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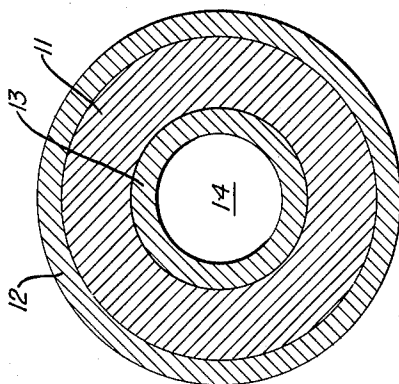


Fig. 2

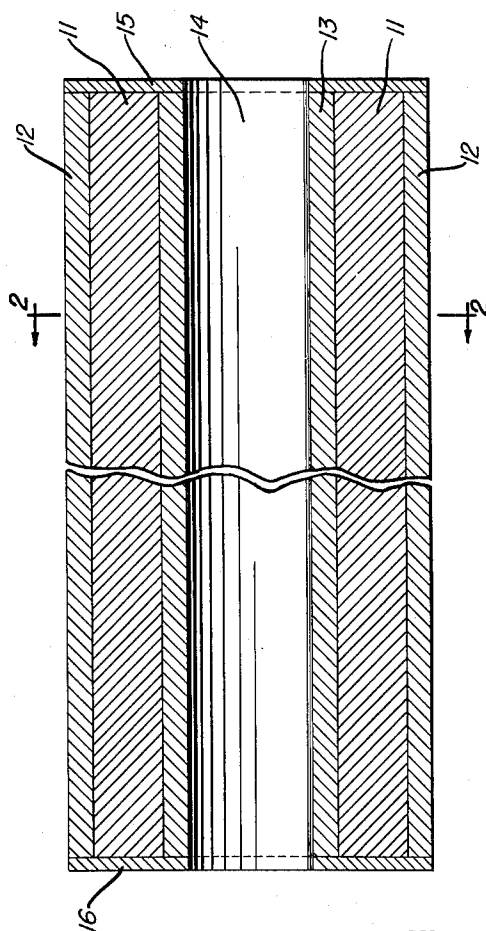


Fig. 1

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3,028,810

PROPELLENT GRAIN

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This invention relates to an article of manufacture suitable for the generation of gases at high pressure by the decomposition of ammonium nitrate. More particularly, the invention relates to an explosive grain consisting of a body portion and an outer surface coating whereby the ignition of the grain at low pressure is facilitated.

Ammonium nitrate is classified as a high explosive even though it is extremely insensitive and cannot be readily ignited by the local application of heat or by a blasting cap. Even when ignited, ammonium nitrate alone does not consistently sustain the propagation of combustion. In order to utilize the excess oxygen available from the decomposition of ammonium nitrate, oxidizable materials are mixed with the ammonium nitrate. However, while these mixtures of ammonium nitrate and oxidizable material are more sensitive than the ammonium nitrate alone, the mixtures are also insensitive or slow burning.

It is known that a smooth burning, readily ignitable ammonium nitrate-oxidizable material mixture can be obtained by the use of chromium-type combustion catalyst. The more common chromium-type combustion catalysts are ammonium or alkali metal chromates or polychromates, chromic oxide, chromic nitrate and copper chromite. The preferred combustion catalyst for commercial mixtures is ammonium dichromate. The relative toxicity of the chromates makes them hazardous unless handled with considerable care. A particular disadvantage to the use of the chromate catalyst is their strong oxidizing property; the chromates react slowly with the oxidizable material in the mixture to give chromate salts which are relatively ineffective catalytically—thus on long storage the chromate containing mixture loses its sensitivity to ignition.

