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[54] QUINONE INHIBITORS IN ORGANOMETALLIC POLYURETHANE PROPELLANT COMPOSITIONS

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[58] **Field of Search** 149/19, 19.4, 19.2

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[57] **ABSTRACT**

A method for inhibiting the soft-center cure phenomenon encountered during the curing process of polyurethane-based propellant compositions. Inhibition is accomplished by including small amounts of an oxidant additive to the propellant mixture prior to the curing process. The addition of the oxidant material of this invention enables the formulation of an improved composite type propellant composition which includes a conventional oxidizer, a polyurethane binder material and a finely ground aluminum metal as basic constituents.

3 Claims, No Drawings

QUINONE INHIBITORS IN ORGANOMETALLIC POLYURETHANE PROPELLANT COMPOSITIONS

BACKGROUND OF THE INVENTION

This invention relates to solid propellant compositions of the composite type and to a method for their preparation. More particularly, this invention concerns itself with polyurethane-based composite solid propellant compositions and to a method for inhibiting the soft-center cure phenomenon encountered during the curing of polyurethane-based rocket fuels.

Generally, composite solid propellants are mixtures of a finely ground inorganic oxidizer dispersed within a matrix of a plastic, resinous or elastomeric material. The plastic matrix provides fuel for the combustion reaction and, in some instances, acts as a binder or adhesive for holding the propellant mixture together before combustion is initiated. In the development of composite propellants various combinations of oxidant and binder have been suggested. For example, potassium and ammonium perchlorate, as well as ammonium, sodium and potassium nitrates, have all been used in combination with various fuels such as asphalt, phenolic resin, polystyrene, butadienes, polysulfides, vinyl polymers, nitrocellulose and other similar materials. The use of these fuels as binders gives a plastic quality to the propellant mixture which allows the propellant to be cast directly into the rocket motor case. This procedure is referred to as case-bonding. It virtually eliminates the craking of solid propellants, a problem of serious proportions in the manufacture of propellant compositions.

Amongst the preferred binder materials for composite type propellants are the polyurethanes, especially when used in combination with small quantities of metal powders, such as aluminum. Oftentimes, however, certain difficulties are encountered when using aluminum powders as a propellant constituent. During the course of propellant mixing, the oxide layer on the surface of the aluminum particles is removed either by abrasion or chemical etching. Metallic aluminum is thereby exposed and reacts spontaneously with the alcohols or moisture in the binder system. A consequence of this reaction is the degradation of the ferric acetylacetonate, curing catalyst utilized in curing polyurethane-based propellants. The degradation of the catalyst results in a low cure potential for the propellant and subsequent rejection for motor manufacture. The propellants, if allowed to cure, develop a cured outer crust with the interior remaining soft or even liquid, hence the name "soft-center cure."

In attempting to overcome the problems encountered during the preparation of aluminum powder-containing polyurethane propellants, it has been found that the inclusion in the propellant mixture of small amounts of a binder soluble oxidant material as a curing additive inhibits the degradation of the ferric acetylacetonate catalyst and thus improves the cures and reproducibility of solid polyurethane propellants. In addition to the above improvement, it has also been found that the addition of binder soluble oxidants enables the manufacture of very highly loaded, 85–87 weight percent, propellants which, without the aid of these additives, are difficult to obtain.

Additive concentrations of about 0.05 to 0.1 weight percent (based on the total propellant weight) of oxidants such as sodium dichromate, lithium perchlorate, potassium ferricyanide, p-benzoquinone, tetrachloroquinone and copper chromite have been found sufficient to insure proper propellant cure.

SUMMARY OF THE INVENTION

In its broad aspect, the present invention concerns itself with an improved polyurethane based solid propellant composition and to the inhibition of the soft-center cure problem which oftentimes occurs during the formulation of aluminum powder-containing polyurethane propellants. During the mixing procedure, the protective oxide layer on the surface of the aluminum powdered particles is abraded, thus exposing the metallic aluminum to the attack of the alcoholic components of the polyurethane binder.

In accordance with the invention, however, it has been discovered that the inclusion of minor amounts of from about 0.05 to 0.1 weight percent of a binder soluble oxidant to the propellant mixture initiates a reoxidation and subsequent deactivation of the aluminum particles, thus eliminating the problem of soft-center cure.

Accordingly, the primary object of this invention is to provide for a new and improved solid propellant composition of the composite type.

Another object of this invention is to provide for a new and improved propellant composition that utilizes polyurethane binder materials together with finely ground aluminum metal as combustion ingredients.

Still another object of this invention is to provide for a method that effectively inhibits the soft-center cure phenomenon encountered during the cure of polyurethane propellants.

A further object of this invention is to provide a method which not only improves the cure and reproducibility of polyurethane propellants but also achieves the formulation and production of very highly loaded 85–87 weight percent, propellants.

The above and still further objects and advantages of the present invention will become apparent upon consideration of the following detailed description thereof.

