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RESTRICTED AMMONIUM NITRATE PROPELLANT

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Fig. 1

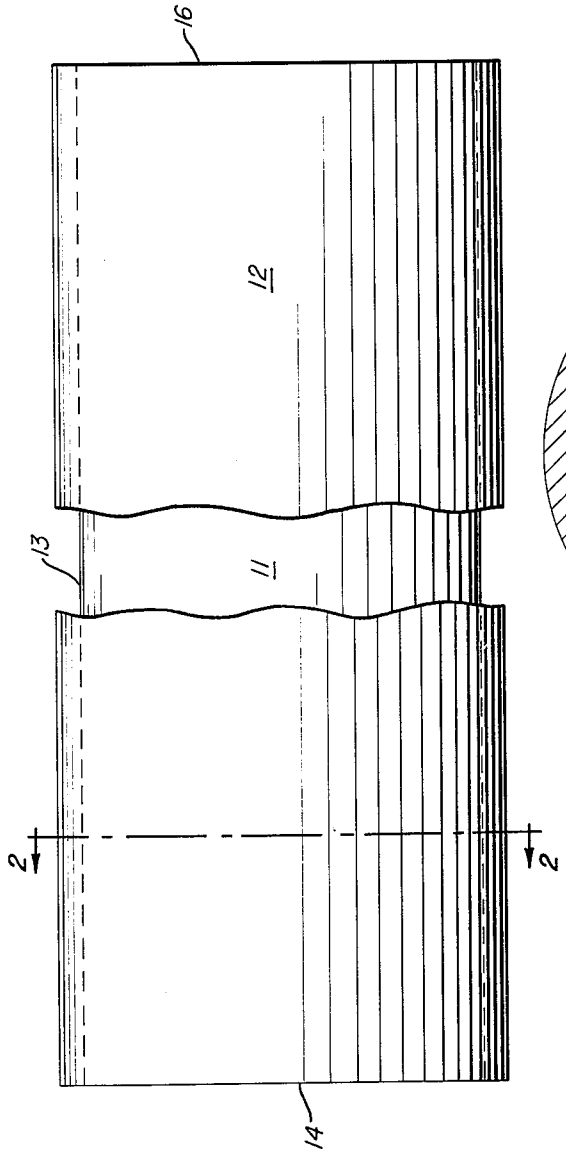
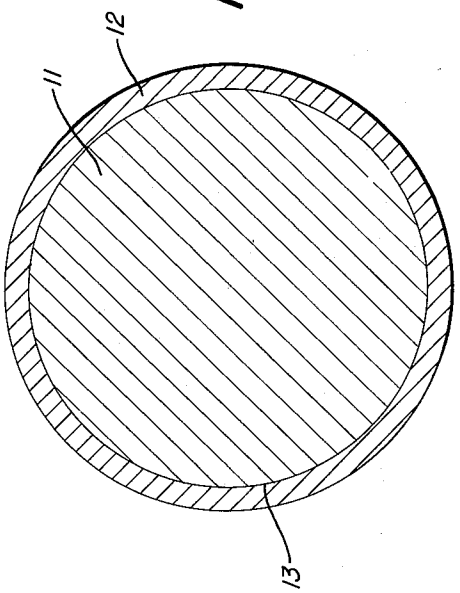


Fig. 2



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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 at +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 epoxide equivalent weight

between about 165 and 215 derived from epichlorohydrin and a bisphenol with (*b*) a liquid polysulfide polymer having an average molecular weight on the order of 1000 derived from alkali metal polysulfide, dichloroethyl formal and a minor amount of trichloro-lower-alkane, and with (*c*) a polyalkylene polyamine, the weight ratio of said epoxy to said polysulfide having been between about 70:30 and 35:65 and the amount of said polyamine having been between about 5 and 15 parts by weight per 100 parts of epoxy plus polysulfide reactants and wherein said restrictor coat is obtained by contacting said surface with a mixture of said reactants.