It has been discovered that certain iron compounds are effective catalysts for the combustion of ammonium nitrate and ammonium nitrate-oxidizable material mixtures. These catalysts are the subject matter of U.S. patent applications filed by Wayne A. Proell and William G. Stanley, Serial Number 273,564, filed February 26, 1952, now Patent No. 2,987,389, and Serial Number 288,065, filed May 15, 1952, now Patent No. 2,955,033. All of the combustion catalysts disclosed in these applications contain the iron cyanide radical, either ferrocyanide or ferricyanide. In addition to the iron cyanide radical, these catalysts contain a second iron ion which may be either ferric or ferro(us). In addition to the iron-iron cyanide complex, the catalyst may contain alkali metal and/or ammonium ions. It has been found that the generic classes of iron-iron cyanide compounds known as soluble Prussian blues and insoluble Prussian blues are effective catalysts for the purposes of this invention. It is known that the better soluble Prussian blues contain alkali metal(s) such as potassium and sodium and/or the ammonium radical. Some of the "compounds" which have been found to be effective are: ferro ferrocyanide, ferric ferrocyanide, ferro ferricyanide, ferric ferricyanide, potassium ferric ferrocyanide, sodium ferric ferrocyanide, ammonium ferric ferrocyanide, potassium soluble Prussian blue, sodium soluble Prussian blue and ammonium-sodium soluble Prussian blue.

The above applications disclose that insoluble Prussian blue is the more effective catalyst at elevated pressures such as exist in the combustion chamber of a rocket motor, e.g., 500 to 2000 p.s.i. However, the insoluble Prussian blue containing ammonium nitrate-oxidizable

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material mixture is very difficult to ignite at low pressure, e.g., about 15 p.s.i. when the catalyst content is below about 6 weight percent. The soluble Prussian blue containing mixture will ignite readily at low pressure when using as little as 3 to 4% of the catalyst, but the combustion is not self-sustaining in an inert atmosphere.

It has been discovered that ammoniated insoluble Prussian blue is an effective catalyst for the combustion of ammonium nitrate or ammonium nitrate-oxidizable material mixtures. The ammoniated insoluble Prussian blue catalyst possesses the ignition characteristics of the soluble Prussian blue catalyst and the burning rate characteristics of the insoluble Prussian blue catalyst. When used in the mixture in amounts of about 3 to 4%, the ammoniated insoluble Prussian blue catalyzed mixture is hard to ignite and does not sustain combustion in an inert atmosphere. The ammoniated insoluble Prussian blue catalyst is produced by exposing an insoluble Prussian blue to the action of ammonia gas. The temperature of the reaction zone containing the insoluble Prussian blue and ammonia gas increases rapidly until a temperature of about 60° C. is reached; as the temperature increases, the rate of increase decreases until at about 60° C. a plateau is reached. As measured by temperature increase, the interaction of ammonia and the insoluble Prussian blue is believed to substantially stop when the temperature of the reaction zone reaches the plateau of about 60° C. The ammoniated insoluble Prussian blue has a strong odor of ammonia after being cooled to room temperature. An ammoniated insoluble Prussian blue of catalytic activity about equal to the odorous material which does not possess any appreciable ammonia odor can be obtained by maintaining the odorous material at a temperature of about 70° C. for several hours. The ammoniation of the insoluble Prussian blue does not change the physical appearance of the material and is noticeable principally in that the catalytic activity of the insoluble Prussian blue, particularly at low operating pressures, is markedly improved. By this treatment various catalytically active grades of insoluble Prussian blue can be converted to materials having about equal catalytic activity, i.e., the normal variation in catalytic activity of Prussian blue obtained from different manufacturers can be eliminated by this ammoniation procedure. The term "ammoniated insoluble Prussian blue" is intended to include both the ammonia-odorous material and the substantially odor-free material.

The above described iron cyanide containing catalysts have a very desirable characteristic in that the burning rate increases only slightly with increase in catalyst content of the mixture. The burning rate is defined as the speed, inches per second, with which a cylindrical grain about 1/4 inch in diameter and about 6 inches long burns. The burning rate increases with increase in pressure at which the burning takes place. The burning rate at elevated pressures is normally determined by the use of a so-called Crawford bomb. When using about 2 weight percent of insoluble Prussian blue as the catalyst, and about 20 weight percent of oxygenated oxidizable material, and the remainder essentially ammonium nitrate, a burning rate at 1000 p.s.i. of about 0.12 in./sec. is obtained. At a catalyst composition of about 10 weight percent, and a corresponding decrease in ammonium nitrate and oxygenated oxidizable material, a burning rate of about 0.15 in./sec. is obtained.

