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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, D.C. 20546

SEP 16 1974

REPLY TO
ATTN OF: GP

TO: KSI/Scientific & Technical Information Division
Attn: Miss Winnie M. Morgan

FROM: GP/Office of Assistant General
Counsel for Patent Matters

SUBJECT: Announcement of NASA-Owned U.S. Patents in STAR

In accordance with the procedures agreed upon by Code GP and Code KSI, the attached NASA-owned U.S. Patent is being forwarded for abstracting and announcement in NASA STAR.

The following information is provided:

U.S. Patent No. : 3,830,673

Government or Corporate Employee : Cal/Tech Pasadena, CA

Supplementary Corporate Source (if applicable) :

NASA Patent Case No. : NPO-11,975-1

NOTE - If this patent covers an invention made by a corporate employee of a NASA Contractor, the following is applicable:

YES ☒ NO ☐

Pursuant to Section 305(a) of the National Aeronautics and Space Act, the name of the Administrator of NASA appears on the first page of the patent; however, the name of the actual inventor (author) appears at the heading of column No. 1 of the Specification, following the words "...with respect to an invention of ..."

Bonnie L. Woerner

Bonnie L. Woerner
Enclosure

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**United States Patent** [19]
**Fletcher et al.**

[11] **3,830,673**
[45] **Aug. 20, 1974**

# [54] PREPARING OXIDIZER COATED METAL FUEL PARTICLES

[76] Inventors: **James C. Fletcher,** Administrator of the National Aeronautics and Space Administration with respect to an invention of; **John I. Shafer,** 775 Linda Vista Ave., Pasadena, Calif. 91103; **George M. Simmons,** 3158 Sawtelle Blvd. No. 1, Los Angeles, Calif. 90066

[22] Filed: **Feb. 2, 1973**

[21] Appl. No.: **329,243**

[52] **U.S. Cl.** ......................... **149/17,** 149/60, 149/76
[51] **Int. Cl.** ............................................ **C06b 19/02**
[58] **Field of Search** ............... 149/5, 19, 20, 60, 76, 149/17

[56] **References Cited**

UNITED STATES PATENTS

| | | | |
|---|---|---|---|
| 2,168,562 | 8/1939 | Davis | 149/17 |
| 3,350,245 | 10/1967 | Dickinson | 149/19 |
| 3,370,537 | 2/1968 | Tepper | 102/87 |
| 3,440,292 | 4/1969 | Allen | 149/19 X |
| 3,706,608 | 12/1972 | Geisler | 149/19 |
| 3,715,246 | 2/1973 | Sayles | 149/19 |

*Primary Examiner*—Leland A. Sebastian
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## [57] ABSTRACT

Solid propellant composition of improved efficiency including an oxidizer, particularly ammonium perchlorate, and a powdered metal fuel, preferably aluminum or beryllium, in the form of a composite, the powdered metal fuel being contained in the crystalline lattice framework of such oxidizer, and hence being occluded within the oxidizer particles, as well as being disposed in the interstices between the oxidizer particles of the composition, such propellant composition produced by a process comprising crystallizing ammonium perchlorate in water, in the presence of finely divided aluminum or beryllium. A suitable binder is incorporated in the propellant composition to bind the individual particles of metal and particles of oxidizer containing occluded metal, together.

