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Brown et al.

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[54] **PROPELLANT INSTABILITY MODIFIER**

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[63] Continuation of Ser. No. 32,432, April 27, 1970, abandoned.

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[51] **Int. Cl.**[2] **C06B 45/34**

[58] **Field of Search** ..... 149/7, 19.9, 76; 117/100 B

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[57] **ABSTRACT**

A composite propellant composition comprising an organic binder; and an oxidizer which has been coated with the following materials: a copolymer of vinylidine and hexafluoropropylene, chlorosulfonated polyethylene, and ethylcellulose.

8 Claims, No Drawings

PROPELLANT INSTABILITY MODIFIER

This is a continuation of application Ser. No. 32,432, filed Apr. 27, 1970 now abandoned.

This invention relates in general to a solid propellant, and more particularly to a solid propellant comprising an oxidizer which has been coated with an inert material in order to stabilize the combustion of the propellant.

Recent studies on the structure of the combustion zone of a propellant has presented evidence that there are significant exothermic processes which occur on and within the solid phase. The results of these studies indicate the combustion process is controlled by two interdependent exothermic reaction zones near and on the surface of the propellant. One zone is in the gas phase at a finite distance away from the solid propellant surface and is characterized by interdiffusion of gasified oxidizer and fuel species and combustion of particles of ejected matter from the surface. The second reaction zone occurs on and within the solid propellant surface. The primary release in this zone probably occurs from chemical reactions between the initial decomposition products of the solid oxidizer and the adjacent fuel surface. Transient and steady-state combustion studies indicate that much of the pressure dependent combustion process is associated with these interfacial reactions.

The interfacial reactions at and within the surface release sufficient heat to expel partially combusted products, pyrolysis products, and fuel and oxidizer fragments into the gas phase zone above the surface where they intermix and burn completely. The maximum flame temperature is reached in the luminous zone where the largest portion of the heat is released. However, because of the relatively large mass flow perpendicular to the surface, only a small amount of heat released in the luminous flame zone reaches the surface to supplement the heat generated by interfacial reactions.

Incorporation of the exothermic chemical processes on and within the solid phase represents an important addition to the analysis of propellant combustion phenomena. Previous theoretical treatments of steady-state combustion as well as combustion instability have considered the exothermic combustion reaction to occur only in the gas phase.

It is an object of this invention to provide and disclose a method for the controlling of the contributions of interfacial reactions to the combustion process.

Other objects and a fuller understanding of the invention may be had by referring to the following description and claims.

Combustion instability has been a serious problem in operational solid propellants. A method of solving this problem in several rocket systems has been the utilization of aluminum in the propellant grain. In rocket systems wherein nonmetallized grains are utilized, attempts to stabilize combustion has involved alterations to the basic combustion chamber or fuel grain. These alterations have in turn generally reduced the reliability of the overall rocket and lowered its performance.

One method for controlling the contributions of interfacial reactions in the combustion process is to change the reactivity of the interface by coating the oxidizer particles with an inert material and preparing the propellant mix in the normal manner. The burning rate characteristics of the propellant are not seriously altered by the presence of the coating. However, the instability characteristics are substantially improved by this coating.

The coatings utilized were selected from the group consisting of Viton A which is a trade name for a copolymer of vinylidine fluoride and hexafluoropropylene; Hypalon-30, a chlorosulfonated polyethylene; and ethylcellulose.

In the conducted experimentation, ammonium perchlorate having an average particle size of 190 microns was utilized as the oxidizer. However, other suitable oxidizers may be utilized. The oxidizer was coated with the polymer utilizing a solvent/nonsolvent technique as disclosed in patent application Ser. No. 727,340 by M. E. Steinle. In the process, the selected polymer is dissolved in a suitable solvent and the required amount of oxidizer is added to the solution in a mixer. The solvent is then evaporated from the mix until the gel state of the polymer is present. A second liquid that is a nonsolvent for the polymer is then added to the polymer solution at a slow rate. This forces the polymer out of solution and around the particles of the oxidizer. A sufficient quantity of the nonsolvent is added to harden the polymer. After stirring for a specified period of time, the liquid is decanted and the coated oxidizer dried.

