June 6, 1961 W. G. STANLEY 2,987,388

RESTRICTED SOLID PROPELLANT GRAIN

Filed Nov. 28, 1955

Fig. 1

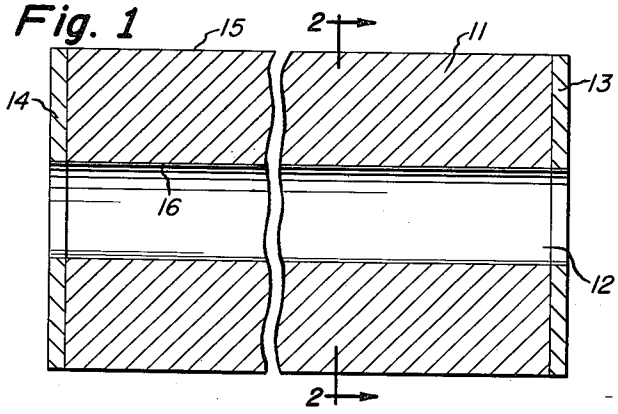


Fig. 2

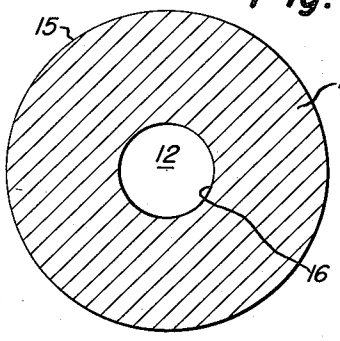


Fig. 3

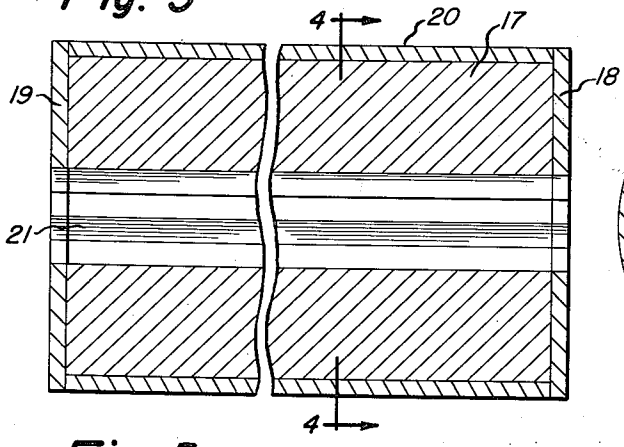


Fig. 4

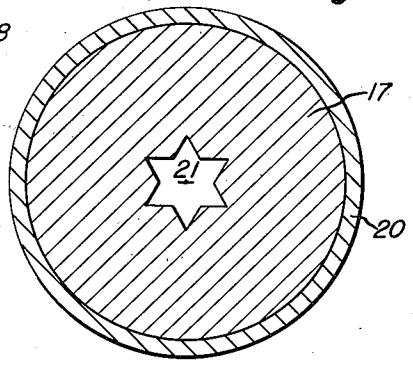


Fig. 5

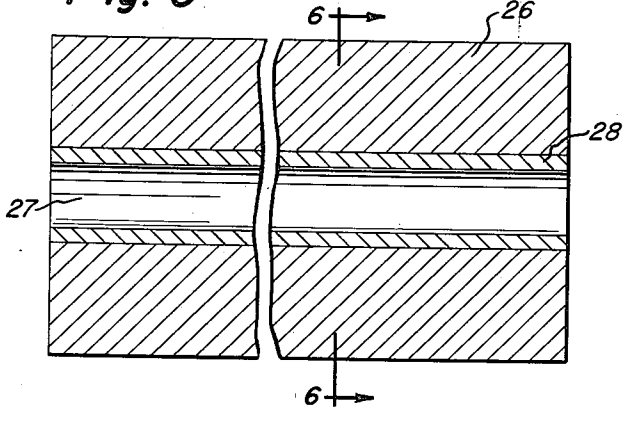
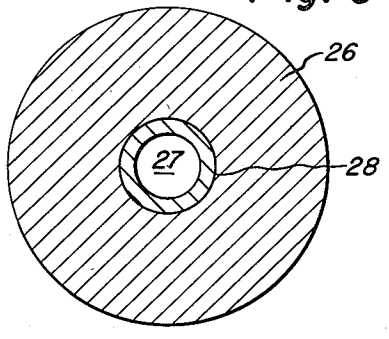