The resinous restrictor utilized in the solid propellant of the invention is a reaction product of a hereinafter defined epoxy resin, a hereinatfer defined liquid polysulfide polymer and a hereinafter defined polyalkylene polyamine. It has been found that in order to obtain the desired characteristics of the restrictor coating it is necessary to control not only the reactants but also the proportions of the reactants. Thus, the epoxy resin and the polysulfide polymer are used in a weight ratio between about 70:30 and 35:65, that is, when 70 parts by weight of epoxy resin are used, 30 parts by weight of polysulfide polymer will be used. The polyalkylene polyamine cross linking reactant is used in an amount between about 5 and 15 parts by weight per 100 parts of the other reactants, i.e. the sum of the epoxy resin plus polysulfide reactant. The particular proportions of epoxy resin and polysulfide polymer used and also the amount of polyamine used will be determined by the particular restricting requirement and also the particular reactant species used.

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-phenol, 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 group. 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 polysulfide polymer reactant has an average molecular weight on the order of 1000. This liquid polysulfide is derived from the reaction of alkali metal polysulfide, a dichloroethyl formal and a minor amount of trichloro-lower-alkane. The preparation and characteristics of these materials are set out by Fettes et al. at chapter XI of "High Polymers," volume X, Schildknecht, in Polymer Processes; Interscience Publishers Inc., 1956. The commercially available liquid polysulfide polymer which is derived from the reaction of sodium polysulfide containing on the average of 2.25 sulfur atoms, bis(2-chloroethyl) formal and about 2 mol percent based on formal of trichloropropane is particularly suitable for use herein.

Restrictor coating meeting the requirements require the use of polyalkylene polyamine curing agents. These polyalkylene polyamines may be of any one of those commonly used in the curing of epoxy resins. For example, polyalkylene polyamines usable herein include diethylene diamine, triethylene tetraamine, tetraethylene penta-amine, hexamethylene tetraamine, and the various polypropylene polyamines and polybutylene polyamines. Tetraethylene

penta-amine is particularly suitable when working with the preferred commercially available epoxy resins and liquid polysulfide polymers set out above.

Particularly good results have been obtained with the above defined preferred epoxy resin, polysulfide polymer and tetraethylene penta-amine used in a weight ratio of epoxy to polysulfide of about 60:40 and penta-amine about 12 parts per 100 parts of epoxy plus polysulfide. Also particularly good results have been obtained using said epoxy and said polysulfide in about equal parts by weight and penta-amine in an amount of about 6 parts per 100 parts of epoxy plus polysulfide.

The solid propellant of the invention comprises a shaped body portion formed of ammonium nitrate as the major component, and an oxidizable binder therefor. This body portion may be any of the configurations commonly used for gas generator purposes or rocket propulsion purposes. For example, a simple cylinder, a tube, a cylinder positioned within a tube, various cruciforms, internal star shaped openings with various types of external surfaces, particularly cylindrical, etc. The restrictor is positioned immediately contiguous to that part of the surface of the propellant body where direct burning is to be prevented. For example, in a tubular grain the annular ends may be coated with a restrictor in order to force the burning to be on the exterior and internal cylindrical surfaces only. In another instance only a particular area of a body portion may be coated with a restrictor to provide a very short term control of burning area; for example, it may be necessary to have all the surface burning but immediately after ignition, pressure surges must be avoided and this is done by restricting only a small portion of the body to control burning for maybe ½ second and at the end of that time the restrictor coating will be removed by the combustion gases. Many methods of restriction are known in this art and it is to be understood that the solid propellant of the invention may assume any one of these shapes.

One embodiment of the invention is particularly described in the figures. In FIGURE 1 there is shown a solid propellant whose body portion **11** is a simple cylinder in shape. A restrictor coating **12** is applied to the cylindrical surface **13** of body portion **11**. In this embodiment the end surfaces **14** and **16** are not restricted. When placed in a rocket motor for example, as shown in FIGURE 2, U.S. 2,539,404, and ignited at surface **16** this grain will burn in cigarette fashion; the restrictor **12** will prevent gases from igniting the cylindrical surface **13** of the body **11**.

It can be seen by examination of the figures that the restrictor coating **12** must adhere tightly to surface **13** or hot gas would pass between the restrictor **12** and surface **13** and cause surface **13** to burn beyond the perpendicular burning surface extending from **16**. This type of burning would tend to produce a conical shaped burning surface which would result in progressively increasing amount of gas production rather than the desired uniform rate.

The thickness of the restrictor coating **11** will be determined by the particular requirements. In general nonporous restrictors are obtained in coats as thin as 1/64 of an inch. It is usual to use a thicker restrictor coat and in general the coat will be between about 1/16 and ¼ inch thick. It is to be understood that the restrictor coat should be no thicker than the requirements of the particular application since excess thickness of material results in uneconomic costs.