**4 Claims, 3 Drawing Figures**

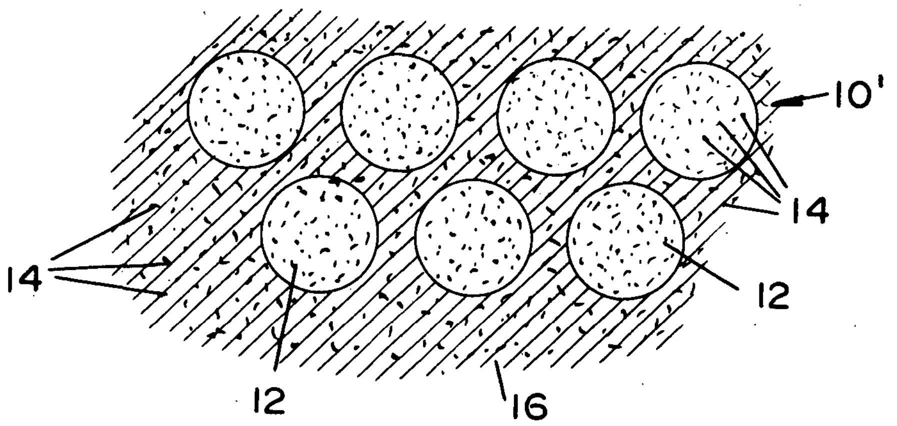


FIG. 1

PRIOR ART

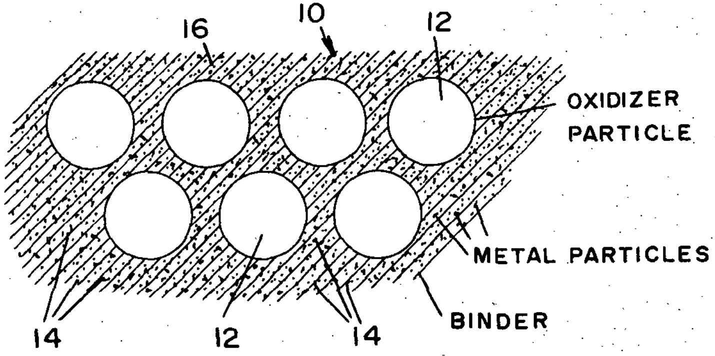


FIG. 2

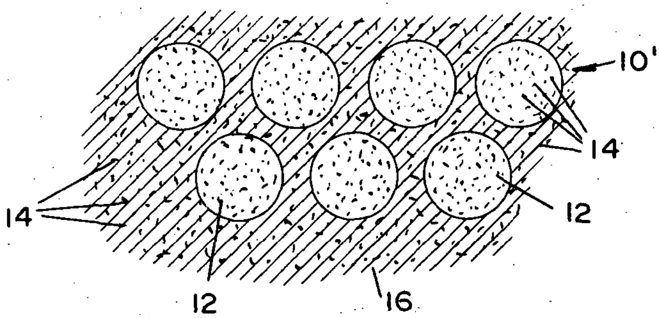
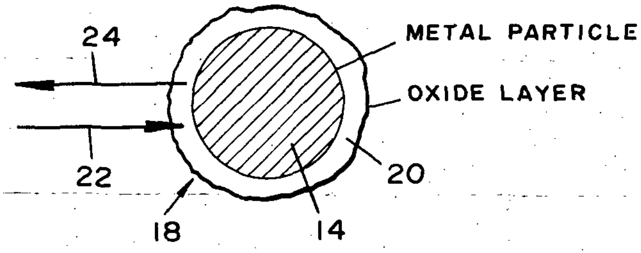


FIG. 3

PRIOR ART



# PREPARING OXIDIZER COATED METAL FUEL PARTICLES

## ORIGIN OF 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 85-568 (72 Stat. 435; 42 USC 2457).

## BACKGROUND OF THE INVENTION

### 1. Field of the Invention

The present invention is directed to new and improved readily ignitable or burnable compositions, particularly solid propellants, and is more particularly directed to the production of a novel solid propellant composition of improved efficiency, comprising ammonium perchlorate oxidizer having finely divided burnable metal, particularly aluminum or beryllium, substantially uniformly distributed throughout the particles of such oxidizer and the propellant composition, and to the method of preparing such composition.

Composite solid propellants generally include an oxidizer, metal fuel and binder. In preparing such solid propellants, it is conventional practice to mechanically mix the oxidizer and the metal fuel, together with the binder, followed by curing the binder in the usual manner. As presently practiced, in the resultant solid propellant the oxidizer occupies the major percentage of the weight and volume of the propellant and the metal is located in the void spaces or interstices between the large oxidizer particles. This arrangement concentrates the metal fuel in a relatively small volume of the propellant. When the propellant is burned, large spheres of metal are observed near the burning surface. These relatively large masses of metal are difficultly removed with the gas phase, and as the oxide layer is formed, it tends to encapsulate the metal, particularly in the case of beryllium, causing lower burning rate and incomplete combustion. The presence of large particles of metal particularly increases the two phase flow losses, the two phase system being that composed of the solid metal particle phase and the gas phase. In metal fueled solid propellants of this type, it is considered that agglomerization of the metal during burning often results in substantially decreased burning efficiency, generally designated as $I_{sp}$ efficiency, where $I_{sp}$ is the impulse delivered per unit mass. This phenomonen is particularly apparent in propellants containing beryllium, and in both beryllium and aluminum propellants when burned at low pressure, e.g. of the order of about 100 psia.