Fig. 6



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RESTRICTED SOLID PROPELLANT GRAIN

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8 Claims. (Cl. 52—.5)

This invention relates to an article of manufacture for the generation of gases at high pressure by the decomposition of ammonium nitrate. More particularly, the invention relates to a gas-generating grain having a body portion and a restrictor coating over a portion of the surface of said body portion whereby combustion of the grain is directed and controlled.

Ammonium nitrate is classified as a high explosive. In order to utilize the excess oxygen available from the decomposition of ammonium nitrate and to obtain relatively slow decomposition of the ammonium nitrate rather than explosion thereof, oxidizable material in the form of a binder and a combustion catalyst are mixed with the ammonium nitrate and the resulting mixture is shaped into grains which can be burned to produce gas under high pressure. The gas so produced may be used for the propulsion of rockets, in the assist-take-off of heavier-than-air aircraft, and for the propulsion of turbines such as for the operation of auxiliary turbine starters for turbojet engines.

Gas-producing ammonium nitrate based grains may be molded or extruded from the propellant material into various shapes. Normally in the generation of gas by burning of an ammonium nitrate gas-producing grain, only a part of the total surface is permitted to become a burning surface. In order to direct the burning of the grain it is necessary to restrict one or more of the burning surfaces of the grain. This is accomplished by superimposing on a portion of the surface a restrictor coating which is relatively non-flammable compared to the flammability of the body portion of the grain. The restrictor coating on the surface delays the burning of the body beneath the coating. By a combination of burning surface, with restriction of portions thereof, the time of combustion of a gas-forming ammonium nitrate based propellant grain of a given composition can be controlled.

Various materials have been used for restricting a part of the burning surface of propellant grains. Cellulose acetate, cellophane tape, petroleum asphalts and asbestos tape have been used. These materials are difficult to apply in a manner to obtain satisfactory bonding of the restrictor coating to the body of the grain and such restrictors give unpredictable results. Grains so restricted are not ballistically dependable. The restrictor coating tends to warp and crack and became detached from the body portion either during storage under extreme temperature change conditions or separate from the body portion during the firing of the grain. Grains which are used in military and commercial service are subjected to extreme temperatures in storage sometimes as low as —75° F. and as high as 170° F. and may require being fired at such extreme temperatures. If the bonding of the restrictor coating to the body of the grain has been damaged causing creeping, warping or peeling of the restrictor, erratic burning properties of the grain results. Non-plasticized cellulose acetate when applied as restrictor coating to ammonium nitrate based grains shows a tendency to warp and peel even at normal ambient temperatures which tendency is increased under extreme temperature changes to which the grain so restricted may be subjected.

An object of this invention is a shaped ammonium nitrate-based propellant grain a part of the burning area of which is restricted. Another object of the invention

is a shaped ammonium nitrate-based grain with restricted burning area which restricted grain is dependable ballistically. Still another object of the invention is a restricted ammonium nitrate propellant grain the restrictor coating of which is easily applied to obtain bonding between said restrictor coating and the body of said grain which bonding will not be damaged by extreme temperature changes. A further object of the invention is a restricted ammonium nitrate based grain the restrictor coating of which will not strip or peel from the body of the grain. An additional object of the invention is an improved method of preparing a restricted ammonium nitrate-based gas-forming propellant grain. Other objects will become apparent from the description of the invention set forth hereinbelow.

Restricted grains of the invention are illustrated by the figures which form a part of this specification:

FIGURE 1 is an elevation section of a cylindrical grain having restricted ends.

FIGURE 2 is a cross section of the grain of FIGURE 1 cut along line 2—2, showing the circular aperture.

