United States Patent

Low et al.

[15] **3,658,608**

[45] **Apr. 25, 1972**

[54] **HYDRAZINIUM NITROFORMATE PROPELLANT STABILIZED WITH NITROGUANIDINE**

[72] Inventors: **George M. Low,** Deputy Administrator of the National Aeronautics and Space Administration with respect to an invention of; **Vernon E. Haury,** 5059 Alta Street, Santa Susan, Calif. 93063

[22] Filed: **Sept. 23, 1970**

[21] Appl. No.: **74,861**

[52] **U.S. Cl.**....................................**149/19,** 149/20, 149/36, 149/92

[51] **Int. Cl.**..**C06d 5/06**

[58] **Field of Search**.............................149/19, 36, 92, 20, 88

[56] **References Cited**

UNITED STATES PATENTS

3,046,829	7/1962	Roemer	149/19 X
3,147,161	9/1964	Abere et al.	149/36 X
3,305,523	2/1967	Burnside	149/19 X
3,418,183	12/1968	Rice	149/19 X
3,476,622	11/1969	Harada et al.	149/19

Primary Examiner—Carl D. Quarforth
Assistant Examiner—E. A. Miller
Attorney—Monte F. Mott, J. H. Warden and John R. Manning

[57] **ABSTRACT**

The stability of solid propellant compositions containing unsaturated carboxyl terminated hydrocarbon binders and hydrazinium nitroformate as an oxidizer will have improved shelf life and stability through the incorporation of nitroquanidine in the mixture.

9 Claims, No Drawings

HYDRAZINIUM NITROFORMATE PROPELLANT STABILIZED WITH NITROGUANIDINE

ORIGIN OF THE INVENTION

The invention described herein was made in the performance of work under a NASA contract and is subject to the provisions of Section 305 of the National Aeronautics and Space Act of 1958, Public Law 83—568 (72 Stat. 435; 42 USC 2457).

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention is in the field of solid propellant compositions. More particularly, the invention relates to improved solid propellant composition containing hydrazinium nitroformate and unsaturated carboxyl terminated hydrocarbon binder.

2. Description of the Prior Art

Hydrazinium nitroformate, HNF, is a very desirable oxidizer for use in solid propellant formulations because it is very energetic, thus providing high performance. One of the most popular binders utilized in solid propellants is carboxyl terminated polybutadiene. This binder has a plurality of double bonds in the backbone. It has been found that HNF cannot be satisfactorily utilized with binders containing such double bonds, since it appears that HNF attacks the backbone of the binder, breaking down the binder chain. Pockets of gas are formed and the propellant thus swells. Further, due to the breakdown of the binder backbone, the material becomes soft. Thus, where a binder containing double bonds is utilized, a typical shelf life with HNF will range from 2 to 15 days at a temperature of 70°–90° F. Such a short shelf life prevents practical utilization of HNF with binders containing double bonds.

An additional problem in utilizing HNF in solid propellants is that it will attack many of the typical curing agents utilized. Particularly it is found that the HNF will attack the aziridine type of curing agent, such as MAPO, which is tris[1-(2-methyl)-aziridinyl] phosphine oxide. One can overcome the problem of the HNF attack on the curing agent by utilizing a curing agent such as triethyelene melamine which is not susceptible to reaction with the HNF. However, it is not possible to readily select a more suitable binder than the carboxyl terminated polybutadiene. As a result, in order to have a practical system, additional means is required to prevent reaction between the HNF and the unsaturated hydrocarbon binder.

