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RESTRICTED AMMONIUM NITRATE PROPELLANT

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Fig. 1

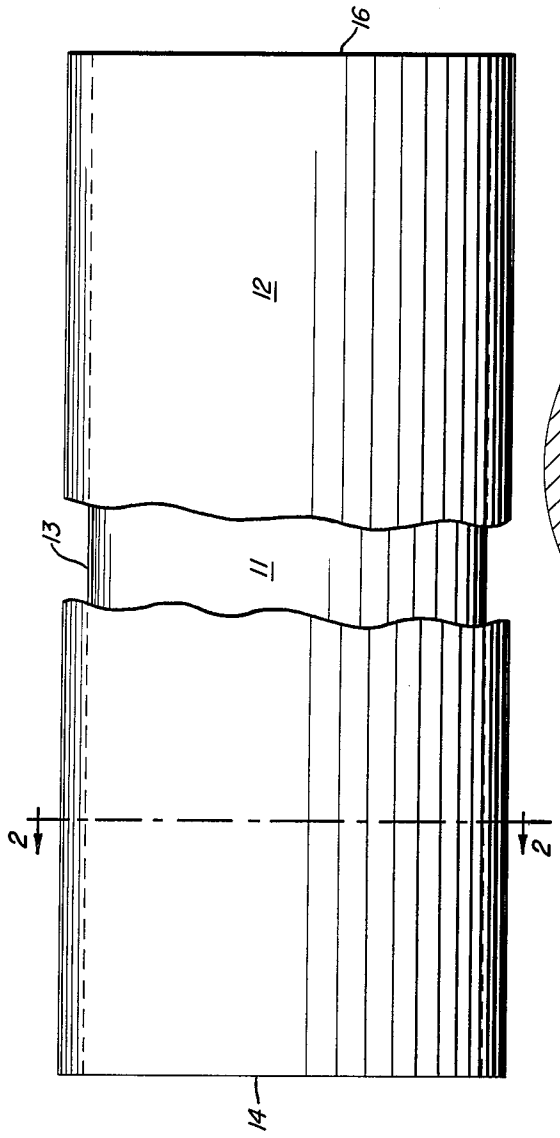
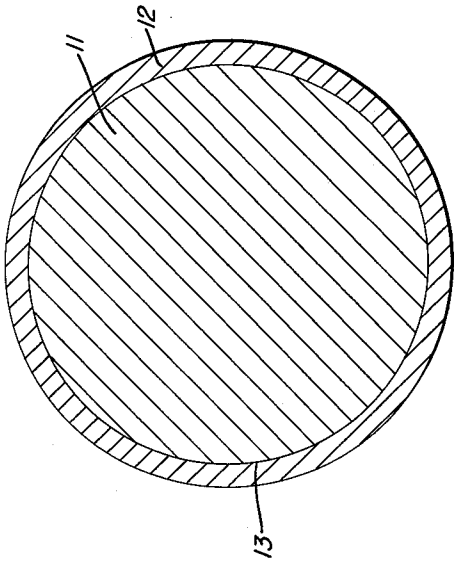


Fig. 2



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RESTRICTED AMMONIUM NITRATE PROPELLANT

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This invention relates to solid propellants based on ammonium nitrate, which propellants are suitable for use in gas generators and rocketry.

A rocket motor and a gas generator have the common requirement namely, that the gas produced in the motor and the generator must be produced at a substantially uniform rate and uniform pressure. The pressure within the motor or gas generator may be determined within limits for the particular gas producing material by the gas exit orifice size or the valve portion. On the other hand the uniform rate of gas production is much more difficult to attain. In order to attain a substantially uniform rate of gas generation it is necessary to utilize a particular type of configuration for the gas generating composition and to control the burning area of the composition. Unless very special precautions are taken all surfaces of the gas generating composition present in the combustion zone will burn. In solid propellants even the narrowest of fissures will result in two burning surfaces, i.e. one on each side of the fissure. To illustrate a solid propellant composition in a cylindrical configuration cannot be fitted so tightly against the wall of the combustion chamber that burning of the cylinder surface is prevented, that is, in the absence of some special precaution a cylindrical grain would burn at both ends and the cylindrical surface.