FIGURE 3 is an elevation section of a grain showing restricted ends and restricted cylindrical surface.

FIGURE 4 is a cross section of the grain of FIGURE 3 cut along the line 4—4 showing restricted cylindrical surface and a star-form aperture.

FIGURE 5 is an elevation section of a cylindrical grain with restricted surface of the internal aperture.

FIGURE 6 is a cross section of FIGURE 5 cut along 6—6.

The shaped propellant gas-forming grain of this invention comprises (1) a body portion consisting of an oxidizable thermoplastic binder composed of plasticized polymeric material said polymeric material being selected from the class consisting of cellulose acetate containing from about 51% to about 57% by weight of acetic acid and cellulose acetate butyrate containing between about 7% and 55% by weight of acetic acid and between about 16 and 61% of butyric acid; an amount of a combustion catalyst sufficient to catalyze the burning of the propellant grain and the remainder of the body portion essentially ammonium nitrate and (2) a restrictor coating over a portion of the surface of said body portion which restrictor coating consists of between about 40% and 60% by weight of cellulose acetate containing between about 54% and 56% by weight of acetic acid and the remainder essentially a citrate plasticizer selected from the class consisting of trimethyl citrate, triethyl citrate, acetyl trimethyl citrate and acetyl triethyl citrate.

The restrictor coating material of this invention consists of cellulose acetate containing between about 54% and about 56% by weight acetic acid said cellulose acetate being plasticized with a citrate plasticizer selected from the class consisting of trimethyl citrate, triethyl citrate, acetyl trimethyl citrate and acetyl triethyl citrate. The term "percent by weight acetic acid" as used herein defines the amount of acetic acid obtained upon saponification of the cellulose acetate and is expressed as percent of the original material. Commercial grades of the cellulose acetate of about 54 to about 56% by weight acetic acid content and also commercial grades of the defined citrate plasticizers may be used in producing the restrictor coating material. The plasticized cellulose acetate contains from about 40% to about 60% by weight of the cellulose acetate the remainder of the restrictor coating material consisting of the citrate plasticizer. It is preferred to use a restrictor consisting of about equal parts of the defined cellulose acetate and acetyl triethyl citrate.

The restrictor coating material may be prepared as follows. The cellulose acetate is charged to a mixer heated to a temperature of about 130°–150° C. and the

citrate plasticizer is added. These components are mixed under reduced pressure, e.g. about 25 inches of mercury vacuum for a period of time sufficient to completely plasticize the cellulose acetate. Reduced pressure is employed in the mixing operation to reduce the inclusion of bubbles of air in the finished product. A bubble-free product is preferred. The time required to plasticize the cellulose acetate may be as long as 2 to 3 hours depending on the temperature used, the relative amounts of cellulose acetate and citrate in the plasticized product and on the efficiency of mixing of the components.

The body portion of the propellant grain consists essentially of an oxidizable thermoplastic binder, a combustion catalyst and ammonium nitrate. The oxidizable thermoplastic binder usually constitutes from about 10% to about 25% by weight of the body portion of the propellant grain. From about 20% to about 40% by weight of the binder is cellulose acetate or cellulose acetate butyrate polymeric material; the remainder of the binder constisting of oxidizable plasticizer material. The plasticizer material preferably contains combined oxygen.

The cellulose acetate of the binder is known commercially as partially esterified cellulose acetate and is defined as having an acetic acid content between about 51 and 57% by weight acetic acid. A particularly suitable cellulose acetate is one which analyzes between about 54 and 56% by weight acetic acid. The cellulose acetate butyrate of the binder material is known as partially esterified cellulose acetate butyrate and is defined as having an acetic acid content between about 7 and 55% by weight and a butyric acid content between about 16 and 61% by weight. A particularly suitable cellulose acetate butyrate is one which analyzes between about 25% and 31% by weight acetic acid and between about 31% and about 35% by weight butyric acid. The terms "percent by weight of acetic acid" and "percent by weight butyric acid" as used herein to define the cellulose acetate butyrate of the binder defines the amount of acetic acid and butyric acid obtained upon saponification of the cellulose acetate butyrate and is expressed as percent of the original material.