### 2. Description of the Prior Art

The following patents are representative of the prior art.

U.S. Pat. No. 3,257,801 discloses a pyrotechnic composition formed by mixing aluminum powder and boron powder and an oxidizer such as potassium perchlorate. U.S. Pat. No. 3,370,537 is directed to a combustible or pyrotechnic composition wherein a metal phase such as aluminum, is dispersed in a continuous solid phase, e.g. a metal chlorate, by slurrying the powdered metal in the molten salt, and the mixture cooled to solidify the molten salt. U.S. Pat. No. 2,168,562 discloses an inorganic nitrate explosive comprising a solid dispersion of ammonium nitrate and a sensitizer such as aluminum, such dispersion resulting from precipitation of the ammonium nitrate with such sensitizer from substantially anhydrous liquid ammonia, followed by expelling the free ammonia.

One method for reducing the amount of agglomerization of the metal fuel in the propellant is to lower the percentage amount of metal therein. However, this decreased metal content also results in decreased $I_{sp}$.

The chief object of the present invention and concept is to spread or distribute the metal fuel, particularly aluminum, uniformly throughout the propellant by incorporating such metal into the oxidizer particles, particularly ammonium perchlorate particles, by simple, convenient and relatively inexpensive procedure, for production of a low burning rate low pressure propellant. Thus, the maximum local concentration of the metal is reduced, thereby substantially reducing undesirable agglomerization, while maintaining the overall level of metal percentage in the propellant.

## DESCRIPTION OF THE INVENTION

In accordance with the invention, an improved solid propellant of increased efficiency is provided, comprising an oxidizer, preferably ammonium perchlorate, and small particles of powdered metal fuel, such as aluminum or beryllium, contained in the crystal lattice of the oxidizer, and thus occluded within the particles of oxidizer, as well as uniformly distributed in the voids or interstices between the oxidizer particles. Thus the high local concentration of metal contained in the voids or spaces between oxidizer particles in conventional propellants, is avoided and a substantially even distribution of the fine metal fuel throughout the entire propellant, including incorporation of the metal within the oxidizer particles, as well as in the spaces between particles, is achieved.

The inorganic metal-oxidizer material of the improved propellant composite according to the invention is obtained by the simple procedure of crystallizing the oxidizer from aqueous solution in the presence of finely divided metal such as aluminum or beryllium, to produce the uniformly occluded product combining burnable metal and an oxidizer, and removing the crystalline product from the water and drying. A suitable binder such as a polyurethane is then mixed with the metal-oxidizer material crystallized from aqueous solution, and the mixture is cured to produce the final propellant composition. The resulting propellant composition is a low burning rate propellant having high efficiency, of the order of 90 percent or greater, when burned at low pressure of the order of about 100 to 200 psia.

The accompanying drawing illustrates the improved propellant composition of the invention over a prior art propellant composition.

In the drawing

FIG. **1** is a simplified illustration of a composite metallized propellant of the prior art;

FIG. **2** illustrates the composite metallized propellant comprised of oxidizer particles with occluded metal fuel, according to the present invention; and

FIG. **3** illustrates the burning of prior art propellant of the type illustrated in FIG. **1**, wherein metal agglomerates with an oxide coating formed on the surface thereof are present, and particularly characteristic of propellant containing beryllium.

In FIG. **1**, illustrating the propellant according to the prior art, it is seen that the propellant indicated at **10** is composed of relatively large oxidizer particles **12** with fine metal particles **14**, such as fine aluminum or beryllium particles, located in the spaces between the large oxidizer particles **12.** The propellant contains a binder **16** which binds the oxidizer particles **12** and metal particles **14** together to form the composite metal propellant. It is seen in FIG. **1** that the concentration of metal particles **14** is localized in the spaces between the large oxidizer particles **12**, and hence in such spaces between oxidizer particles, the metal concentration is substantially higher than the overall concentration of metal in the propellant composite.

