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15 Claims 10

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3,697,340 HOMOGENEOUS SOLID SOLUTION OXIDIZING

COMPOSITION Clyde J. Swedenberg, Oxon Hill, Md., and Manfred J. Cziesla, Washington, D.C., assignors to the United States of America as represented by the Secretary of

the Navy No Drawing. Filed May 13, 1969, Ser. No. 826,081 Int. Cl. C06f 1/04 15 Clair

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ABSTRACT OF THE DISCLOSURE

A homogeneous solid solution oxidizing composition which is the result of the admixture of a hydroxylam- 15 monium salt and a hydrolyzed polymer or certain other polar polymer binder materials, e.g., polar polymers containing poly-hydroxyl, poly-amine, poly-ester and polycarboxyl functionality.

BACKGROUND OF THE INVENTION

This invention relates generally to oxidizing compositions and more particularly to a homogeneous solid solution oxidizing composition useful for propellants and 25 explosives.

In the past, propellant compositions which employed solid oxidizing compositions have been of the non-homogeneous composite type wherein the crystalline oxidizers were suspended in a resinous binder. One significant disadvantage of these composite type propellants is the influence of the particle size of the ingredients upon the total efficiency of the propellant. For example, at times it is necessary to use combinations of particle sizes of an ingredient (i.e., bimodal or multimodal distributions) in order to achieve optimum packing and processibility. Furthermore, changes in particle size result in variations in the available surface of ingredients and therefore affect the rates of reaction involved. Even more important, the variation in rate of reaction affects the burning rate of the propellant, which must be carefully controlled in order to fulfill the mission. Obviously, all these checks on the control of particle sizes are tedious and time consuming.

Recently, a new class of solid oxidizers, in the form of hydroxylammonium salts, such as hydroxylammonium perchlorate (HAP) and hydroxylammonium nitrate (HAN) have been found to be extremely useful as such in liquid monopropellant compositions. However, attempts to employ these hydroxylammonium salts as solid oxidizers in conventional composite type propellant compositions (i.e., with conventional resinous binder materials) have met with very little success. In addition to the general disadvantages of composite type compositions as hereinbefore discussed, several other factors may be attributed to this unsuccess. Firstly, the hydroxylammonium salts are such chemically strong oxidizing agents that they disrupt the cross-linking of these conventional binder materials. Secondly, because of the low 60 melting points of the hydroxylammonium salts, the solid oxidizing compositions containing them exhibit changes in properties during their utilization which cause unstable burning and other deleterious effects. For example, when the hydroxylammonium salts are combined with conventional binders and incorporated within a rocket motor casing, the crystals of the salt oxidizer change in apparent volume at their melting point and cause the binder material to break up and form cracks, which allow for increased internal pressure and eventual rupturing of the motor. Furthermore, the low melting points of the hydroxylammonium salts completely preclude their utiliza2

tion in air-launched missiles or launching vehicles because the heat encountered from air friction alone causes the salts to melt.

Another problem which exists with the use of solid hydroxylammonium salt oxidizing composition is the extreme hygroscopicity of the salts.

SUMMARY OF THE INVENTION

It is therefore one object of this invention to provide new hydroxylammonium salt oxidizing compositions.

Another object of this invention is to provide a hydroxylammonium salt oxidizing composition wherein no influence of particle exists.

Still another object of this invention is to provide an oxidizing composition which comprises a hydroxylammonium salt in solid form but which does not exhibit any deleterious changes in properties at the melting point temperature of the salt.

It is a further object of this invention to provide a hydroxylammonium salt oxidizing composition which is 20 substantially non-hygroscopic.

These and other objects are accomplished by providing a homogeneous solid solution of a hydroxylammonium salt oxidizer dissolved in a suitable polymer binder material.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The solid solution oxidizing compositions of the present invention are prepared by dissolving, preferably at ele-30 vated temperatures, a melted hydroxylammonium salt such as hydroxylammonium perchlorate (HAP), hydroxylammonium nitrate (HAN) or derivatives thereof, e.g., the N-methyl, N-ethyl, O-methyl and O-ethyl derivatives, and mixtures thereof in a suitable polymer binder 35 material or vice versa, i.e., wherein the binder is dissolved in the oxidizer salt. Although, any polymer material that is capable of forming a solid solution with the hereinbefore identified hydroxyl-ammonium salt oxidizers may be employed in the practice of this invention, prefer-40 ably polymers containing polyhydroxyl, poly-amine, polyester and poly-carboxyl functionality are used. Specifically, some of these are polyvinylalcohol, polyvinylacetate, partially hydrolyzed polyvinylacetate, and polyvinylpyrrolidone and copolymers of these materials. The molecular weights of the polymers employed are not critical but

preferably are in the range of from about 20,000 to 200,000.

The ratio of the materials comprising the oxidizing compositions of the present invention may vary within 50 a wide range, e.g., about 30-85 percent-by-weight oxidizer to 70-15 percent-by-weight binder may be used, but preferably the ratio employed is that which provides the greatest amount of oxidizer salt to the least amount of binder polymeric material and the greatest efficiency. 55 This, of course, is dependent upon the particular binder polymer employed and its solubility relationship with the particular hydroxylammonium salt employed.