Any oxidizable plasticizer for the cellulosic may be used. Plasticizers for the body portion of the grain may be classified generally as polymeric esters, esters of polyhydric alcohols, ethers of nitrophenols, nitromonocyclic aromatics, esters of polycarboxylic acids, alkyl ethers of polyglycol, and polyglycols. Specific examples of such plasticizers are ethylene glycol diglycolate, acetin (mono, di and tri), nitromethylpropanediol diacetate, triethylene glycol di-2-ethylbutyrate, triethylene glycol di-2-ethylhexoate and polyethylene glycol di-2-ethylhexoate. Specific examples of esters of polycarboxylic acids are alkyl citrates such as triethyl citrate, acetyl triethyl citrate, trimethyl citrate, acetyl trimethyl citrate, and the dialkyl phthalates such as dibutyl phthalate and dioctyl phthalate. Specific examples of nitrophenyl ethers which may be incorporated in the binder of the body portion are dinitrophenyl allyl ethers, dinitrophenoxyethanols and the dinitrodiphenyl ethers such as bis(dinitrophenoxy)ethane and 2,4-dinitrodiphenyl ethers. Such nitromonocyclic aromatics as dinitrotoluenes and dinitrobenzenes may be used in the body portion of the grain formulation. Combinations of two or more of the plasticizers may be used.

I prefer to use in the binder material of the body portion of the grain a cellulosic polymeric base material plasticized with a critrate plasticizer which cellulosic polymeric material and plasticizer are also present in the restrictor. Thus when cellulose acetate having an acetic acid content of 54–56% by weight acetic acid plasticized with acetyl triethyl citrate is used as restrictor, it is preferred that the cellulose ester of the body portion be cellulose acetate of this grade and that at least a part of the plasticizer of the cellulose ester in the body portion of the grain be acetyl triethyl citrate. Duplication of the components of the restrictor material in the body portion

of the grain tends to minimize the migration of the components either to or from the restrictor which may take place particularly under hot storage conditions. A better bond is obtained by duplicating components in the restrictor in the body portion and the bond tends to improve under hot storage conditions.

The body portion of the grain of this invention may also contain a minor amount of aromatic amines, usually not more than 10% of the binder material, to inhibit chemically the decomposition of the grain when stored under high temperature storage conditions. Other components may be added in minor amounts to the body portion to improve ignition properties and to improve resistance to physical change in the structure of the grain caused by variable temperatures to which the grain is subjected in storage and in use. Thus the polymeric solids from GR–S latex may be added in amounts less than 1.0% by weight of the body portion. A surfactant may be added to the grain material in an amount up to about 0.2% by weight of the body portion. Sorbitan sesquioleate has been found to be effective to improve contacting of the components in the mixture thereof.

The combustion catalyst of this invention may be an inorganic combustion catalyst such as Prussian blue (insoluble or soluble grades), chromate or dichromate catalysts such as ammonium chromate, ammonium dichromate or the alkali metal chromates or dichromates. I may also use organic type catalysts such as the monosodium salt of barbituric acid in the body portion of the grain. The amount of catalyst used is usually in the range of from about 1 to 10% by weight, based on the weight of the body portion of the grain. Amounts of catalyst within the range of from about 2 to about 6% by weight are preferred. Mixtures of these combustion catalysts may be used.

From about 0.5% to 3% by weight of finely divided carbon, based on the weight of body portion, may be added to improve the burning properties of the grain. Examples of carbon which may be used are the carbon blacks, that is, channel blacks and furnace combustion blacks. Finely divided petroleum coke may also be used in the body portion of the grain composition.

Up to about 2% by weight of an asphalt or asphaltic resin obtained from petroleum residuum stock by propane precipitation may be added in an amount up to about 2% by weight of the body portion to improve the ignition properties.