A uniform rate of burning or a controlled change in rate of burning is attained by applying a relatively non-combustible coating to the surface of the propellant body where direct burning is to be prevented. This coating is commonly referred to as a restrictor or combustion restrictor. The requirements for satisfactory restrictors are stringent. In the first instance the restrictor must adhere to the surface of the solid propellant body. Also, the restrictor must be substantially non-porous; the presence of pores or holes in the coat results in combustion of the solid propellant at that point with resultant variation in the gas production rate. Also the restrictor must not develop fissures or cracks under prolonged storage conditions. It is an ordinary military requirement that solid propellants be able to withstand repeated changes of temperature from as much as −70° F. to as much as +170° F. without changing the gas production rate. Of course, it is understood that the restrictors must be relatively simple to apply to the surface to be prevented from burning and also relatively inexpensive.

An object of the invention is a restricted solid propellant grain using ammonium nitrate as the major gas producing material. Other objects will become apparent in the course of the detailed description.

FIGURE 1 shows one embodiment of the invention namely, a solid propellant body having a cylindrical configuration with a restrictor applied to the cylindrical surface.

FIGURE 2 shows a cross-section at 2—2 of FIGURE 1.

The gas generating solid propellant of the invention comprises a shaped body portion, formed of ammonium nitrate as the major component and an oxidizable binder therefor, and a combustion restrictor coat positioned immediately contiguous to that part of the surface of said body where direct burning is to be prevented, which restrictor consists essentially of the resin reaction product

of (*a*) an epoxy resin having an epioxide equivalent weight between about 165 and 215 derived from epichlorohydrin and a bisphenol with (*b*) a liquid polymeric polyamide reaction product of polyene fatty acids and an aliphatic polyamine, said polyamide having an amine number between about 250 and 350 and with (*c*) a polymethoxy acetal having the formula

$$CH_3-\left(\begin{matrix}CHCH_2\\ |\\ OCH_3\end{matrix}\right)_n-CH(OCH_3)_2$$

where n is an integer having an average value between 3 and 10, said reactants having been present in said resin producing reaction mixture, in parts by weight per 100 parts of reaction mixture, as follows: said epoxy between about 50 and 25, said polyamide between about 15 and 65, and said acetal between about 35 and 10, and wherein said restrictor coat is obtained by contacting said surface with a mixture of said reactants.

The epoxy resin utilized in the restrictor coating of the instant propellant is derived from the reaction of epichlorohydrin and a bisphenol. The bisphenols utilized may be bi-phenol, a substituted bi-phenool, particularly those containing alkyl substituents having from 1 to 4 carbon atoms, or complex bi-phenol ethers or the more complex bisphenols having alkyl group joining the two phenyl groups. A particularly suitable bisphenol reactant is 2,2'-bis-(p-hydroxyphenylpropane) which is commonly known as Bisphenol A. The particular epoxy resin produced from these reactants has an epoxide equivalent weight between about 165 and 215. The commercially available material derived from the reaction of epichlorohydrin and Bisphenol A and having an average epoxide equivalent weight of about 185 is particularly suitable. The term "epoxide equivalent weight" as used herein is in accord with the usage of Stivala in chapter 10 of "High Polymers" volume X, Schildknecht in Polymer Processes; Interscience Publishers Inc., 1956.

The liquid polymeric polyamide used as a reactant for the preparation of the resin reaction product is a reaction product of polyene fatty acids and aliphatic polyamines. This polyamide is one of the well known class of polymers whose method of preparation from polyene fatty acids and alkylene polyamines is described in U.S. 2,450,-940. A particularly suitable class of polyamides is described in U.S. 2,705,223 at column 3. For the purposes of this invention the polyamides are liquid materials, i.e. materials which are liquid at temperatures below about 100° F. and preferably are liquid at ordinary atmospheric temperatures in the region of 30 to 75° F. In addition to being liquid materials the polyamides used in this invention have an amine number between about 165 and 215. The amine number is a measure of the free amine groups present in the polymer and is defined as the number of milligrams of potassium hydroxide equivalent to the free amine groups present in one gram of the polymer.

The third reactant present in the reaction mixture which produces the resin reaction product used as the restrictor is a polymethoxy acetal. The polymethoxy acetals have the formula:

$$CH_3-\left(\begin{matrix}CHCH_2\\ |\\ OCH_3\end{matrix}\right)_n-CH(OCH_3)_2$$

The actals which are suitable for use herein are those where n is an integer having an average value between 3 and 10. In general these acetals are available as mixtures of compounds and are sold on the basis of an average molecular weight as defined by the value of n. Those acetals wherein the average value of n is 4 or 5 are particularly suitable.

