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INHIBITING SURFACE OXIDATION OF SOLID PROPELLANTS BY ADDING KETOXIMES

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ABSTRACT OF THE DISCLOSURE

The method of inhibiting changes that occur during storage at the surface of solid propellant grains that have a binder with unsaturated linkages, the method involving incorporating a ketoxime in the propellant composition from which the grain is made.

One of the problems presented in handling and storage of solid propellant grains in rocket motors is deterioration in properties of grain surfaces exposed to oxygen. Many of the polymers used as binders for solid propellants, for example, polybutadiene, contain unsaturated linkages, and a reaction with oxygen occurs at these sites. As a result, the chemical bond is broken or cross-linked in an unfavorable manner, and the characteristics of the grain surface are substantially altered. The surface becomes hardened, and small cracks are formed.

The most serious consequence of these changes is that ignitability of the grain is decreased so that reliability of the grain becomes questionable. After extended storage in contact with oxygen, the propellant grain must be removed and replaced with a new grain to assure reliable operation. The permissible shelf life of propellant grains, at present about 3 to 5 years for typical compositions, could be extended significantly by inhibiting the changes which occur at the surface of the grain.

It is, therefore, an object of this invention to provide a method of inhibiting changes in the surface properties of solid propellant grains.

Another object is to provide a method of inhibiting the reaction of unsaturated polymers with oxygen.

Still another object is to provide a method of extending the shelf life of solid propellant grains.

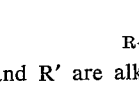
Other objects and advantages will be apparent from the following description.

In the present invention, oxidative surface changes in solid propellant grains are inhibited by providing in the grain a small amount of a ketoxime of the formula

where R and R′ are alkyl radicals. This additive decreases the extent of reaction between the surface of solid propellant grains and the oxygen to which the grains are exposed during handling and storage. The duration for which propellant grains can be stored in the presence of oxygen without loss of ignitability is substantially extended.

Although this invention is not to be understood as limited to a particular theory, it is postulated that the ketoxime inhibits surface changes primarily by preventing the cross-linking reaction which occurs between alkenic linkages in the presence of oxygen.

Any ketoxime falling within the formula



wherein R and R′ are alkyl radicals may be employed, and ethylmethyl ketoxime is preferred.

The ketoxime is provided in the propellant composition at a proportion of about 0.05 to 1.0 weight percent of the polymeric binder, a proportion of about 0.1 weight percent being preferred. Larger amounts can be used, but no further advantage is realized.

The ketoxime additive is effective for any propellant composition having an unsaturated polymer as the binder component. In general, propellant compositions comprise about 10 to 25 weight percent polymer binder, the balance of the composition being oxidizer, plasticizer, fuel particles, ballistic modifiers and the like. Unsaturated polymer binders for which the present invention is effective include carboxyl-terminated polybutadiene, hydroxyl-terminated polybutadiene, polybutadiene-acrylic acid, polysulfides and polybutadiene acrylic acid-acrylonitrile. The remaining ingredients of the propellant composition are not critical to this invention since the ketoxime does not significantly react with or affect the performance of these components.

The ketoxime can be incorporated in the propellant grain by adding it to the remaining ingredients during the usual mixing stage in preparation of the grain composition. Being a liquid, the ketoxime disperses readily throughout the propellant mixture. The processing steps normally employed for the particular propellant composition, for example, casting or extrusion and curing are not affected by the ketoxime additive.

The invention is illustrated by the following example.

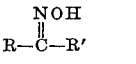
EXAMPLE

The effect of added ethylmethylketoxime on the reaction of carboxyl-terminated polybutadiene polymer with oxygen was determined by the following procedure. Commercially available carboxy-terminated polybutadiene (HC–434, Thiokol Chemical Company) was contacted with benzene to remove the beta-naphthylamine which was present as the anti-oxidant in the polymer. Tris (methylaziridinyl)phosphine oxide curing agent and the carboxyl-terminated polybutadiene were mixed in equivalent amounts, and 0.1 weight percent ethylmethylketoxime was added to one portion of the mixture. The mixtures with and without the ketoxime were cast between Teflon-coated metal plates to form films 20 to 30 mils thick. The films were exposed to oxygen at one atmosphere at a temperature of 120° C. for an extended period, and the amount of oxygen absorbed by each film was determined periodically. The film without ketoxime absorbed oxygen rapidly after an initial induction period, 170 milliliters of oxygen being absorbed in 110 hours. The film containing added ketoxime absorbed only about 42 milliliters in the same period under these conditions and only 80 milliliters in 180 hours. Reaction of the polymer with oxygen is thus substantially decreased by the additive.

The above example is merely illustrative and is not to be understood as limiting the scope of the invention, which is limited only as indicated by the appended claims.

What is claimed is:

1. The method of inhibiting surface changes in a solid propellant grain that is made of a propellant composition that has an unsaturated polymer binder as a propellant ingredient thereof, said method comprising incorporating in said propellant composition an effective amount of a ketoxime sufficient to reduce oxidation at the surface of the propellant grain, said ketoxime having the formula



wherein R and R′ are alkyl radicals.

2. The method of claim 1 wherein the concentration of said ketoxime is about 0.05 to 1.0 weight percent of said polymer binder.

3. The method of claim 2 wherein the concentration of said ketoxime is about 0.1 weight percent of said polymer binder.

4. The method of claim 1 wherein said unsaturated polymer is carboxyl-terminated polybutadiene, hydroxyl-terminated polybutadiene, polybutadiene acrylic acid, a polysulfide or polybutadiene acrylic acid-acrylonitrile.

5. The method of claim 1 wherein said ketoxime is ethylmethylketoxime.

6. The method of claim 4 wherein said ketoxime is ethylmethylketoxime.

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