DESCRIPTION OF THE PREFERRED EMBODIMENT

In the preferred form of this invention, it has been found that the inclusion of from about 0.05 to 0.1 weight percent of a binder soluble oxidant in a conventional aluminum powder containing polyurethane propellant composition can effectively inhibit the soft-center cure problem oftentimes encountered during the curing process of these propellants. Oxidant additives which have proved most effective as soft-center cure inhibitors are sodium dichromate, lithium perchlorate, copper chromite and potassium ferricyanide. Hydrogen acceptors such as p-benzoquinone and tetrachloroquinone have also proved sufficient in effecting a proper propellant cure. Although the hydrogen acceptors do not stop the initial aluminum-alkoxide formation, they do prevent the consequent reductive degradation of the ferric acetylacetonate catalyst used during the propellant cure.

The cure phenomenon has been aptly named soft-center or surface cure because during cure, the propellant batch frequently developed a hard crust on the surface exposed to the atmosphere. Beneath the crust, however, it remained soft, and in "heavy cases" even liquid. Extending the duration of cure will not produce any change. It is due to excess diisocyanate in the propellant which acts as chain terminator but polymerizes with moisture through formation of used linkages. The skin of such a propellant is often of a mirror-like smoothness and non-sticky. This distinguishes soft-center cure from other forms of "bad or soft-cure," in which the propellant remains more or less uniformly soft with a sticky, messy surface (probably in most cases due to excessive hydroxyl groups).

Soft-center cure is by no means a rare phenomenon. Probably 50% of the scrapped propellants and motors may be charged to its account. The particular "danger" of surface cure is its difficult detection in the accelerated cure tests, which are used for propellant qualification prior to casting. Small propellant slabs seldom show the effect, and also the temperature gradient of soft-center cure appears to be smaller than that of the urethane reaction. When a propellant exhibiting surface cure is cut, each new surface will develop a new crust of cured propellant. This however is hardly a practical way of solving the problem.

Unless deliberately provoked by excess diiscoyanate (15 and more equivalent percent excess of diiscoyanate) surface cure is only encountered with aluminized polyurethane propellants. A basic study of this cure failures of polyurethane propellants revealed that one of the most adverse factors was the result of the reaction of aluminum powder with the alcoholic ingredients of the polymeric binder system.

$$Al + 3\ ROH \rightarrow Al(OR)_3 + 3/2\ H_2 \qquad (1)$$

It also has been found that a consequence of this reaction is the degradation of the $Fe(AA)_3$ catalyst which leads to the aforementioned cure failure. The degradation of the $Fe(AA)_3$ may proceed via reduction of the Fe^{3+} to Fe^{2+} by the hydrogen evolved.

(2) $Fe(AA)_3 + \frac{1}{2} H_2 \rightarrow Fe(AA)_2 + HAA$
ferrous acetylacetone acetylacetonate (unstable)

The mechanism is based on the experimental fact that 80% and more of the $Fe(AA)_3$ has been found to be reduced to Fe^{2+} in poorly cured propellants. Also, the action of hydrogen acceptors, like p-benzoquinone, is difficult to explain by other mechanisms.

The Al-alcohol side reaction is, as said before, initiated particularly by mechanical abrasion. Highly loaded propellants are particularly sensitive. During high shear mixing, the protective oxide layer on the surface of the aluminum particles is partly abraded, thus exposing the metallic aluminum to the attack of the alcoholic binder components. If binder soluble oxidants such as $Na_2Cr_2O_7$, $LiClO_4$ and the like are present, a reoxidation and subsequent deactivation of the Al-particles occurs, thus eliminating this problem. Also, it has been found that H_2-acceptors (p-benzoquinone) are sufficient to insure propellant cure. They do not stop the initial side reaction (Al-alkoxide formation) but prevent the consequent reductive degradation of the $Fe(AA)_3$ catalyst.

The following examples are illustrative of preferred embodiments of the present invention. It should be understood, however, that these examples are not intended to limit the invention and that obvious changes may be made by those skilled in the art without changing the basic concept of the invention.

EXAMPLE I

A propellant composition was made by mixing together the following ingredients. The two modifications differ only in the quantity of cure catalyst and the grade of aluminum powder.

Ingredient	Wt %	Mod I Wt %	Mod II Wt %
$NH_4\ ClO_4$	67.000	67.000 (aluminum (123)	67.000
Aluminum (140)	18.000	18.000	18.000
$MgSO_4$ (Anh.)	0.100	0.100	0.100
Sulfur	0.100	0.100	0.100
P-benzoquinone	0.050	0.050	0.050
*FeAA	0.020	0.020	0.017
*L-45	0.005	0.005	0.005
*IDP (20%)	2.945	2.945	2.946
*PPG (70 eq)	7.824	7.824	7.826
*LHT-42 (15 eq)	2.670	2.670	2.670
*TEA (15 eq)	0.092	0.092	0.092
*TDI, Gr.II (112 eq)	1.194	1.194	1.194
	100.000	100.000	100.000

*FeAA = Ferric acetyl acetonate
IDP = Isodecyl pelargonate
PPG = Poly (1,2 oxypropylene) glycol 2000 MW
LHT-240 = Triol based on adduct of propyleneoxide and 1,2,6-hexanetriol
TEA = Triethanolamine
TDI = Toluene diioscyanate

The cured propellants, using standard JANAF dumbbell specimens in the uniaxial tension test on the Instron tensile tester, gave the following results

Tensile strength (max)	125 psi
Elongation to break	65%
Initial modulus (tangent)	550 psi
Constant strain held:	20% at 40°F and 70% RH for 2 wks.