In order to have a restrictor coating meet the particular requirements it is necessary that the proportions of the

ıree reactions be controlled. Based on 100 parts of re-
:tion mixture the parts by weight of each reactant pres-
ıt is as follows: the defined epoxy reactant between
ɔout about 50 and 25; the defined liquid polyamide be-
veen about 15 and 65 and the defined acetal between
ɔout 35 and 10. To illustrate one end of the range of
roportions contains said epoxy 50 parts, said polyamide
5 parts and said acetal 35 parts. At the other end of
ıe range the proportions are said epoxy 25 parts, said
olyamide 65 parts and said acetal 10 parts. The amount
f each reactant present may be varied between these
mits as required by the particular use and by the particu-
ır epoxy or polyamide or acetal used.

The solid propellant of the invention comprises a
ıaped body portion formed of ammonium nitrate as the
ıajor component, and an oxidizable binder therefor. This
ody portion may be any of the configurations commonly
sed for gas generator purposes or rocket propulsion pur-
oses. For example, a simple cylinder, a tube, a cylinder
ositioned within a tube, various cruciforms, internal star
ıaped openings with various types of external surfaces,
articularly cylindrical, etc. The restrictor is positioned
nmediately contiguous to that part of the surface of
ıe propellant body where direct burning is to be pre-
ented. For example, in a tubular grain the annular ends
ıay be coated with a restrictor in order to force the burn-
ıg to be on the exterior and internal cylindrical surfaces
nly. In another instance only a particular area of a
ody portion may be coated with a restrictor to provide a
ery short term control of burning area; for example, it
ıay be necessary to have all the surface burning but
nmediately after ignition, pressure surges must be avoid-
d and this is done by restricting only a small portion of
he body to control burning for maybe ½ second and at
ıe end of that time the restrictor coating will be re-
ıoved by the combustion gases. Many methods of re-
triction are known in this art and it is to be understood
hat the solid propellant of the invention may assume any
ıne of these shapes.

One embodiment of the invention is particularly de-
cribed in the figures. In FIGURE 1 there is shown a
olid propellant whose body portion **11** is a simple cylin-
er in shape. A restrictor coating **12** is applied to the
ylindrical surface **13** of body portion **11**. In this em-
odiment the end surfaces **14** and **16** are not restricted.
Vhen placed in a rocket motor for example, as shown in
'IGURE 2 U.S. 2,539,404 and ignited at surface **16** this
rain will burn in cigarette fashion; the restrictor **12** will
ırevent gases from igniting the cylindrical surface **13** of
he body **11**.

It can be seen by examination of the figures that the
estrictor coating **12** must adhere tightly to surface **13** or
ıot gas would pass between the restrictor **12** and surface
3 and cause surface **13** to burn beyond the perpendicular
ıurning surface extending from **16**. This type of burn-
ng would tend to produce a conical shaped burning sur-
ace which would result in progressively increasing
ımount of gas production rather than the desired uni-
orm rate.

The thickness of the restrictor coating **11** will be de-
ermined by the particular requirements. In general non-
ɔorous restrictors are obtained in coats as thin as 1/64
nch. It is usual to use a thicker restrictor coat and in
eneral the coat will be between about 1/16 and ¼ inch
hick. It is to be understood that the restrictor coat should
ɔe no thicker than the requirements of the particular ap-
ɔlication since excess thickness of material results in un-
ɛconomic costs.

Another embodiment of the solid propellant of the in-
vention consists of a number of gas generating composi-
ion pieces which are bonded into a unitary solid propel-
ant by using the restrictor of the invention as a mortar
ɔetween the individual gas generator composition pieces.
For example, a large motor may require an amount of
solid propellant of a size that cannot be produced in one
piece. For example, a cigarette burning cylinder may be
too large to be handled in one piece. This cylinder may be prepared in 3 or 4 sections. These individual sections may be formed into, in effect, a single cylinder by using the restrictor material as the adhesive between each section. To illustrate: a cylinder having a diameter of about 9 inches and about 20 inches long was sawed into four-quarters lengthwise. The four-quarters were then cemented into a cylinder using restrictor material and then the cylindrical surface was restricted as shown in FIGURES 1 and 2. This composited grain was burned in a rocket motor for a period of several minutes and burned at a constant pressure indicating that under this severe duty the restrictor coating completely prevented passage of gas and burning down the sides of the individual pieces.

