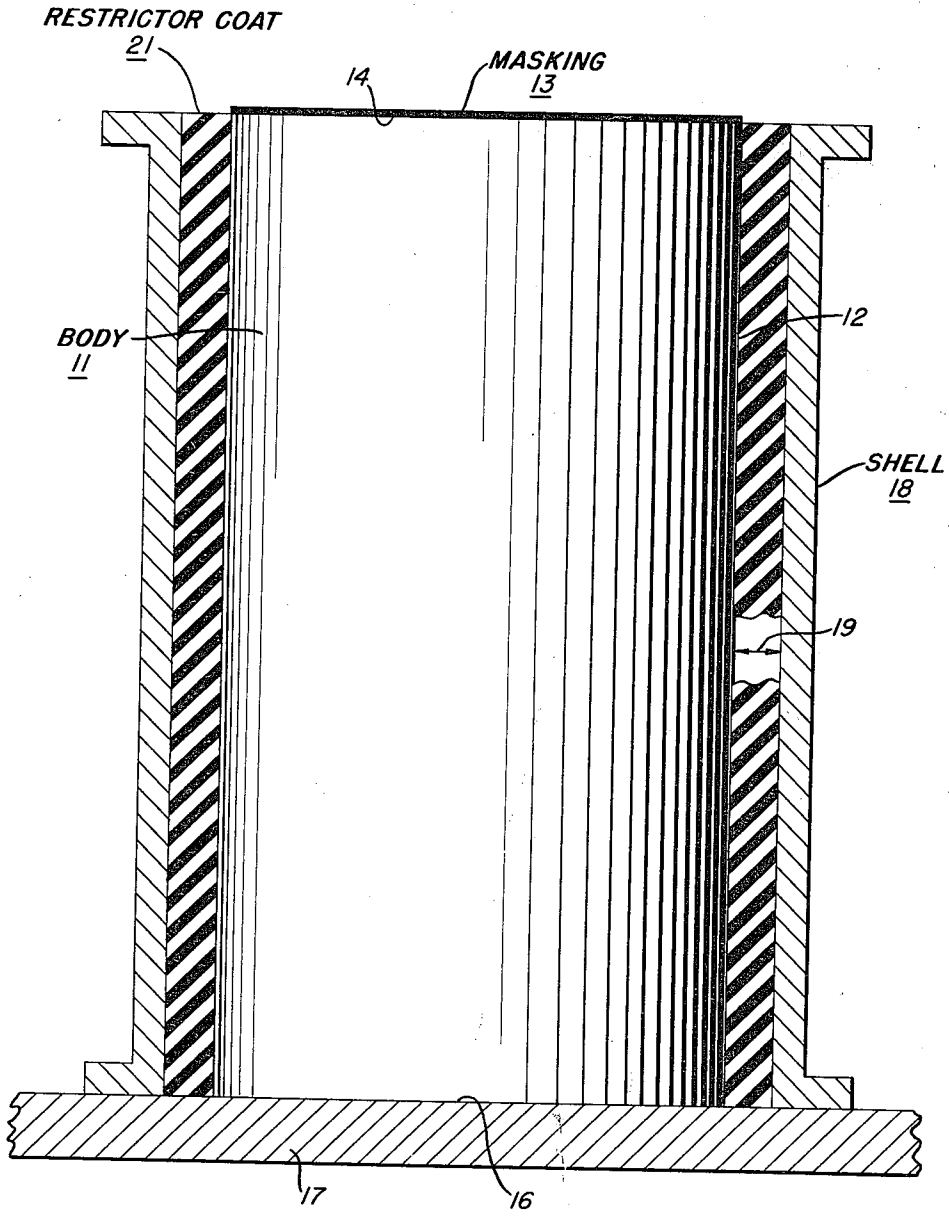
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RESTRICTED PROPELLANT BODY

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RESTRICTED PROPELLANT BODY

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This invention relates to ammonium nitrate base solid propellants provided with a restrictor coating over a portion of the propellant body.

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.

An object of the invention is an ammonium nitrate type solid propellant body provided with a restrictor coating over a portion thereof. A particular object is a process for preparing a restricted ammonium nitrate solid propellant utilizing a polyurethane elastomer as the restrictor. Other objects will become apparent in the course of the detailed description of the invention.

The figure shows a partial sectional view of one embodiment of the restricted propellant of the invention positioned in a shell wherein the restrictor coating is applied.

The ammonium nitrate base solid propellant of the invention comprises an ammonium nitrate base body provided with a polyurethane elastomer restrictor coating on a predetermined portion of the body. The process of preparing the restricted ammonium nitrate solid propellant comprises masking the surface area which are not to be restrictor coated of a shaped ammonium nitrate propellant body, positioning the body in a shell spaced therefrom a distance essentially equal to the desired thickness of the restrictor coating, adding to some void space a

restrictor coating producing mixture consisting essentially of an aromatic diisocyanate and a saturated polyester having terminal hydroxyl groups and a molecular weight between about 600 and 3000, wherein between about 1 and 1.5 isocyanate groups are present per hydroxyl group, and a catalyst from the class consisting of N-cocomorpholines, pyridines, quinolines, isoquinolines, and ethoxylated amines, said catalyst being characterized by an activity such that said reaction mixture flows into all the void space before the set point of the mixture is reached, maintaining the shell, body and reaction mixture for a time needed to form a substantially solid polyurethane restrictor coating on the exposed surface of said body and then removing said shell and said masking to obtain a restricted propellant grain.