It is preferred for the purposes of gas generation at high pressures to use a minimum amount of combustion catalyst such as 0.5 to about 4 weight percent, preferably 1 to 3 weight percent. At these low catalyst contents the mixture is virtually non-ignitable at ordinary pressures. A shaped grain having this preferred low catalyst content can be made to operate by pressuring the combustion

chamber to an elevated pressure prior to the application of the ignition means to the surface of the grain. A common procedure for this pressuring is to have a charge of black powder present in the combustion chamber; the burning of the black powder raises the pressure in the chamber to in excess of 500 p.s.i. and also ignites the explosive grain. The use of this pressuring means is undesirable because (1) it requires the presence of an additional item in the chamber and (2) normally there exists in the chamber prior to the ignition of the explosive grain a pressure surge in excess of the desired operating pressure of the gas generating apparatus.

An object of this invention is an ammonium nitrate-oxidizable material explosive grain that is readily ignitable at ordinary pressures. Another object is the manufacture of an explosive grain which is readily ignitable at ordinary pressures and does not require a high combustion catalyst content. Still another object is the manufacture of a composite explosive grain consisting of a body portion having a desirably low catalyst content and an outer surface coating which permits easy ignition at low pressures and which coating has a burning rate about that of the body portion.

The above objects and other objects which will be apparent in the detailed description of the invention are achieved as follows: The novel explosive grain of this invention consists of a body portion and an outer surface coating portion, which coating has a thickness between about 1 and 20 millimeters. The body portion comprises essentially a mixture of ammonium nitrate, about 71 to 95 weight percent; oxidizable material, about 5 to 25 weight percent; combustion catalyst, between about 0.5 and 4 weight percent. The outer surface coating comprises essentially ammonium nitrate, about 63 to 89 weight percent; oxidizable material, between about 5 and 25 weight percent; and combustion catalyst, between about 6 and 12 weight percent. The combustion catalyst used in the composite explosive grain of this invention is selected from the group consisting of iron-iron cyanide complexes, soluble Prussian blues, insoluble Prussian blues and ammoniated insoluble Prussian blues.

While the amount of combustion catalyst needed to obtain easy ignition at ordinary pressures of the surface coating will vary somewhat dependent on the particular catalyst and a particular oxidizable material, in general about 6% is sufficient. With increase in catalyst content the ease of ignition improves, but no real advantage is gained by using more than about 12%.

The surface coating performs two functions which are (1) permits easy ignition at ordinary temperatures, i.e., about atmospheric pressure, and (2) produces sufficient gas to pressure the combustion chamber to a pressure such that the body portion will ignite. Thus the minimum thickness of the outer surface coating will vary with the composition of the body portion and also with the free volume of the combustion chamber, i.e., the larger the free volume, the more gas needed to bring the combustion chamber to the desired elevated pressure. In general the thickness of the outer surface coating may be from about 1 mm. to about 20 mm. or more. Preferably the thickness of the outer surface coating should be between about 2 and 10 mm. Further, it may be desirable to increase the thickness of the outer surface coating when operating with very large diameter grains such as 8 inches or 12 inches.

Normally in the generation of gas by the burning of an ammonium nitrate explosive, only a part of the total surface is permitted to burn. This result is achieved by coating some of the surface with an inhibiting material which prevents the ignition of the ammonium nitrate beneath the inhibiting material. Examples of suitable inhibiting material are cellulose acetate, Scotch cellophane tape and petroleum asphalts. For example: A cylindrical grain can be burned cigarette-fashion by inhibiting the cylindrical surface and one end of the grain. On the

other hand, a cylindrical grain can be burned along the cylindrical surface only by inhibiting both ends of the grain. A cylindrical grain which is provided with a coaxial longitudinal opening throughout the length of the grain can be made to burn on both the outer and inner cylindrical surfaces by inhibiting the annular area of both ends. The explosive grain of this invention is not limited to a perforated cylinder (tubular) grain, but may be utilized with any shaped grain such as cruciform, tri-form, hexaform, slab, etc. It is normal practice to inhibit a part of the outer surface of all grains used for propelling rockets. A grain which consists of a body portion and inhibitor placed on part of said body portion and the outer surface coating of this invention over the uninhibited surface is within the scope of the invention. It has been found that all of the burning surface of the body portion need not be coated in order to obtain ignition of the entire uninhibited surface of the body portion; however, at least about 70% of the uninhibited burning surface should be coated in order to obtain complete and uniform ignition.

FIGURE 1 shows a longitudinal cross-sectional view of one embodiment of the invention.