The body portion of the solid propellant of the invention consists essentially of ammonium nitrate as the major component and oxidizable binder or matrix forming material is also present to permit the ammonium nitrate to be formed into shaped configurations or grains.

The improved composition of the invention contains ammonium nitrate as the major component. The ammonium nitrate may be ordinary commercial ammonium nitrate such as is used for fertilizers. This commercial grade material contains a small amount of impurities and the particles are usually coated wth moisture resisting material such as paraffin wax. Military grade ammonium nitrate which is almost chemically pure is particularly suitable. The ammonium nitrate is preferably in a finely divided particulate form which may be either produced by prilling or by grinding. The ammonium nitrate is the major component of the gas-generator composition and usually the composition will contain between about 65 and 80% of ammonium nitrate.

In order to permit the shaping of the ammonium nitrate composition into definite configurations a matrix former or binder material is present. When ammonium nitrate decomposes free-oxygen is formed. Advantage of the existence of this free-oxygen is taken and oxidizable organic materials are used as the binders. These oxidizable organic materials may contain only carbon and hydrogen, for example, high molecular weight hydrocarbons such as asphalts or residuums, and rubbers either natural or synthetic. Or, the oxidizable organic material may contain other elements in addition to carbon and hydrogen for example, Thiokol Rubber and Neoprene. The stoichiometry of the composition is improved, with respect to smoke production, by the use of oxygenated organic materials as the binders. The binder or matrix former may be a single compound such as a rubber or asphalt or it may be a mixture or compounds. The mixtures are particularly suitable when special characteristics are to be imparted to the grain which cannot be obtained by the use of a single compound.

The multi-component binder or matrix former commonly consists of a polymeric base material and a plasticizer therefor. Particularly suitable polymeric base materials are cellulose esters of alkanoic acids containing from 2 to 4 carbon atoms such as cellulose acetate, cellulose acetate butyrate and cellulose propionate; the polyvinyl resins such as polyvinylchloride and polyvinyl acetate are also good bases; styreneacrylonitrile is an example of a copolymer which forms a good base material. In general the binder contains between about 15 and 45% of the particular polymeric base material.

The plasticizer component of the binder is broadly defined as an oxygenated hydrocarbon. The hydrocarbon base may be aliphatic or aromatic or may contain both forms. The oxygen may be present in the plasticizer in ether linkage and/or hydroxyl group and/or carboxyl groups; also the oxygen may be present in inorganic substituents particularly nitro groups. In general any plasticizer which is suitable for work with the defined polymers may be used in the invention. Exemplary classes of plasticizers which are suitable are set out below.

It is to be understood that these classes are illustrative

only and do not limit the types of oxygenated hydrocarbons which may be used to plasticize the polymer.

Di-lower alkyl-phthalates, e.g. dimethyl phthalate, dibutyl phthalate dioctyl phthalate and dimethyl nitrophthalate.

Nitrobenzenes, e.g. nitrobenzene, dinitrobenzene, nitrotoluene, dinitrotoluene, nitroxylene, and nitrodiphenyl.

Nitrodiphenyl ethers, e.g. nitrodiphenyl ether and 2,4-dinitrodiphenyl ether.

Tri-lower alkyl-citrates, e.g. triethyl citrate, tributyl citrate and triamyl citrate.

Acyl tri-lower alkyl-citrates where the acyl group contains 2–4 carbon atoms, e.g. acetyl triethyl citrate and acetyl tributyl citrate.

Glycerol-lower alkanoates, e.g. monoacetin, triacetin, glycerol, tripropionate and glycerol tributyrate.

Lower alkylene-glycol-lower alkanoates wherein the glycol portion has a molecular weight below about 200, e.g. ethylene glycol diacetate, triethylene glycol dihexoate, triethylene glycol dioctoate, polyethylene glycol dioctoate, dipropylene glycol diacetate, nitromethyl propanediol diacetate, hydroxyethyl acetate and hydroxy propyl acetate (propylene glycol monoacetate).

Dinitrophenyl-lower alkyl-lower alkanoates, e.g. dinitrophenyl ethylacetate, and dinitrophenyl amyloctoate.

Lower alkylene-glycols wherein the molecular weight is below about 200, e.g. diethylene glycol, polyethylene glycol (200), and tetrapropylene glycol.

Lower alkylene-glycol oxalates, e.g. diethylene glycol oxalate and polyethylene glycol (200) oxalate.