EXAMPLE II

Propellant formulation using $Na_2Cr_2O_7$

NH_4ClO_4	69%
Al-123	8
Al-140	8
*IDP	4.0
*GTRO	0.93
*C-1	0.30
*B-2000	8.35
*HDI	1.18
Sulfur	0.08
$Na_2Cr_2O_7$	0.08
$CuSO_4$	0.08

*IDP = Isodecyl pelargonate
*GTRO = glycerol triricinoleate
*C-1 = bis(cyanoethyl)dihydroxypropylamine
*B-2000 = poly(1,2 oxybutylene)glycol 2000 MW
*HDI = hexamethylenediisocyanate.

The cured propellants gave the following uniaxial tension test results:

Temperature	77°F	−75°F
Tensile strength, psi	119	557
Elongation at break, %	60	46
Young's Modulus, psi	429	4725

The propellant batch in which Na_2Cr_2O was left out failed to cure.

EXAMPLE III

NH_4ClO_4	70%
Al-140	17%
*FeAA	0.015
$Na_2Cr_2O_7$	0.1
$CuSo_4$	0.08
Sulfur	0.05
*IDP	4.78
*TP-4040	3.40
*B-2000	2.60
*C-1	0.30
*HDI	0.67

*TP-4040 = polyoxypropylene adduct on trimethylol propane.

The cured propellant gave the following uniaxial tension test results:

Temperature	77°F	−75°F
Tensile strength, psi	117	502
Elongation, %	21	25
Young's Modulus, psi	845	4260

The propellant not containing $Na_2Cr_2O_7$ failed to cure.

There is no maximum quantity with respect to the quantity of p-benzoquinone. However, concentrations of more than 0.1% failed to further improve the cure of the propellant. In case of $Na_2Cr_2O_7$, which may be substituted for the Quinone, 0.2% appears to be the upper useful limit. The lower limit depends on the severity of the soft-center cure effect but usually no less than 0.5% was found suitable. The purpose of the additives is to obtain a positive cure of the batches. In a cure reliability study, thirty 60-lb batches of the above (modI) formulation of Example I were made not using any of the soft-center cure inhibitors. They all failed to cure, yielding approximately a ¼–178 inch crust under which the propellant remained mushy. Analysis for soluble iron of these batches showed zero $Fe(AA)_3$ i.e., all of the catalyst had been degraded to Fe_2O_3. On the other hand, over two hundred 2,000-lb batches of this formulation were mixed and cured successfully using the p-benzoquinone additive. Soluble iron content was theoretical. Less than one percent of the batches containing the p-benzoquinone failed to cure.

The following mixing procedure was used with all of the above examples. In the mix procedure, all propellant ingredients, with the exception of oxidizer, TDI and FeAA, were blended together and added to a sigma-blade mixer capable of a mix temperature that could be controlled between the desired temperatures — usually ambient to 135°F. The oxidizer was added from a hopper to the stirred fuel premix. This operation, depending on the size of the propellant batch, took from 5 to 30 minutes. After the oxidizer addition was completed, the mix temperature was usually raised to 110°F while the batch was mixed in vacuum for about 30 minutes. At this time, the toluene diisocyanate containing all the cure catalyst dissolved, was added and the mixing continued for 10 to 15 minutes. The completed batch was transferred to a casting station by means of a transfer pot. There the pot was hooked up to a casting bell and casting into the required molds was accomplished.

While the present invention has been illustrated by reference to propellant compositions formulated from specific oxidants and polyurethanes, it is to be understood that other conventional oxidizers may be employed as well as other urethane polymers provided they possess suitable combustion characteristics and comparable plasticity. The propellants may also include any of the well known and conventional additives used to obtain specific effects with composite type solid propellants.

From the foregoing description, it becomes apparent that the present invention provides for a new and improved polyurethane based solid propellant composition as well as a means for inhibiting the soft-center cure phenomenon encountered during the curing process for these propellants.

What is claimed is:

1. In an improved composite type solid propellant composition comprising a finely ground inorganic oxidizer, a polyurethane binder fuel, aluminum powder and a ferric acetylacetonate curing catalyst, the improvement which comprises the addition of about 0.05 to 0.1 weight percent of a binder soluble, soft-center cure inhibiting additive selected from the group consisting of p-benzoquinone and chloroquinone.

2. A method for inhibiting the soft-center cure phenomenon encountered during the cure of aluminum powder-containing polyurethane binder-based solid propellants comprising the step of adding to the propellant prior to curing a small amount of a binder soluble inhibiting agent selected from the group consisting of p-benzoquinone and chloroquinone.

3. A method in accordance with claim **2** wherein said inhibiting agent is added in amounts of from about 0.05 to 0.1 weight percent.

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