On the other hand, according to FIG. **2** illustrating a propellant **10′** according to the present invention, the metal, e.g. aluminum particles **14**, are occluded within the oxidizer particles **12**, as well as being distributed in the voids or interstices between the oxidizer particles, and hence the metal particles are substantially uniformly distributed or dispersed throughout the entire propellant composite, and such lowering of the localized metal concentration in the binder **16** between oxidizer particles markedly affects and reduces the agglomerization of the metal particles during burning.

FIG. **3** shows a metal agglomerate **18** comprising a metal particle of beryllium **14** having an oxide coating or layer **20** thereon, produced during the burning of a conventional composite metal propellant containing beryllium particles illustrated in FIG. **1.** During burning, the oxidizer gases from the oxidizer particles **12** must diffuse through the oxide layer **20** to reach the metal fuel particles **14**, as indicated by the arrow **22**, or the metal vapor from the metal particles **14** must diffuse through the oxide layer **20** outwardly, to meet the oxidizer gases, as indicated by the arrow **24.** The effect of the oxide layer is proportional to its thickness. The greater the thickness of the oxide layer the lower the burning efficiency, and the presence of such large particles of metal oxide also increases the two phase losses, that is the losses resulting from the large solid phase particles being accelerated by the gas phase out the rocket nozzle. In the case of aluminum, the oxide formed does not completely encapsulate the free metal particles, but rather forms a cap on one side of the particle, and also contributes to two phase flow losses, the amount of which is proportional to the size of such metal agglomerate.

The composite of the invention illustrated in FIG. **2**, containing occluded metal within the oxidizer particles substantially reduces or hinders the formation of large metal agglomerates of the type illustrated in FIG. **3**, and decreases the thickness of any oxide layer **20** formed on the respective metal particles, and increases the total surface area available for combustion, thus improving combustion efficiency. Two phase flow losses are reduced by the reduction in size of the metal oxide particles formed.

The preferred oxidizer for producing the propellant composition of improved efficiency according to the invention, is ammonium perchlorate. However, ammonium nitrate has also been found effective. These oxidizers are readily soluble in water to form a saturated solution, perferably at elevated temperature for example 50° to 90°C, from which crystallization of the ammonium perchlorate or ammonium nitrate can occur by suitable cooling, and the crystals of such oxidizer, together with occluded metal fuel such as aluminum, are readily removed from the aqueous medium, as described in greater detail below.

The metal fuels employed in producing the solid propellant composition of the invention are aluminum and beryllium. Aluminum is the preferred metal fuel, since in propellants employing beryllium as the metal fuel, an oxide layer of the type illustrated at **20** in FIG. **3** tends to form, wherein oxidizer gases must diffuse through the oxide layer to reach the metal fuel or the metal vapor must diffuse to meet the oxidizer gases, such diffusion process decreasing the speed at which the particle burns and thus decreasing performance. On the other hand, when employing aluminized propellants according to the invention, utilizing aluminum as the metal fuel, the mass of such oxide layer on the metal fuel, as previously noted, is decreased due to reduced size of the metal agglomerate formed. Moreover, where beryllium is employed, since beryllium metal is not readily wetted by water, it is necessary to employ a passivated beryllium, for example beryllium containing a chromate coating, which is suitably wetted when in contact with water used as the solvent for the oxidizer.

As previously noted, the method for achieving the metal dispersion, e.g. an aluminum dispersion, throughout the above-noted oxidizer, preferably ammonium perchlorate, comprises crystallizing the oxidizer from aqueous solution in the presence of small particles of the suspended metal fuel. Water is saturated with oxidizer at an elevated temperature e.g., 80°C and the metal is incorporated. The entire solution is agitated or stirred by suitable means to maintain the metal suspended, and is cooled slowly to a reduced temperature to produce crystallization. Thus, for example, cooling of the metal suspended-oxidizer aqueous solution can be carried out down to any lower temperature below the elevated initial temperature of the solution, for example down to as little as 5°C below such elevated temperature, or such cooling can be carried out down to a temperature at or below room temperature, e.g. down to about 5°C or lower, crystallization at these lower temperatures taking place in a short period from about 5 minutes, and up to a couple hours at higher temperatures. The resulting product consists of the crystallized oxidizer, particularly ammonium perchlorate, with metal, preferably aluminum, occluded in and/or on the surfaces of the particles of the oxidizer.