Lower alkylene-glycol maleates, e.g. ethylene glycol maleate and bis-(diethylene glycol monoethyl ether) maleate.

Lower alkylene-glycol diglycolates, e.g. ethylene glycol diglycolate and diethylene glycol diglycolate.

Miscellaneous diglycollates, e.g. dibutyl diglycollate, dimethylalkyl diglycollate and methylcarbitol diglycollate.

Lower alkyl-phthalyl-lower alkyl-glycollate, e.g. methyl phthalyl ethyl glycollate, ethyl phthalyl ethyl glycollate and butyl phthalyl butyl glycollate.

Di-lower alkyloxy-tetraglycol, e.g. dimethoxy tetra glycol and dibutoxy tetra glycol.

Nitrophenylether of lower alkylene glycols, e.g. dinitrophenyl ether of triethylene glycol and nitrophenyl ether of polypropylene glycol.

Nitrophenoxy alkanols wherein the alkanol portion is derived from a glycol having a molecular weight of not more than about 200. These may be pure compounds or admixed with major component bis(nitrophenoxy)-alkane.

A single plasticizer may be used or more usually two or more plasticizers may be used in conjunction. The particular requirements with respect to use will determine not only the polymer but also the particular plasticizer or combination of plasticizers which are used.

In addition to the basic components, i.e. ammonium nitrate binder and catalyst, the gas generator propellant composition may contain other materials. For example, materials may be present to improve low temperature ignitability, for instance oximes may be present or, asphalt may be present. Surfactants may be present in order to improve the coating of the nitrate with the binder and to improve the shape characteristics of the composition. Various burning rate promoters, which are not catalyst per se, may also be present.

The aromatic hydrocarbon amines are known to be gas evolution stabilization additives. Examples of these aromatic amines are toluene diamine, diphenyl amine, naphthalene diamine, and toluene triamine. In general the aromatic hydrocarbon amines are used in amounts between about 0.5 and 5 percent.

The mixture of ammonium nitrate, cellulose ester and oxygenated hydrocarbon is essentially as insensitive to shock as is ammonium nitrate itself. It is extremely difficult to get this particular mixture to burn. Smooth burning is attained by the addition of a catalyst to the mixture. This catalyst is distinguished from the well known sensitizers. For example, nitro starch or nitroglycerin may be added to ammonium nitrate in order to increase its sensitivity to shock and enable it to be more easily detonated for explosive use. Catalysts as a class do not promote sensitivity and are used to cause the ammonium nitrate composition to burn for example like a cigarette. The effectiveness of the catalyst is in general measured by its ability to impart a finite burning rate to a cylindrical strand of ammonum nitrate composition. The burning rate is specified as inches per second at a given pressure and temperature; usually these burning rates are obtained by a bomb procedure operating at 1000 p.s.i. and about 75° F. temperature.

Many catalysts which promote the burning of ammonium nitrate compositions are known. The inorganic chromium salts form the best known classes of catalysts. The better known members of this class are ammonium chromate, ammonium polychromate, the alkali metal chromates and polychromates, chromic oxide, chromic nitrate, and copper chromite. Ammonium dichromate is the most commonly used chromium salt. Various hydrocarbon amine chromates such as ethylene diamine chromate and piperidine chromate are also excellent chromium catalyst. Certain heavy metal cyanides particularly those of cobalt, copper, lead, nickel, silver and zinc are effective catalysts. The cyanamides of barium, copper, lead, mercury and silver are effective catalysts. The various Prussian blues are excellent catalysts.

In addition to the above primarily inorganic catalysts various organic catalysts are known. The organic catalysts are particularly useful when it is desired to have combustion products which are gases or vapors and thereby do not erode gas exit orifices. Two catalysts which do not contain any metal components are pyrogene blue (Color Index 956–961) and methylene blue. Particularly suitable catalysts are the alkali metal barbiturates. Finely divided carbon such as carbon black present in amounts of several percent is effective alone as a catalyst however, carbon is generally used in combination with another catalyst as a burning rate promoter.

Test

The propellant body portion to which the restrictor coatings were applied in this test was a cylinder about 9 inches in diameter and about 20 inches long. The restrictor coating which was applied to the cylindrical surface had a thickness of approximately 3/16 inch. The solid propellant grains were then placed into a rocket motor and fired using an orifice such that the internal pressure in the combustion chamber was about 800 p.s.i. The particular propellant composition gave a burning time of about 200 seconds. In all cases the grain was carefully inspected after having been subjected to thermal cycling tests over the temperature range −50° F. to +150° F. in order to detect restrictor cracking and spalling.