SUMMARY OF THE INVENTION

The herein invention is based upon the discovery that if a relatively small amount of nitroguanidine is added to solid propellant formulations having unsaturated hydrocarbon binders and containing HNF, then the shelf life of the propellant is significantly increased. Thus, unexpectedly it has been discovered that if at least 2 weight percent of the nitroguanidine is utilized, the shelf life of the propellant containing HNF can be increased up to at least 5 months at ambient temperatures. The nitroguanidine is added to the propellant during its mixing phase and will remain in the composition to prevent the undesirable reaction of the HNF with the binder. It is believed the invention will be further understood from the following detailed description and example:

DESCRIPTION OF THE PREFERRED EMBODIMENTS

As has been pointed out, HNF, though being a very energetic oxidizer, appears to attack the double bonds that exist in various hydrocarbon binders utilized in solid propellants. The result of this attack is the production of a gas which swells the propellant, making it spongy or porous. The material is then no longer utilizable for rocket motors, since it will have completely unpredictable burning rates. Further, the strength of the propellant is so greatly weakened that it cannot sustain the high *g*-loads encountered in rocket motors without further disintegrating. The most typical binder that is utilized with HNF is carboxyl terminated polybutadiene. Another binder which is useful, but not as preferred is polyisoprene, which also contains double bonds susceptible to attack by the HNF. There are other solid oxidizers known to attack solid unsaturated binders, such as hydroxylamine perchlorate and hydrazine perchlorate. These other oxidizers however are not as energetic as HNF and thus the herein invention is not directed toward preventing the attack of these materials upon the unsaturated binders. These other materials are merely illustrative of the existence of the herein problem in solid propellant systems.

A typical solid propellant formulation utilizing HNF as a solid particulate oxidizer will contain on the order of 50 to 65 weight percent of the material. The unsaturated hydrocarbon binder will comprise from 5 to 25 weight percent. Additionally, there will be a solid particulate fuel such as aluminum, ranging from 5 to 20 weight percent. Propellant compositions will preferably additionally contain other materials, such as plasticizers, including hydrocarbon oils, certain esters and some nitro compounds which can range from 0 to 20 weight percent. Representative of hydrocarbon oils are Conoco H–35, a product of Continental Oil Co. and Oronite Polybutene No. 6, a product of California Chemical Co. Esters, in order to be miscible with the hydrocarbon polymer binder, must have a carbon to oxygen ratio of about 3 to 1 or higher. Dioctyl azelate and isodecyl pelargonate are typical of the preferred esters.

Nitro and nitrato compounds also are not soluble to a great extent in the polybutadiene binder when the carbon to oxygen ratio is less than about 3 to 1. Thus, the low solubility of triethylene glycol dinitrate and trimethylol ethane trinitrate where the c/o ratio is less than 1 to 1 limits their use to less than 5 parts per 100 parts of the polymer.

Further, a small amount varying from 0.2 to 1.0 weight percent of the curing agent, preferably triethylene melamine, is present to cross link the unsaturated hydrocarbon binder. It is particularly preferred to use the melamine as a curing agent since it neither attacks or reacts with HNF, unlike other various conventional curing agents that are used with the unsaturated binders.

Without further additive materials, the above general composition of a solid propellant containing HNF will decompose within a relatively short time at ambient conditions. However, upon the addition of nitroguanidine to the formulation, shelf life can be increased to the point where the propellant is useful. It has been found that at least 2 weight percent of nitroguanidine is required in the propellant formulation. This amount can vary up to 20 weight percent of the formulation, at which point no further improvement in propellant stability is seen upon further addition of the nitroguanidine. Generally it is preferred to add about 10 weight percent of the nitroguanidine to assure inhibition of gas formation due to the aforegoing reaction of the HNF.

Nitroguanidine has been previously added to various solid propellant compositions mainly to serve as a means to control the burning rate of the propellant. In the herein compositions, the nitroguanidine however performs unexpected results, since other similar materials which have been tried do not affect the reaction of HNF with the binder at all or to a minor degree as compared to the nitroguanidine. For example, two nitrocellulose stabilizers, ethyl contralite and 2-nitrodiphenylamine, when added to the composition herein in fact increased the rate of deterioration of the HNF containing propellants. Another material that had been added was resorcinol, which in some tests appeared to slightly increase the shelf life but was not nearly as effective as the nitroguanidine. Various other materials that had also been tested had no effect, or in fact accelerated the deterioration. Thus, unexpectedly nitroguanidine inhibited the reaction of the HNF with the binder to provide a useful propellant composition.