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 one half second and at the end of that time the restrictor coating will be removed by the combustion gases.

The polyurethane restrictor coating of the invention is produced by slow setting reaction involving an aromatic diisocyanate, a saturated polyester having terminal hydroxyl groups and a molecular weight between about 600 and 3000 and a catalyst. The restrictor coating must be free of holes and thin spots therefore precautions should be taken to keep the reaction mixture essentially free of materials that produce foam by reaction with the isocyanate group. It is preferred to use a polyester which is essentially free of carboxyl groups for this reason. The isocyanate groups are present in an amount of at least the theoretical for reaction with the hydroxyl groups of the polyester; an excess is preferable and as much as 1.5 times the theoretical requirement may be used.

The catalyst used in the preparation of the polyurethane is a slow acting catalyst. A slow acting catalyst is necessary because the manner of producing a restrictor coating requires flow of the rection mixture through narrow void spaces between the surface of the propellant body and the shell positioned at the portion of the body which is to be restricted. The thickness of the restrictor coating will be determined by the particular requirements. In general non-porous restrictors are obtained in coats as thin as 1/16 inch. It is usual to use a thicker restrictor coat and in general the coat will be between about 1/8 and 1/16 inch thick, circumstances may require coating 3/8 inch or more. 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. In general it is preferred that the set time of the reaction mixture in a beaker containing about 100 grams of polyester of molecular weight about 1700 with 10 grams of tolylene diisocyanate (80:20 commercial mixture) and 1 gram of catalyst in-

termingled at 70–80° F. be at least about 30 minutes; the time being determined from the moment of adding the catalyst to the mixture of isocyanate compound and polyester and the moment when the material in the beaker is too thick to flow appreciably when the beaker is turned on its side. It is to be understood that the set time of the reaction mixture will be determined by the particular application; a long relatively wide void space may require a far slower setting mixture than a short thin void space. In general for ease in operation the catalyst type and usage will be determined to give a setting time only a few moments longer than the time needed for the reaction mixture to flow into the space farthest from the point of introduction of the liquid reaction mixture.

Suitable catalyst for the practice of the invention are selected from the class consisting of N-cocomorpholines, pyridines, quinolines, isoquinolines, and ethoxylated amines. The usage of catalyst is determined by the particular reactants and by the setting time requirements. The amount of catalyst, based on 100 parts by weight of polyester, may vary from as little as 0.1 or less to as much as 10 parts by weight. It is usual to use between about 1 part and 3 parts by weight.

The ethoxylated amines are available as commercial materials known as ethamines. These may be either the product of reaction with mono-amines, di-amines or mixtures thereof.

N-cocomorpholine itself is an excellent catalyst; substituted N-cocomorpholines may also be used .

In addition to pyridine, quinolines and isoquinoline per se various substituted members of these compounds are useful as catalysts in the process. The substituted pyridines may be the picolines, lutidines, or collidines. In addition to the pyridines etc. containing these simple lower alkyl substituents higher molecular weight alkyl substituents such as nonyl, dodecyl or pentadecyl may be present. In general one or more alkyl groups having from 1 to 15 carbon atoms may be present. Alkanol substituents wherein the group is joined to the ring through a carbon atom are suitable; one or more of these alkanol groups each having from 1 to 15 carbon atoms in the group may be present. Substituent(s) may be an alkaryl group or an aralkyl group. The substituent may be positioned on the ring at any point but it is preferred that the substitutents be in a position to stericly hinder the nitrogen atom in the ring—especially suitable are substituents on the carbon atom(s) ortho to the nitrogen atom. In the case of pyridine it is preferred that the substituents be on the 2 and/or 6 positions.

The isocyanate affording compound contains at least two of these groups. The compound may be an aromatic diisocyanate such as tolylene diisocyanate, naphthalene diisocyanate, phenylene diisocyanate, diphenylmethane diisocyanate, triphenylmethane triisocyanate; substituted aromatic diisocyanates may be used such as methoxyphenylene diisocyanate, phenoxyphenylene diisocyanate, and chlorophenylene diisocyanate. The isocyanate affording compound may be a pre-polymer adduct such as the product of the reaction of tolylene dissocyanate with trimethyolpropane.

The hydroxyl group affording reactant is a saturated polyester terminated with hydroxyl groups and having a molecular weight between about 600 and 3000. The polyester condensation product of adipic acid and ethylene glycol is particularly suitable. The branched polyesters such as are derived from the reaction of adipic acid, ethylene glycol and some glycerol are also suitable. In addition to the polyesters the higher molecular weight ether glycols may also be used.