Specifically, 6 grams of a polymer, e.g., ethylcellulose, are dissolved in 300 grams of methylene chloride. The OH groups in the cellulose utilized have been partially or completely replaced by ethoxyl groups. The solution and 394 grams of ammonium perchlorate having a particle size of about 190 microns are added to a mixer bowl and agitated on a modified Hobart mixer at ambient temperature. During agitation, a nitrogen flush is utilized to draw off the excess methylene chloride. When the methylene chloride has been substantially removed and the mixture has the appearance of a thick gel, an initial portion of a total of 1000 ml. of Freon (1,1,2 - trichloro-1,2,2, - trifluoroethane) is added slowly with agitation to bring the ethylcellulose out of solution and to coat the ammonium chloride. At this point a small amount of a hardening agent, e.g., 0.06 gram of tetrabutyl titanate, may be added. After the mixture is agitated for a period of 15 minutes, the agitation is stopped and the liquid phase removed. A second portion of Freon is added and the coated ammonium perchlorate agitated for a period of 10 minutes. Subsequently, the liquid phase is removed and the recovered wet polymer coated ammonium perchlorate dried.

In order to evaluate the effectiveness of the coated oxidizer, a conventional propellant composition comprising 78 parts by weight of ammonium perchlorate and 22 parts by weight of an organic binder, e.g., a carboxy - terminated polybutadiene was prepared. Formulations were then prepared consisting of 78 parts by weight of ammonium perchlorate coated with 1 to 1.5 parts by weight of a polymer selected from the group consisting of: a copolymer of vinylidine fluoride and hexafluoropropylene, a chlorosulfonated polyethylene, and ethylcellulose. The coated ammonium perchlorate was then mixed with 22 parts by weight of a carboxy-terminated polybutadiene and the propellant prepared in the conventional manner.

Experimentations were conducted utilizing a "T-burner" apparatus to study the instability properties of the above prepared propellants. A measurement of the acoustic admittance was obtained. Said acoustic admit-

tance is an expression of the instantaneous burning rate exponent as a function of the frequency. This type of apparatus, which is utilized in industry for acoustic measurements, consists of a cylindrical combustion bomb with end burning charges of propellant in either or both end. By measuring the oscillating pressure at the ends of the burner, it is possible to derive the acoustic response function for the propellant under study. An example of said apparatus is disclosed by R. Stittmater, L. Watermeier and S. Pfaff, "Virtual Specific Acoustic Admittance Measurements of Burning Solid Propellant Surface by a Resonant Tube Technique," *Ninth Symposium (International) on Combustion*. New York: Academic Press (1963) pp. 311–315.

It was found that the effects of the coatings tended to reduce the surface activity and thereby the pressure sensitivity of the propellant. It was found that coating the oxidizer with 1.5 parts by weight with a copolymer of vinylidine fluoride and hexafluoropropylene reduced the maximum value of the acoustic admittance by about 50% along with a shift in the frequency at which the maximum value occurred. These effects are considered to be due entirely to the coating of the oxidizer material and not to fact that an inert material was incorporated into the propellant mix. It was found that while a polymer of chlorosulfonated polyethylene or ethyl cellulose did not significantly alter the maximum response function, they altered the frequency at which the maximum response occurred.

Although we have described our invention with a certain degree of particularity, it is understood that the present disclosure has been made by way of example and that any appropriate combinations of oxidizer and binder components may be utilized in conjunction with the inert materials without departing from the spirit and scope of the invention.

Having described our invention we claim:

1. In a propellant composition comprising an oxidizer and an organic binder component, the improvement wherein the oxidizer particle has been coated with ethylcellulose.

2. A composition in accordance with claim **1** wherein the oxidizer is ammonium perchlorate.

3. A composition in accordance with claim **2** wherein the binder is a carboxy-terminated polybutadiene.

4. A composition in accordance with claim **3** that contains the materials in the approximate weight ratio of 78 parts of ammonium perchlorate to 22 parts of carboxy-terminated polybutadiene.

5. A method of inhibiting the combustion instability characteristic of a non-aluminized propellant having an oxidizer and organic binder component; comprising the coating of the oxidizer particles with ethylcellulose.

6. A method in accordance with claim **5** wherein the oxidizer is ammonium perchlorate.

7. A method in accordance with claim **5** wherein the binder is a carboxy-terminated polybutadiene.

8. A method in accordance with claim **7** containing the approximate weight ratio of 78 parts of ammonium perchlorate to 22 parts of carboxy-terminated polybutadiene.

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