The nitroguanidine is obtained in a powder form and can be added at any time during the mixing of the propellant ingredients. In the mixing of the propellant, normally the binder and plasticizer are first mixed with the fuel then the oxidizer is added thereto. The nitroguanidine is often added with the fuel.

It is believed the invention will be further understood from the following detailed examples.

EXAMPLE I

A propellant formulation was made by mixing in weight percent 10.92 percent of carboxy terminated polybutadiene, 0.34 weight percent triethylene melamine, 4.74 percent Conoco H–35, which is a hydrocarbon oil with a low viscosity, 16 percent aluminum powder, and 68 percent HNF. The carboxy terminated polybutadiene, plasticizer and aluminum fuel were mixed for five minutes in a Baker-Perkins vertical mixer. The HNF was added thereto in three increments, mixing for 10 minutes after each addition. Finally, the curing agent was added and mixing was continued for 10 minutes in vacuum to obtain a void-free mix. This propellant cured in about 24 hours at ambient temperature. Swelling and porosity of the propellant mixture became evident after 6 days at ambient temperature.

EXAMPLE II

A composition containing 13.9 weight percent carboxyl terminated polybutadiene, 0.6 weight percent triethylene melamine, 3.5 weight percent Conoco H–35, 10 percent aluminum powder and 62 percent HNF was formulated as described in Example I. To this composition during the mixing thereof was added 10 percent nitroguanidine. The propellant was cast into plastic containers which had a length to diameter ratio of 3. The propellant cured in about 24 hours at ambient temperature then was stored at ambient temperature and was examined frequently.

The above formulation of this example showed no deterioration such as swelling or softening after 5 months storage at ambient temperatures.

EXAMPLE III

To indicate that nitroguanidine appeared to particularly achieve the unexpected results of the herein invention a related compound, cyanoguanidine, was utilized as an additive to the propellant formulation. A composition was thus formulated containing 12.4 percent carboxy terminated polybutadiene, 0.5 percent triethylene melamine, 3.1 percent Conoco H–25, 10 percent aluminum powder, 68 percent HNF, and 6 percent cyanoguanidine. The resulting cured composition began swelling 13 days after mixing at ambient temperature.

Thus, as can be seen from the examples and above description, nitroguanidine unexpectedly and peculiarly serves to inhibit a reaction between HNF and unsaturated hydrocarbon binders, particularly carboxyl terminated polybutadiene. No theoretical explanation for the effect of nitroguanidine has been developed. The possibility that the stabilizing effect might be due to the nitramino group ($-NHNO_2$) was considered. Ethylene dinitramine, containing two of these groups, however, was not effective.

I claim:

1. A solid propellant composition comprising:
an unsaturated carboxyl terminated polymeric hydrocarbon binder,
hydrazinium nitroformate is an amount sufficient to act as an oxidizer,
a suitable curing agent for said binder,
and nitroguanidine as an amount sufficient to improve the shelf life of the composition.

2. The composition of claim 1 wherein said binder is carboxyl terminated polybutadiene.

3. The composition of claim 1 wherein said curing agent is triethylene melamine.

4. The composition of claim 1 further comprising:
a solid particulate metal fuel.

5. A solid propellant composition comprising:
5 to 25 weight percent of unsaturated carboxyl terminated polymeric hydrocarbon binder,
50 to 65 weight percent hydrazinium nitroformate,
0.2 to 1.0 weight percent of a curing agent for said binder,
and 2 to 20 weight percent nitroguanidine.

6. The composition of claim 5 further comprising:
5 to 20 weight percent of a solid particulate metal fuel.

7. The composition of claim 6 wherein said binder is carboxyl terminated polybutadiene.

8. The composition of claim 7 wherein said curing agent is triethylene melamine.

9. The composition of claim 5 additionally comprising:
up to 20 weight percent of a suitable plasticizer for said binder.

* * * * *