The resultant oxidizing composition is a homogeneous solid solution wherein the hydroxylammonium salt oxidizer is completely enveloped by the polymer binder material. An alternative procedure which may be used to prepare the solid solution oxidizing compositions of the present invention is to dissolve both the hydroxylammonium salt or mixtures thereof and the binder pol-65 ymeric material in a common solvent, such as methanol, ethanol, water, etc., and subsequently evaporate the solvent.

Many additives may be added to the oxidizing compositions without departing from the scope of the present 70 invention. For example, the compositions may be modified by the addition of (a) fuels such as aluminum,

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beryllium and additional polymers, (b) plasticizers, (c) burning rate modifiers, (d) stabilizers, and (e) small amounts of other soluble oxidizers such as lithium perchlorate, ammonium perchlorate and ammonium nitrate. Preferably, however, the additives should not comprise more than 50 percent by weight of the total oxidizing composition.

A preferred oxidizing composition within the scope of the present invention is the homogeneous solid solution of hydroxylammonium perchlorate (HAP) in poly- 10 vinyl alcohol, modified by the addition of aluminum.

The general nature of the invention having been set forth, the following examples are presented as specific illustrations thereof. It will be understood that the invention is not limited to these examples, but is susceptible 15 monium nitrate, N - methyl-hydroxylammonium perto different modifications that will be recognized by one of ordinary skill in the art.

EXAMPLE 1

Composition percent weight

HAP 81.0

Polyvinyl alcohol 19.0

The composition of Example 1 has a specific impulse of 250 seconds.

EXAMPLE 2

Composition percent weight

HAN 80.0

Polyvinyl alcohol 20.0

The composition of Example 2 has a specific impulse of 236 seocnds.

EXAMPLE 3

Composition percent weight

HAP 60.0 Polyvinyl alcohol 15.0

Aluminum 25.0

The composition of Example 3 has a specific impulse of 262 seconds and a density impulse of 509 seconds.

EXAMPLE 4

Composition percent weight

HAN 55.0 Polyvinyl alcohol 15.0 Aluminum 30.0

The composition of Example 4 has a specific impulse of 264 seconds.

EXAMPLE 5

Composition percent weight

HAP 70.0

Polyvinyl alcohol 30.0

The composition of Example 5 has a burning rate of 1.35 inches/sec. at 77° F. and 500 lb./sq. in. pressure 55 and 3.9 inches/sec. at 77° F. and 2500 lb./sq. in.

Obviously numerous modifications and variations of the present invention are possible in light of the above teachings. It is therefore to be understood that within the scope of the appended claims the invention may be 60 practiced otherwise than as specifically described herein.

What is claimed and desired ot be secured by Letters Patent of the United States is:

We claim:

1. An oxidizing composition comprising a hydroxyl- 65 S. J. LECHERT JR., Assistant Examiner ammonium salt and a polymeric binder material capable of forming a solid solution with said salt; wherein said salt is selected from the group consisting of hydroxyl-

4

ammonium perchlorate, hydroxylammonium nitrate, Naminohum perchlorate, hydroxylaminohum mrate, N-methyl-hydroxylammonium perchlorate, N-ethyl-hydroxylam-monium nitrate, N - ethyl - hydroxylammonium nitrate, O - methyl - hydroxylammonium per-chlorate, O-ethyl-hydroxylammonium perchlorate, O-methyl-hydroxylammonium nitrate, O-ethyl hydroxylammonium nitrate, and mixtures thereof and said polymeric binder material is selected from the group consisting of polyhydroxyl polymers, poly-ester polymers, poly-carboxyl polymers, and poly-amine polymers.

2. The oxidizing composition of claim 1 wherein said hydroxylammonium salt is selected from the group consisting of hydroxylammonium perchlorate, hydroxylamchlorate, N - ethyl-hydroxylammonium perchlorate, Nmethyl-hydroxylammonium nitrate and N-ethyl-hydroxylammonium nitrate and mixtures thereof.

3. The oxidizing composition of claim 1 which fur-20 ther includes a material selected from the group consisting of fuels, plasticizers, burning rate modifiers, stabilizers and other soluble oxidizers.

4. The oxidizing composition of claim 2 wherein the hydroxylammonium salt is hydroxylammonium per-25 chlorate.

5. The oxidizing composition of claim 2 wherein said hydroxylammonium salt is hydroxylammonium nitrate. 6. The oxidizing composition of claim 2 wherein said polyhydroxyl polymer is polyvinylalcohol.

7. The oxidizing composition of claim 2 wherein said polyamine polymer is polyvinylpyrrolidone.

8. The composition of claim 1 wherein the weight of said salt varies from about 30-85 percent by weight of said composition and the weight of said binder material 35 varies from about 70-15 percent by weight of said composition.

9. The composition of claim 10 wherein the weight of said salt varies from about 30-85 percent by weight of said composition and the weight of said binder ma-40 terial varies from about 70-15 percent by weight of said composition.

10. The composition of claim 9 comprising hydroxylammonium perchlorate as the salt and polyvinyl alcohol as the polymeric binder material.

11. The composition of claim 10 additionally containing a fuel.

12. The composition of claim 11 wherein said fuel is aluminum.

13. The composition of claim 11 wherein said fuel 50 not comprise more than 50 percent by weight of the total oxidizing composition.

14. The composition of claim 13 wherein said aluminum does not comprise more than 50 percent by weight of the total oxidizing composition.

15. The composition of claim 9 comprising hydroxylammonium nitrate as the salt and polyvinyl alcohol as the polymeric binder material.

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