In carrying out the above process, small particle size metal fuel, e.g. fine aluminum or aluminum powder, is employed. The particle size of the metal fuel, e.g. aluminum, ranges generally from about 1 to about 30 microns, preferably about 3 to about 20 microns, with mixtures of varying sizes within these ranges being suitable.

The particle size of the oxidizer, e.g. ammonium perchlorate, initially employed for solution in the water, can be any size which will readily dissolve in water in a short time, for example ammonium perchlorate or ammonium nitrate having a particle size of the order of about 200 microns. However, following crystallization of the inorganic composition comprising the oxidizer particles with occluded metal such as aluminum, it is preferred to control the size of the resulting particles of oxidizer and occluded metal. Generally such particle size can range up to 400 microns, and usually the propellant composition following its crystallization from water is processed by screening to a mixture having varying particle sizes ranging from about 10 to about 200 microns. The smaller particles of metal occluded oxidizer in such mixture are intended to be introduced into and fill in the voids between the larger particles of metal occluded oxidizer, as described in detail below. Thus for example mixtures of oxidizer such as ammonium perchlorate and aluminum metal fuel having the exemplary distribution of particle sizes noted below can be employed:

a. 75 percent composed of 200 micron particles, 25 percent composed of 12 micron particles;
b. 50 percent composed of 400 micron particle size, 35 percent of 200 micron size and 15 percent of 50 micron size.

The oxidizer, e.g. ammonium perchlorate, is employed in major proportion, generally ranging from about 65 to about 99 percent, preferably about 75 to about 90 percent, by weight of combined oxidizer plus metal. The metal fuel, e.g. aluminum, is employed in minor proportion generally from about 1 to about 35 percent, preferably about 10 percent to about 25 percent, by weight of the combined oxidizer plus metal. In carrying out the procedure for producing the propellant composition according to the invention, as noted above, the amount of metal fuel, e.g. aluminum, incorporated in the oxidizer, preferably ammonium perchlorate, is calculated with respect to the amount of oxidizer to be crystallized from the aqueous solution, so that the final propellant will contain the desired proportions of metal fuel and oxidizer within the above-noted ranges.

As previously noted, water is the preferred solvent for crystallizing out the metal fuel occluded-oxidizer particles employed for producing the propellant composition of the invention, since as previously pointed out, ammonium perchlorate and ammonium nitrate are highly soluble in water and can be readily crystallized therefrom, with the fine particles of metal fuel, e.g. aluminum, incorporated in the crystal lattice of the oxidizer and hence occluded in the particles of the oxidizer. In addition, the crystals of metal fuel occluded-oxidizer formed in the aqueous medium can be readily removed therefrom as by decantation or filtration. Further, the use of water is convenient, safe and economical. Although tap water can be employed, high purity water, such as deionized or distilled water preferably is employed. Thus, the use of expensive and dangerous solvents such as the anhydrous liquid ammonia of the prior art as illustrated in above U.S. Pat. No. 2,168,562 is avoided, together with any problems inherent in freeing ammonia from the precipitated propellant.

Following crystallization, the crystallized oxidizer particles, e.g. ammonium perchlorate, containing occluded metal fuel, e.g. aluminum, together with free aluminum particles, are removed from the aqueous medium by suitable means such as decantation, followed by filtration, and the resulting mixture is dried, as by washing with ethyl alcohol, followed by heating, e.g. in a vacuum oven. The resulting composition containing the ranges of proportions of oxidizer and metal fuel noted above is adapted for use in a solid propellant by addition of a binder.

Any suitable conventional organic binder material which burns and is readily decomposable can be employed for binding the metal fuel particles and oxidizer particles containing occluded metal fuel of the above-described novel composition, to form the solid propellant of the invention. Such binder in effect adds to the fuel of the propellant. Thus, suitable organic polymeric binders include thermoplastic, thermosetting, elastomeric, polymeric and plastic materials of various types. Such materials can be either naturally occurring, or synthetically produced.

