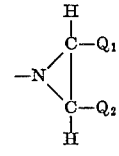
2. The reaction product formed by reacting phosphine oxides of the general formula



with organic molecules of the general formula



in the presence of an organic solvent, and where X_1 represents an aziridine group of the structure



and Q_1 and Q_2 are selected from the group consisting of hydrogen or alkyl groups of one to four carbon atoms, X_2 is an organic radical, R is selected from the group consisting of an alkyl containing an active hydrogen atom and an organic entity of molecules some of which contain at least one hydroxyl group, and n is a whole number between 1 and 5, said reaction product being combined with ammonium perchlorate, hydroxy terminated polybutadiene and a diisocyanate curing agent to form a cured propellant composition.

3. The combination as defined in claim 2 wherein said reaction product is present in the amount of about 0.05 to about 1.0 weight percent, said ammonium perchlorate is present in an amount of about 60 to 90 weight percent and said hydroxy terminated polybutadiene is present in an amount of about 10 to 20 weight percent.

4. The combination as defined in claim 3 wherein said propellant composition also contains a powdered metal of about 2 to 20 weight percent.

5. The combination of claim 4 wherein said powdered metal is aluminum.

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U.S. Cl. X.R.

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