The term "ammonium nitrate" as used in this specification and claims is defined as either commercial grade ammonium nitrate, such as conventionally grained ammonium nitrate containing a small amount of impurities and which is generally coated with a small amount of moisture-resistant material such as petrolatum or paraffin or military grade ammonium nitrate or a mixture of other inorganic nitrates with ammonium wherein the ammonium nitrate is the preponderant material, that is, constitutes at least about 90% of the nitrate. Relatively pure C.P. grade ammonium nirate is preferred. It is preferred that at least a major part of the ammonium nitrate be finely ground to pass through a #80 U.S. standard sieve.

Referring now to the figures, FIGURE 1 is an elevation section of a cylindrical grain and FIGURE 2 is a cross section of the grain of FIGURE 1 cut at **2—2**. The body portion **11** is provided with internal cylindrical aperture **12** extending longitudinally through the grain. The grain is provided with restrictor coating **13** and **14** consisting of the plasticized cellulose acetate covering the annular ends of the grain. Thus when the grain is fired only cylindrical surfaces **15** and **16** become burning surfaces since the restrictors **13** and **14** prevent the end-burning of the grain.

FIGURE 3 is an elevation section of a cylindrical grain consisting of body portion **17** restricted with restrictor coating **18** and **19** covering the annular ends and

also having the external cylindrical surface covered with restrictor coating **20**. The aperture **21** of this grain is star-shaped as shown by FIGURE 4 which is a cross section of the grain of FIGURE 3 cut along the line **4—4**. The star-shaped aperture can be designed to provide internal burning area adapted to the desired period of time for total combustion of the grain and to give substantially constant burning area during the combustion of the grain.

FIGURE 5 represents an elevation section of a cylindrical grain consisting of a body **26** provided with an internal cylindrical aperture **27** the cylindrical surface of which is restricted with restrictor coating **28**. FIGURE 6 is a cross section of the restricted grain of FIGURE 5 cut along line **6—6**. When the grain represented by FIGURES 5 and 6 is fired initial burning of the grain is limited to external surfaces, that is, external cylindrical surface and annular ends.

It is to be understood that the embodiments shown in the figures are merely representative of methods of restriction and do not limit the scope of the invention, which concerns a body portion having a restrictor coating applied to any desired part thereof.

The restrictor coating may be applied to the body portion of the grain by many methods. Thus the plasticized cellulose acetate may be sprayed or brushed on those surfaces of the grain which are to be restricted. Then the grain with the restrictor coating may be submitted to pressure to insure a satisfactory bonding to the body portion. The thickness of the restrictor coating applied to the body of the grain is from about 2 mm. to about 10 mm. depending on the size of the propellant grain and on the service in which it is used.

The plasticized restrictor coating material may be molded or extruded into transparent sheets. Shaped restrictor coating in the form of plates may be cut or stamped from the sheets. These preshaped plates may be bonded to the preshaped body portion, using an oxidizable cementing material to bond the plates to the body portion, followed if desired, by applying pressure to the grain to improve the bond.

An excellent method for bonding the preshaped plates of restrictor coating to the body portion of the grain is to bond the plates and shape the body portion simultaneously when using a molding technique for shaping the grain. The preshaped plates are inserted in the mold suitably placed to restrict that portion of the surface of the grain which is to be restricted. I have discovered that the temperature, pressure and time required to shape the body portion in the molding operation correspond to the conditions necessary to obtain a well bonded restrictor coating having the defined composition.

The fabrication of a grain similar to that shown in FIGURES 1 and 2 is described below, to illustrate the molding technique of preparing restricted grains. Preshaped restrictor plates of suitable thickness, for example 4 mm., are dipped in acetone or other suitable solvent to remove superficial dirt or grease contamination and are dried. A annular disc plate having a diameter of about 5" and a centrally located circular aperture of suitable diameter to pass over the cylindrical inset in the mold, is placed in the bottom of the mold in contact with the piston plate. If desired the plates may be warmed before inserting them in the mold. A weighed amount of grain material, about 1800 grams, of body portion material sufficient to fabricate the 5" diameter grain, is poured at a temperature of 115° C.±5° C. into the mold and tamped to provide an upper surface. A second restrictor plate is then placed on the surface of the material in the mold and pressure is applied for a period of ½ minute to 15 minutes, the temperature of the material in the mold being maintained within the range of 100° C.–120° C. during the pressing operation. Pressures in the range of from about 1500 p.s.i. to about 6000 p.s.i. may be used. When using a restrictor material containing 50% by weight of the cellulose acetate the pressure applied will usually be in the range of from about 3000 p.s.i. to about 5000 p.s.i. The pressure is released and the grain, restricted on the annular ends, is ejected.