The invention is described in connection with the embodiment shown in the annexed figure which forms a part of this disclosure. In the figure the ammonium nitrate propellant body **11** consists of a solid cylinder of ammonium nitrate base propellant. This body is to be restricted along the cylindrical surface **12** so that the grain will when ignited burn cigarette fashion. The body **11** is provided with a masking **13** on end surface **14**. The masking **13** may be any material which will protect surface **14** from contact with the polyurethane affording reaction mixture. The opposite surface **16** of body **11** may or may not be masked dependent upon the visocosity of the reaction mixture and the setting time with respect to the overall length of body **11**.

The masked body is positioned vertically on a flat surface **17**, for example a metal plate. Shell **18** which is a tube having an internal diameter such that a void space **19** essentially equal to the thickness of the desired restrictor coating is provided when shell **18** is positioned on surface **17** about body **11**. Shell **18** may be of any rigid material to which polyurethane does not readily adhere. Shell **18** should be of a rigidity great enough to provide a substantially uniform thickness of restrictor.

Restrictor coat **21** is obtained by pouring into void space **19** the desired polyurethane affording reaction mixture. When the restrictor coating has hardened enough to permit handling of the restricted body shell **18** is removed and masking **13** is also removed affording the finished restricted propellant.

One particular embodiment of the polyurethane affording reaction mixture consisted of 10 parts of a commercial mixture of tolylene diisocyanate isomers containing 80 percent of the 2,4- isomer and 20 percent of the 2,6- isomers. The polyester was a commercially available condensation reaction product of adipic acid and ethylene glycol; the polyester had a hydroxyl number of 65, an acid number of 1.5 and a Brookfield viscosity at 77° F. of 14,000 centipoises and a molecular weight of close to 1700. One hundred parts by weight of the polyester was used. The catalyst in this particular embodiment consisted of 1 part by weight of N-cocomorpholine, which was added at room temperature of about 75° F. to the mixture of polyester and diisocyanate. This ratio of polyester and diisocyanate gives a slight excess of isocyanate groups over the hydroxyl groups and produces a tough, dense elastomer. This system has an exotherm upon the introduction of the catalyst and a setting time of 45 minutes. The reaction mixture was proportioned to fill a 3/16 inch void space about a solid cylinder of propellant 9 inches in diameter and 24 inches long. The potted propellant body was permitted to stand at room temperature overnight and the shell was then removed. The usual tests for adherence of the restrictor coating to the body were applied as well as visual testing of the continuity of the coating. The grain passed the cycling tests without visible deterioration of the coating. The final proof of good restriction was firing the grain in a motor; the production of a uniform pressure-time curve showed that not only did the restrictor coating maintain continuity but it was not removed from the surface by the hot gases in the motor. The burnout time of this particular grain which consisted of ammonium nitrate 62%, cellulose acetate 12%, acetyl triethyl citrate 9%, dinitrophenoxyethanol mixture 9%, carbon black 4%, toluene diamine 1%, and sodium barbiturate catalyst 3% was about 200 seconds.

Equally satisfactory results were obtained using 2-ethanol pyridine and quinoline as catalysts using the same polyester and diisocyanate reactants.

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 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 be-

tween 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 FIGURE 1. Ths 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 C.P. or 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 material 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; 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 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 oxolates, e.g. diethylene glycol oxolate and polyethylene glycol (200) oxolate.

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 mix-

ture. 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 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.

Thus having described the invention, what is claimed is:

1. A process of preparing a restricted ammonium nitrate solid propellant which comprises masking the surface area which are not to be restrictor coated of a shaped ammonium nitrate propellant body, positioning the body in a shell spaced therefrom a distance essentially equal to the desired thickness of the restrictor coating, adding to said void space a restrictor coating producing mixture consisting essentially of an aromatic diisocyanate and a saturated polyster having terminal hydroxyl groups and a molecular weight between about 600 and 3000, wherein between about 1 and 1.5 isocyanate groups are present per hydroxyl group, and a catalyst from the class consisting of N-cocomorpholines, pyridines, quinolines, isoquinolines, and ethoxylated amines, said catalyst being characterized by an activity such that said reaction mixture flows into all the void space before the set point of the mixture is reached, maintaining the shell, body and reaction mixture for a time needed to form a substantially solid polyurethane restrictor coating on the exposed surface of said body and then removing said shell and said masking to obtain a restricted propellant grain.

2. A restricted ammonium nitrate solid propellant obtained by the process of claim 1.

3. The process of claim 1 wherein said diisocyanate is a tolylene diisocyanate.

4. The process of claim 1 wherein said polyester is a condensation reaction product of adipic acid and an ethylene glycol having a molecular weight of about 1700.

5. The process of claim 1 wherein said catalyst is N-cocomorpholine.

6. The process of claim 1 wherein said catalyst is 2-ethanol pyridine.

No references cited.

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