Another embodiment of the solid propellant of the invention consists of a number of gas generating composition pieces which are bonded into a unitary solid propellant by using the restrictor of the invention as a mortar between 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 to 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 either 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 with 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 of compounds. The mixtures are particularly suitable when special characterisitics 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; styrene-acrylonitrile 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 many 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 diglycoate.

Miscellaneous diglycolates, e.g. dibutyl diglycolate, dimethylalkyl, diglycolate and methycarbito diglycolate.

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

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

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

Nitrophenylether of lower alkyene glycols, e.g. dinitro-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 ammonium 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 catalysts. 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.

Tests

The propellant body portion to which the restrictor coatings were applied in these tests 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%.

Test 1.—In this test an epoxy resin purchased commercially which had an epoxide equivalent weight of 179–194 and is produced by the reaction of epichlorohydrin and Bisphenol A was used as the epoxy reactant. The liquid polysulfide polymer was a commercial material produced by the reaction of sodium polysulfide containing an average of 2.25 atoms of sulfur, bis(2-chloroethyl)-formal and 2% of trichloropropane based on formal. This polymer had a molecular weight of about 1000 and a viscosity at 25° C. of about 10 poises. The polyamine curing agent was tetraethylene penta-amine. In this test 40 parts by weight of the polysulfide polymer and 12 parts

by weight of the penta-amine were mixed; this mixture was then mixed with 60 parts by weight of the epoxy resin. Prior to this the body portion which was to be restricted had been placed within a shell enclosing the cylindrical surface and spaced about 3/16 inch from the surface. The mixture of reactants at room temperature of about 80° F. was then poured into the space between the cylindrical surface of the body portion and the shell. In general, it is best to bring the reactants into contact with the surface to be restricted almost immediately after the final mixing of the reactants. However, there is an appreciable time before the initial setting of the reactants and some delay may be tolerated. It is observed that a fair temperature rise takes place during the setting of the resin reaction product. In this instant the solid propellant was permitted to set overnight to allow for completion of the resin reaction. The shell was removed and the restrictor coating carefully inspected for bubbles and incomplete coverage of the surface. This procedure gives a complete coverage of the surface with a bubble free impervious resin coat. This solid propellant was subjected to the temperature cycling test required by military specifications and was then fired in a rocket motor. A very uniform pressure was maintained in the rocket motor for the duration of the firing indicating that the restrictor coat successfully prevented burning of the cylindrical surface of the grain.

Test 2.—In another test a restrictor coating was applied using 100 parts by weight of the polysulfide polymer, 12 parts by weight of the penta-amine and 100 parts of the epoxy. This material was applied as set out in Test 1 and produced a completely satisfactory restrictor coating as demonstrated by firing in the rocket motor.

It is to be understood that the restrictor coating may be applied to the surface by means other than the potting technique of the above tests, for example, thin layers may be built up by applying a succession of coats of the reactant mixture by spraying or brushing before the reactants have begun to set. Even after an appreciable amount of reaction has taken place the incompletely reacted mixture may be applied to the surface and obtain satisfactory restriction.

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 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 epoxide equivalent weight between about 165 and 215 derived from epichlorohydrin and a bisphenol with (*b*) a liquid polysulfide polymer having an average molecular weight on the order of 1000 derived from alkali metal polysulfide, dichloroethyl formal and a minor amount of trichloro-lower-alkane, and with (*c*) a polyalkylene polyamine, the weight ratio of said epoxy to said polysulfide having been between about 70:30 and 35:65 and the amount of said polyamine having been between about 5 and 15 parts by weight per 100 parts of epoxy plus polysulfide reactants 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 and said polysulfide polymer is derived from sodium polysulfide dichloroethyl formal and about 2 mole percent based on formal of trichloropropane.

3. The propellant of claim 2 wherein said weight ratio of epoxy to polysulfide is about 60:40 and tetraethylenepentamine is used in an amount of about 12 parts.

4. The propellant of claim 2 wherein the weight ratio of said epoxy to said polysulfide is about 50:50 and tetraethylene pentamine is used in an amount of about 6 parts.

5. 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.

6. The propellant of claim 5 wherein said body portion 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.