The following tests illustrate the utilility of restricted gas-propellant grains fabricated according to the invention.

Test 1

Equal weights of commercial lacquer grade cellulose acetate having an acetic acid content of 54–56% and a commercial grade acetyl triethyl citrate were mixed at a temperature of 140° C. under reduced pressure (25 inches of mercury vacuum) for a period of about two and one-half hours. This plasticized material was introduced at ambient temperature to a steam-jacketed molding press and heated for several minutes to soften the material and bring it to the temperature of the press which was heated with 30 pounds' steam. Pressure of 100 pounds per square inch was applied for 90 seconds after which the pressure was released and the press was cooled with tap water. A flexible, tough, transparent sheet was obtained having a thickness of 4 mm. Discs having a diameter of 4 15/16" and a centrally located circular aperture of 1 9/16" diameter were cut from the prepared sheet for use in restricting the annular ends of cylinders.

Cellulose acetate of the same acetic acid content as incorporated in the above restrictor material and a commercial C.P. grade ammonium nitrate, 80% of which was finely ground to pass through a #80 U.S. standards sieve, were dried at a temperature of 120° C. under reduced pressure for about one hour. To 70.2 parts by weight of the dried nitrate was added 6.5 parts by weight of the dried cellulose acetate. These were mixed and to the mixture was then added 7.8 parts by weight of acetyl triethyl citrate, 6.8 parts by weight of crude 2,4-dinitrophenoxyethanol, 1.7 parts by weight of a resinous asphalt product, 3 parts by weight of monosodium barbiturate catalyst, 3 parts by weight of easy processing channel black carbon, and 1 part by weight of 2,4-diaminotoluene. These body portion components were mixed at a temperature of 110° C. and at reduced pressure (25 inches of mercury vacuum) for a period of one and one-quarter hours. The product was in the form of bead-like particles having diameters within the range of about ⅛" to about ⅜". The particles were homogeneous with respect to internal structure. The crude 2,4-dinitrophenoxyethanol product contained about 63% by weight of the dinitrophenoxyethanol and about 37% by weight of bis(2,4-dinitrophenoxy)ethane. The asphalt product was a propane-insoluble asphaltic resin having an A.S.T.M. softening point of 162° F., and A.S.T.M. penetration of 7 at 77° F. i.e. 0.7 mm. absolute penetration and an A.S.T.M. ductility greater than 100 at 77° F Tests for determining these properties are described in the 1954 edition of "A.S.T.M. Standards on Bituminous Materials for Highway Construction Waterproofing and Roofing."

Restrictor discs prepared as described above, were dipped in acetone to remove superficial dirt and grease contamination after which they were dried. One of these clean discs was placed in the bottom of a 5" inside diameter mold on top of the bottom piston. The mold was provided with a centrally located cylindrical inset having a diameter of 1½" thus providing a clearance of about 1/32" between the periphery of the aperture of the restrictor disc and the inset. Seventeen hundred seventy-five grams of the above bead-like particles was poured into the mold at a temperature of 110° C. The particles in the mold were tapped lightly to give a flat surface and a second clean restrictor disc was placed on top of the material. The piston was inserted and a pressure of 3400 p.s.i. was applied for 10 minutes. The restricted hot grain was ejected from the mold as a finished product. The annular ends showed no defects in the bonding of the transparent restrictor plates to the body material.