Among thermoplastic material which can be employed as binders are polymers and copolymers of mono-olefinic hydrocarbons such as polyethylene, polypropylene and polybutene. Illustrative examples of thermosetting polymers include polyurethane resins, epoxide resins and polyesters. In addition, elastomers such as the natural and synthetic rubbers may be employed which are generally polymers and copolymers of a diolefin with other olefin constituents which can be cured or vulcanized to cross link the polymer. These include polybutadiene, butadiene-styrene and butadiene-acrylonitrile polymers and copolymers. Preferred binders employed according to the present invention include polyether polyurethane and hydroxy terminated polybutadiene.

Additional binders which can be employed include polyamides, vinyl polymers such as polyvinyl acetate, polyvinyl chloride and the like, cellulose esters such as cellulose acetate and cellulose acetate-butyrate, ethylcellulose, formaldehyde resins such as urea-formaldehyde resin, phenol-formaldehyde and melamine-formaldehyde resin, and silicone resins.

A detailed list of binder materials is given in U.S. Pat. No. 3,257,801, noted above, and such materials can be employed as binders for the solid propellant of the present invention.

If desired, plasticizers such as the phthalates, e.g. dibutyl phthalate or dioctyl phthalate, can also be incorporated in the binder, but are not necessary.

Burning catalysts to obtain a higher burning rate such as metal oxide burning catalysts, e.g. ferric oxide or chromic oxide, can be used in the propellant composition of the invention, but are not necessary. For producing the propellant of the invention, it is preferred not to employ a burning catalyst since the solid propellant of the present invention is specifically designed as a low pressure-low burning rate propellant.

The amount of binder material which can be employed in the solid propellant can vary. However, generally about 5 to about 25 percent, preferably about 10 to about 20 percent, of polymeric binder is employed by weight of the total composition of propellant, including metal fuel and oxidizer, and binder.

The resulting finished propellant composition contains the metal fuel, e.g. aluminum, particles uniformly distributed or dispersed throughout the mass of the propellant including the spaces or voids between the oxidizer particles, as well as occluded in such oxidizer particles, the metal occluded oxidizer particles and free metal particles in such spaces being bonded together by the binder filling such spaces.

The following are examples of practice of the invention. The amounts set forth in the examples are in terms of parts or per cent by weight unless otherwise specified.

## EXAMPLE 1

(batch procedure)

Forty parts of ammonium perchlorate and 10 parts of aluminum powder having a particle size ranging from 5 to 10 microns are added to a pot containing 55 parts of water, and the mixture is heated to about 80°C while maintaining the aluminum particles in suspension by stirring. Sufficient ammonium perchlorate is employed to form a saturated solution at 80°C. It is desirable not to have a super saturated solution. The mixture is then cooled while stirring to about 20°C over a period of about 1 hour.

Ammonium perchlorate crystallizes out on the suspended aluminum, forming particles of ammonium perchlorate with occluded aluminum, such particles as well as particles of aluminum trapped between particles or crystals of the ammonium perchlorate with occluded aluminum, being removed by decantation and filtration. The resulting mixture is dried by heating in a vacuum oven at about 150° to about 110°C for 24 hours.

## EXAMPLE 2

(continuous procedure)

A warm saturated solution of ammonium perchlorate containing crystals of ammonium perchlorate is maintained in a separate first container at 60°C.

A second container or crystallizer is provided having aluminum powder of 5 to 10 microns particle size suspended in water at temperature ranging from about 5 to about 70°C, specifically about 40°C, cooler than the warm ammonium perchlorate solution in the first vessel.

The warm solution of ammonium perchlorate is continuously passed into the second vessel or crystallizer containing the cooler aluminum powder suspension, which is maintained in suspension by suitable agitator means. Ammonium perchlorate solution is continuously pumped out of the cooler crystallizer container via a filter, leaving all aluminum solids in the crystallizer. The liquid ammonium perchlorate solution leaving the crystallizer is pumped back to the warmer container and the cycle is repeated.