FIGURE 2 shows a cross-sectional view along the line 2—2 of this embodiment.

In the figures the body portion 11 of the propellant grain is provided with an external coating 12. An internal coating 13 covers the cylindrical surface of a coaxial longitudinal perforation 14. The grain was forced to burn only on the curved interior and exterior surfaces by the presence of a layer of inhibitor, 15 and 16 respectively, positioned on the annular end surfaces of the grain. Thus the grain burns both on the inner surface and the outer surface with the direction of burning proceeding toward the center of the body portion 11.

The term ammonium nitrate as used in this specification and in the claims is intended to mean either ordinary commercial grade ammonium nitrate, such as, conventionally grained ammonium nitrate containing a small amount of impurities and which is then generally coated with a small amount of moisture-resisting material such as petrolatum or paraffin, or military grade ammonium nitrate, or a mixture of other inorganic nitrates and ammonium nitrate wherein the ammonium nitrate is the preponderate nitrate.

The decomposition of ammonium nitrate produces free-oxygen in addition to the other decomposition products. Additional energy can be obtained by having present in the combustion zone an oxidizable material which combines with the free-oxygen. It is to be understood that the combustion catalysts utilized in the explosive grain of this invention contain oxidizable materials which will consume some of the free-oxygen. The oxidizable material may be any material which contains a deficiency of combined oxygen. Metals such as aluminum and magnesium may be used. The non-metallic elements, sulfur and carbon, may be used. Nitrogen-containing organic compounds that do not unduly sensitize the explosive mixture are particularly good; examples of these are urea, nitroguanidine, mononitrate naphthalene, dinitrodiphenyl oxide, etc. Hydrocarbon materials are an excellent oxidizable material and are preferred where low cost is a matter of concern. Examples of hydrocarbon oxidizable materials are waxes, tars, asphalts, bitumen, coal tar, shale oil residue, viscous higher boiling hydrocarbon oils, etc.

Oxygenated materials are very useful as oxidizable materials for certain applications of the explosive grain. For use in rockets, a material that is dimensionally stable is desirable. It has been found that the various cellulose acetates which have been plasticized to improve workability are a particularly suitable oxidizable material. It is desirable to use an oxygenated plasticizer and a polyester of a glycol and a dicarboxylic acid is a particularly suitable plasticizer material. The term "oxygenated oxidizable material" is intended to include all organic materi-

als which contain oxygen as well as carbon and hydrogen—other elements such as nitrogen and sulfur may also be present.

The amount of oxidizable material that is added to the ammonium nitrate-catalyst mixture is dependent upon the amount of catalyst present and the particular type of oxidizable material itself. Normally it is desirable to have present a sufficient amount of oxidizable material so that the explosive mixture is about stoichiometrically balanced with respect to oxygen content. This preferred composition may be exceeded, but in general no more oxidizable material should be present than can react with the available oxygen to yield a soot-free gas. The presence of some oxidizable material is desirable so that the explosive mixture of this invention should contain between about 5 and 25% of oxidizable material, and preferably between about 15 and 25% of oxygenated oxidizable material.

A cylindrical grain of about 4 inches in diameter by 12 inches long and having a 1 inch diameter coaxial longitudinal perforation was made of the following composition: ammonium nitrate, 74 weight percent; cellulose acetate, 6%; polyester of ethylene glycol and diglycolic acid, 9%; dinitrodiphenyl oxide, 9%; insoluble Prussian blue combustion catalyst, 2%. This grain could not be ignited at atmospheric pressure, but did ignite quite readily at 1000 p.s.i. and gave a burning rate of 0.13 in./sec. Another grain of the above dimensions and composition was prepared. To this grain there was applied a 5 mm. coating over the outer and inner cylindrical parts thereof; the annulus of both ends was inhibited with a thin film of asphalt. The surface coating consisting of 12% of insoluble Prussian blue; ammonium nitrate, 70%; and 18% of the oxygenated oxidizable materials as described for the body portion. The coated grain was placed in a miniature rocket motor and the grain was ignited by applying through the nozzle opening the flame from an ordinary match to a portion of the coated surface. The combustion spread rapidly over the entire uninhibited surface and the entire grain was consumed.