Restricted grains prepared as described above were fired

at −75° F., +70° F. and +170° F. in a test motor having an efflux nozzle of 0.236" diameter. Pressure-time traces for the firing indicated no restrictor failure. These restricted grains also passed the thermal shock test known as the cycle test. In this test the restricted grain was heated for a period of two hours in an oven held at a temperature of 170° F. after which the hot grain was immediately chilled for a period of two hours in a refrigerator held at a temperature of −75° F. to complete one cycle. The grain was immediately subjected to the high and low temperatures for a second cycle after which the grain was allowed to cool to ambient temperature. No defects in the grain, in the bonding of the restrictor or the restrictor itself were produced in this cycle testing of the restricted grain as evidenced by the fact that the cycled grains fired successfully.

Test 2

Restrictor material and restrictor plates were produced in the same manner as the restrictor material and plates described in Test 1 except that the restrictor material consisted of only 40 parts by weight of the lacquer grade cellulose acetate and 60 parts by weight of acetyl triethyl citrate. The plates were softer, less rigid and less tough than the plates containing 50% cellulose acetate.

Propellant material for the body portion of the grain was prepared in the same manner as the body portion of Test 1. The composition was approximately that of the composition of the body portion of Test 1 except that a small amount of sorbitan sesquioleate was added as a surfactant to aid in the mixing of the materials and a small amount of polymeric solids from GR–S latex, tackified with a p-tertiary-butylphenol-acetylene resinous product, was added to the composition.

Restricted grains of the above product were prepared by molding under the same conditions as the product of Test 1 applying the 40% cellulose acetate–60% acetyl triethyl citrate restrictor plates at the ends of the body portion.

Samples of the cylindrical restricted grains having the annular ends restricted with the 40% cellulose acetate-containing restrictor plates were aged at a temperature of 170° F. for a period of 30 days. The restrictor plates showed no tendency to peel from the body portion of the grains and the bonding of the restrictor plates was not damaged by the prolonged high temperature treatment. The grains were fired in the test motor at −75° F., +70° F. and +170° F. Substantially identical pressure-time traces were obtained by firing, at ambient temperature, grains which had been subjected to the prolonged (30 day) high temperature treatment and grains which had not been subjected to the prolonged high temperature treatment.

Test 3

Restrictor material containing 60% of lacquer grade cellulose acetate (54–56% by weight acetic acid) and 40% by weight acetyl triethyl citrate was prepared. Sixty parts by weight of cellulose acetate and 40 parts by weight of the acetyl triethyl citrate were mixed at a temperature of about 150° C. under reduced pressure (25 inches of mercury vacuum) for a period of about three hours. The mixture was considerably stiffer than the plasticized product obtained in Test 1 from 50%–50% mixture of these components and the plasticized product was more cheese-like, that is, tended to crumble at ambient temperatures. This material was introduced at ambient temperatures to the steam-jacketed molding press and was heated several minutes to soften the hard material and to bring it to molding temperature i.e., about 135° C. A pressure of 150 pounds per square inch was applied for about 90 seconds after which the pressure was released and the press was cooled with tap water as in Test 1. A transparent sheet was obtained having a thickness of about 4 mm. which sheet resembled the sheet of restrictor material obtained in Test 1, except that the sheet was less flexible and less tough. Discs having a diameter of 4 15/16" were cut from the prepared sheet for use in restricting the annular ends of cylinders as described above. Body-forming material having the same composition as the body material of Test 2 was used in fabricating a grain restricted with the 60% cellulose acetate–40% acetyl triethyl citrate discs. After washing the discs in acetone and drying the same, one of the discs was placed in the bottom of the pressure mold and the body portion material was poured into the mold after which the material was tamped and a second disc was placed on top of the material. The molding operation was carried out under the same conditions of time, temperature and pressure used in Test 1. Inspection of the annular ends showed no defects in the bonding of the plates to the material.

Restricted grains were cycled in the thermal shock test and no defects in the grain structure or in the bonding of the restrictor thereon was produced in this rigorous test. Pressure-time trace for the firing of the grain in the test motor showed no restrictor failure. The restrictor plate showed no tendency to peel from the body portion of the grain. However, the difficulty of preparing the plasticized restrictor material and molding the same indicates a close approach to the maximum percentage of cellulose acetate content in the restrictor consistent with efficient preparation and desirable dependability of a propellant grain so restricted.