As ammonium perchlorate solution is pumped into the crystallizer containing suspended aluminum, the aluminum perchlorate crystallizes out on the suspended aluminum, forming particles of ammonium perchlorate with occluded aluminum. Such particles together with trapped particles of aluminum between the oxidizer particles are removed by decantation and filtration, and the particles are dried by washing with ehtyl alcohol, followed by heating in a vacuum oven at about 105° to about 110°C.

The above continuous process is controlled so that the resulting oxidizer-metal mixture or composition contains 85 percent ammonium perchlorate and 15 percent aluminum, by weight.

## EXAMPLE 3

The procedure of Example 1 is substantially repeated, employed passivated beryllium having a chromate coating, of a particle size of about 5 to about 20 microns, sufficient passivated beryllium being employed to produce a crystallized composition containing particles of beryllium occluded in the crystallized ammonium perchlorate, comprising 75 percent ammonium perchlorate and 25 beryllium by weight of the oxidizer-metal combination.

## EXAMPLE 4

The procedure of Example 1 is repeated employing ammonium nitrate oxidizer in place of ammonium perchlorate, the amounts of ammonium nitrate and aluminum metal fuel employed being such as to obtain a crystallized oxidizer-metal composition containing aluminum occluded in the ammonium nitrate and on the surfaces thereof, and composed of 75 percent ammonium nitrate and 25 percent aluminum by weight.

## EXAMPLE 5

The procedure of Example 2 is repeated, employing ammonium nitrate, while controlling the continuous procedure to obtain a crystallized oxidizer-metal composition of ammonium nitrate with occluded aluminum metal fuel, composed of 80 percent ammonium nitrate and 20 percent aluminum, by weight.

## EXAMPLES 6–11

The following are examples of oxidizer-metal compositions containing metal occluded oxidizer prepared according to the invention by crystallizing from aqueous solution, and containing ammonium perchlorate or ammonium nitrate as oxidizer, and aluminum or beryllium as metal fuel, the metal fuel being occluded within the particles of oxidizer.

| | EXAMPLES (percent by weight) | | | | | |
|---|---|---|---|---|---|---|
| | 6 | 7 | 8 | 9 | 10 | 11 |
| Ammonium perchlorate | 90 | 70 | | 85 | | 95 |
| Ammonium nitrate | | | 85 | | 80 | |
| Aluminum | 10 | 30 | 15 | | | 5 |
| Beryllium | | | | 15 | 20 | |

## EXAMPLE 12

(combining inorganic material with binder to form propellant)

The oxidizer-metal composition of Example 1 is screened to provide a distribution of particle sizes wherein 75 percent of the mixture is composed of particles having an average size of 200 microns and 25 percent is composed of particles having an average size of 12 microns. A binder is added to the resultant mixture employing an amount of binder which is 20 percent by weight of the total propellant composition, the ammonium perchlorate and aluminum fuel together comprising 80 percent of the total propellant composition.

As a specific binder there is employed a polyether polyurethane composed of the following.

89 percent polypropylene glycol (90–93 percent total hydroxyl content)
0.35 percent trimethylol propane (7–10 percent of the total hydroxyl content)
10.15 percent toluene 2,4-diisocyanate
0.25 percent ferric acetylacetonate
0.25 percent phenyl beta naphthylamine

The above viscous mixture of binder, oxidizer and metal is placed in a mold and cured at a temperature of about 60°C for about 5 days. The resulting cured binder which binds the particles of aluminum and ammonium perchlorate oxidizer with aluminum occlusions together, is a polyether polyurethane.

## EXAMPLE 13

A finished propellant composition is produced by the procedure of Example 12, employing the ammonium perchlorate-occluded aluminum mixture produced in Example 2, and employing 15 percent of the polyurethane binder and 85 percent of the mixture of Example 2.

## EXAMPLE 14

The ammonium perchlorate-occluded aluminum mixture of Example 1 is screened to form a mixture composed of 50 percent of particles of an average 400 micron size, 35 percent of an average 200 micron size and 15 percent of an average 50 micron size particles.

To this mixture is added 15 percent by weight of the total composition, of a binder composed of 83 percent hydroxy terminated polybutadiene (R45M, Arco Chemical Co.) and 17 percent of a diisocyanate (General Mills DDI diisocynnate 1410) as curing agent, such diisocyanate understood as having the structure OCN(D)NCO where D is a 36 carbon hydrocarbon chain radical.