The body portion consisted of an ammonium nitrate composition as follows: cellulose acetate 12%, acetyl triethyl citrate 9%, 9% of a 2:1 mixture of dinitrophenoxyethanol and bis(dinitrophenoxy)ethane, carbon black 4%, toluene diamine 1%, sodium barbiturate catalyst 3% and ammonium nitrate 62%.

In this test the epoxy resin was a commercial material which had an epoxide equivalent weight of 179–194 and is produced by the reaction of epichlorohydrin and Bisphenol A. The liquid polymeric polyamide was a commercial material having an amine number in the range of 290–320 and averaging about 305; this material is commonly known as Versamid 125. The polymethoxy acetal used has an average *n* value of 4 and is available commercially as PMAC–5; this material is a condensation product of methylvinyl ether and methanol. In this test the reaction mixture consisted of 45 parts by weight of

ersamid 125, 35 parts by weight of epoxy and 20 parts weight of PMAC–5.

This particular mixture has a reaction time of about hours prior to setting to a semi-solid material. In about –24 hours, dependent on atmospheric temperature, the action mixture sets to a hard tough solid. Prior to this e body portion which was to be restricted had been aced within a shell enclosing the cylindrical surface id spaced about 3/16 inch from the surface. The mixture reactants at room temperature of about 80° F. was then oured into the space between the cylindrical surface of e body portion and the shell. In general it is best to ing the reactants into contact with the surface to be stricted almost immediately after the final mixing of the actants. However, there is an appreciable time before ie initial setting of the reactants and some delay may be lerated. It is observed that a fair temperature rise takes ace during the setting of the resin reaction product. In is instant the solid propellant was permitted to set for 4 hours to allow for completion of the resin reaction. he shell was removed and the restrictor coating carefully ispected for bubbles and incomplete coverage of the surce. This procedure gives a complete coverage of the irface with a bubble free impervious resin coat. This olid propellant was subjected to the temperature cycling st required by military specifications and was then fired i a rocket motor. A very uniform pressure was maintined in the rocket motor for the duration of the firing idicating that the restrictor coat successfully prevented urning of the cylindrical surface of the grain.

Thus having described the invention, what is claimed is:

1. A solid propellant comprising a shaped body portion, formed of ammonium nitrate as the major component and an oxidizable binder therefor, and a combustion restrictor coat positioned immediately contiguous o that part of the surface of said body where direct burnng is to be prevented, which restrictor consists essentially f the resin reaction product of (*a*) an epoxy resin having n epoxide equivalent weight between about 165 and 215

derived from epichlorohydrin and a bisphenol with (*b*) a liquid polymeric polyamide reaction product of polyene fatty acids and an aliphatic polyamine, said polyamide having an amine number between about 250 and 350 and with (*c*) a polymethoxy acetal having the formula

$$CH_3-\left(\begin{matrix}CHCH_2\\ |\\ OCH_3\end{matrix}\right)_n-CH(OCH_3)_2$$

where *n* is an integer having an average value between 3 and 10, said reactants having been present in said resin producing reaction mixture, in parts by weight per 100 parts of reaction mixture, as follows: said epoxy between about 50 and 25, said polyamide between about 15 and 65, and said acetal between about 35 and 10, and wherein said restrictor coat is obtained by contacting said surface with a mixture of said reactants.

2. The propellant of claim 1 wherein said epoxy resin has an epoxide equivalent weight of about 185 derived from epichlorohydrin and Bisphenol A, said polyamide has an amine number of about 305 and said acetal is the defined polymethoxy acetal wherein *n* is 4.

3. The propellant of claim 2 wherein the weight ratio of epoxy to polyamide to acetal is about 35:45:20.

4. The propellant of claim 1 wherein said shaped body portion is a cylinder and said restrictor coat is positioned immediately contiguous to the cylindrical surface of said cylinder, said coat being between about 1/16 and 1/4 inch thick.

5. The propellant of claim 4 wherein said body portion consists essentially of ammonium nitrate as a major component, and ammonium nitrate combustion catalyst in an amount between about 1 and 8 weight percent and between about 10 and 40 weight percent of a binder consisting essentially of cellulose acetate and an oxygenated hydrocarbon plasticizer therefor.

No references cited.