Test 4

Attempts to produce satisfactory restrictor material containing 30% of the cellulose acetate and 70% of the acetyl triethyl citrate failed. Restrictor material containing 35% by weight of the cellulose acetate and 65% by weight of the acetyl triethyl citrate were also unsatisfactory. In molding the restrictor material containing these low percentages of cellulose acetate, the citrate flashed around the edge of the pressure plate in the molding operation. Soft restrictor materials were obtained which when molded produced limp sheets rather than the desired tough, rigid sheets. Restrictor materials containing these low percentages of cellulose acetate tend to warp and deform when grains restricted therewith are heated in preparation for firing at 170° F. and during cycling of the grains in the cycle test and during storage of such grains to high temperature (at 170° F.).

The term "percent" where used in this specification and in the claims based thereon refers to percent by weight.

Having thus described my invention, I claim:

1. A shaped propellant grain consisting essentially of (1) a body consisting of (*a*) an oxidizable thermoplastic binder composed of a plasticized cellulosic material said cellulosic material being selected from the class consisting of cellulose acetate containing from about 51% to about 57% by weight of acetic acid and cellulose acetate butyrate containing between about 7% and 55% of acetic acid and between about 16% and 61% of butyric acid, (*b*) an ammonium nitrate combustion catalyst from the class consisting of Prussian blue, ammonium chromate, ammonium dichromate, alkali metal chromate, alkali metal dichromate and monosodium barbiturate, said catalyst being present in an amount between about 1 and 10 percent by weight of said body and (*c*) the remainder essentially ammonium nitrate and (2) a restrictor coating positioned on a portion of the surface of said body whose burning is to be delayed with respect to the burning of surface of said body which is not restrictor-coated which restrictor coating is on the order of 2 to 10 millimeters in thickness and consists of between about 40% and 60% of cellulose acetate containing between about 54 and 56% of acetic acid and the remainder essentially a citrate plasticizer selected from the class consisting of trimethyl citrate, triethyl citrate, acetyl trimethyl citrate and acetyl triethyl citrate.

2. The grain of claim 1 wherein said catalyst is Prussian blue.

3. The grain of claim 1 wherein said catalyst is ammonium dichromate.

4. The grain of claim 1 wherein said catalyst is monosodium barbiturate.

5. The grain of claim 1 wherein said binder contains a citrate plasticizer selected from the class consisting of trimethyl citrate, triethyl citrate, acetyl trimethyl citrate and acetyl triethyl citrate.

6. The grain of claim 1 wherein said restrictor coating consists of about 50 weight percent of cellulose acetate containing from about 54% to about 56% of acetic acid and the remainder essentially acetyl triethyl citrate.

7. The grain of claim 1 wherein said restrictor coating is applied to said body portion by means of a pressure of 1500 to 6000 p.s.i. at a temperature of 100° to 120° C. said pressure being applied for a period of ½ to 15 minutes.

8. An article of manufacture consisting essentially of (1) a tubular body consisting of (*a*) an oxidizable thermoplastic binder composed of about 31% of cellulose acetate containing between about 54 and 56% of acetic acid, about 37% of acetyl triethyl citrate, and about 32% of a mixture consisting of about 63 weight percent of 2,4-dinitrophenoxyethanol and about 37 weight percent of bis(2,4-dinitrophenoxy)ethane, said binder being present in an amount of about 21% based on said body, (*b*) between about 1 and 4 weight percent, based on said body, of monosodium barbiturate catalyst, and (*c*) the remainder essentially ammonium nitrate and (2) positioned at the ends of said tubular body annular plates adapted for restricting the burning of the body which annular plates are on the order of 2 to 10 mm. in thickness and consist of about equal weight percentages of acetyl triethyl citrate and cellulose acetate containing from about 54 to about 56 weight percent acetic acid.

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