The mixture of binder and propellant is placed in a mold and cured at 60°C for about 10 days, to provide a finished solid propellant according to the invention.

## EXAMPLE 15

The procedure of Example 14 is repeated but employing the mixture of Example 3 instead of that of Example 1, resulting in a finished propellant composition of ammonium perchlorate containing beryllium as metal fuel.

## EXAMPLE 16

A conventional solid propellant is prepared by placing all of the components of the binder described in Example 12 in a container, except for the toluene diisocyanate component. Then aluminum powder having a particle size of 5 to 10 microns is added, following which ammonium perchlorate is added, the formulation being mixed between each addition. The proportions of aluminum and ammonium perchlorate employed in the mixture are 75 percent ammonium perchlorate and 25 aluminum, by weight of the total of these two components, the same relative proportions of these components as employed in Example 1. Then the toluene diisocyanate component is added last.

The amount of binder employed is 20 percent by weight of the total composition of ammonium perchlorate, aluminum and binder. The components of the binder are employed in the same proportions to each other as set forth in Example 12.

The resulting mixture is placed in a mold and cured at 60°C for 5 days.

The resulting solid propellant in which the metal fuel is simply added to the propellant during physical mixing, and a second propellant composition of Example 12 produced according to the invention and employing the same ammonium perchlorate, aluminum and binder components and in the same proportions, except that the aluminum is added by incorporating it first with ammonium perchlorate in aqueous solution followed by crystallization thereof according to the invention, are each burned under the same conditions and at 100 and 200 psia. Photographs taken at 4,000 frames per second during burning of these two propellants showed in the case of the first propellant produced by conventional procedure, the presence of large radiant spheres of aluminum of the order of about 600 microns in size. On the other hand, such photographs of the propellant of Example 12 according to the invention, containing occluded aluminum in the ammonium perchlorate and produced according to the procedure of Example 1, showed the absence of the above-noted large aluminum spheres, indicating that agglomerization of the aluminum particles accompanied by the formation of large particles of aluminum oxide is greatly reduced.

From the foregoing, it is seen that the invention provides an improved solid propellant containing oxidizer and metal particles, having increased efficiency for use as a low burning low pressure propellant, comprising a more uniform distribution of metal fuel throughout the propellant, by crystallizing the oxidizer, perferably ammonium perchlorate, from aqueous solution in the presence of fine particle size metal fuel, preferably aluminum, and forming a propellant in which the metal, i.e., aluminum, particles are occluded within and/or on the surface of the oxidizer, i.e. ammonium perchlorate, particles, as well as being distributed in the interstices or voids between such oxidizer particles.

While we have described particle embodiments of our invention for the purpose of illustration within the spirit of the invention, it will be understood that the invention is not to be taken as limited except by the scope of the appended claims.

We claim:

**1.** The process for preparing a composition adapted for use in a solid propellant, which comprises forming a first saturated aqueous solution of an oxidizer at elevated temperature, said oxidizer selected from the group consisting of ammonium perchlorate and ammonium nitrate, said first solution containing crystals of said oxidizer, forming a second suspension of particles of a metal fuel selected from the group consisting of aluminum and beryllium, in water, maintained at temperature ranging from about 5° to about 70°C cooler than said first oxidizer solution, continuously passing said oxidizer solution at elevated temperature into said aqueous suspension of metal fuel particles, crystallizing particles of said oxidizer containing said metal fuel occluded in said oxidizer particles from said second aqueous suspension, recovering said metal fuel-occluded particles of said oxidizer from said aqueous suspension, and continuously passing cooled aqueous oxidizer solution from said second aqueous suspension to said first saturated oxidizer solution maintained at elevated temperature.

**2.** The process as defined in claim **1**, said oxidizer being ammonium perchlorate and said metal fuel being aluminum, the particle size of said aluminum ranging from about 1 to about 30 microns.

**3.** The process as defined in claim **1**, including filtering said cooled aqueous oxidizer solution prior to passage thereof to said first saturated oxidizer solution, to leave all metal fuel particles in said second aqueous suspension.

**4.** The process as defined in claim **1**, said first oxidizer solution being maintained at 60°C.

* * * * *