The outer surface coating may be applied to the body portion in the form of a pasty mixture by means of a putty knife in experimental work, or by means of an automatic machinery for commercial production. Also, the coating could be added to the body portion by placing the body portion in the mold of an injection molding machine and injection molding the coating onto the burning surface of the body portion. Still another method is to slurry the composition of the surface coating in a solvent such as acetone and painting the slurry onto the body portion. Many methods of applying this surface coating will be readily apparent to those skilled in the art.

I claim:

1. An article of manufacture that is suitable for the generation of gas at elevated pressures, which article consists of a body portion, which body comprises essentially ammonium nitrate between about 71 and 95 weight percent, an oxidizable material between about 5 and 25 weight percent, and between about 0.5 and 4 weight percent of a combustion catalyst selected from the group consisting of iron-iron cyanide complexes, soluble Prussian blues, insoluble Prussian blues, and ammoniated insoluble Prussian blues; and an outer surface coating portion of a thickness between about 1 and 20 millimeters, which coating comprises essentially ammonium nitrate between about 63 and 89 weight percent, an oxidizable material between about 5 and 25 weight percent, and between about 6 and 12 weight percent of a combustion catalyst selected from the group consisting of iron-iron cyanide complexes, soluble Prussian blues, insoluble Prussian blues, and ammoniated insoluble Prussian blues.

2. The article of claim 1 wherein said coating covers at least about 70% of the burning surface of said body portion.

3. The article of claim 1 wherein at least one combustion catalyst is ammoniated insoluble Prussian blue made by treating insoluble Prussian blue with ammonia until the temperature of the reaction zone reaches about 60° C. and substantially no further temperature rise takes place.

4. The article of claim 1 wherein at least one combustion catalyst is insoluble Prussian blue.

5. The article of claim 1 wherein at least one combustion catalyst is soluble Prussian blue.

6. The article of claim 1 wherein the catalyst in said body portion is insoluble Prussian blue and the catalyst in said coating is ammoniated insoluble Prussian blue.

7. An article of manufacture that is suitable for the generation of gas at elevated pressures, which article consists of a body portion, which body comprises essentially between about 1 and 3 weight percent of a combustion catalyst selected from the group consisting of iron-iron cyanide complexes, soluble Prussian blues, insoluble Prussian blues, and ammoniated insoluble Prussian blues, between about 15 and 25 weight percent of an oxygenated oxidizable material, and the remainder essentially ammonium nitrate; and an outer surface coating having a thickness between about 2 and 10 millimeters, which coating comprises essentially between about 6 and 12 weight percent of a combustion catalyst selected from the group consisting of iron-iron cyanide complexes, soluble Prussian blues, insoluble Prussian blues, and ammoniated insoluble Prussian blues, between about 15 and 25 weight percent of an oxygenated oxidizable material, and the remainder essentially ammonium nitrate.

8. The article of claim 7 wherein said oxygenated oxidizable material is a cellulose acetate plasticized with a polyester of a glycol and a dicarboxylic acid.

9. The article of claim 8 wherein said oxygenated oxidizable material also contains a nitrodiphenyl oxide.

10. A propellant grain for use in a rocket motor, which grain has a cylindrical shape and is provided with a coaxial longitudinal opening throughout the length of the grain, which grain consists of a shaped body portion comprising essentially between about 0.5 and 4 weight percent of a combustion catalyst selected from the group consisting of iron-iron cyanide complexes, soluble Prussian blues, insoluble Prussian blues, and ammoniated insoluble Prussian blues, between about 5 and 25 weight percent of an oxidizable material, and the remainder essentially ammonium nitrate; and a surface coating which covers a predominant percentage of the burning surface of said body portion, which coating is between about 2 and 10 millimeters in thickness and which comprises essentially between about 6 and 12 weight percent of a combustion catalyst selected from the group consisting of iron-iron cyanide complexes, soluble Prussian blues, insoluble Prussian blues, and ammoniated insoluble Prussian blues, between about 5 and 25 weight percent of an oxidizable material, and the remainder essentially ammonium nitrate.

11. The grain of claim 10 wherein an amount of the outer area of said body portion is inhibited against combustion.

12. The grain of claim 10 wherein the combustion catalyst is ammoniated insoluble Prussian blue and the oxidizable material is an oxygenated oxidizable material.

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