METHOD FOR RestrictING PROPellant GRAINS

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ABSTRACT OF THE DISCLOSURE

Improved method for producing polyurethane restricted solid propellant grains wherein the heated, restricted grain is subjected to the additional critical step of repressing, at a pressure in excess of 2,000 p.s.i.

This invention relates to solid propellants having a polyurethane restricter, and more particularly to an improved method for producing said propellants.

In gas generation for rocket or missile usage, it is desirable that the gas affording composition develop gas at a controlled rate. In order to attain a substantially controlled 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 a 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 controlled 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 restricter or combustion restricter. The requirements for satisfactory restrictors are stringent. In the first instance the restricter must adhere to the surface of the solid propellant body. In fact, the strength between the propellant and the restricter should be stronger than the restricter body itself. Also, the restricter must be substantially non-porous; the presence of pores or holes in the coat results in combustion of the solid propellant at the point with resultant variation in the gas production rate. Also the restricter 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 —65° F. to as much as +160° F. without materially changing the ambient gas production rate.

Polyurethane has been found to be an excellent material for the purpose of restriction and is used extensively; however, polyurethane restricted grains have not met with complete success because of the large number of failures in not being able to withstand such repeated changes of temperature. In the past, rejections of nearly 1/2 to 1/4 of such grains were not uncommon because of these failures.

This involves the application of the restricter by forcing the fluid polyurethane around the grain under pressure. These processes have been able to form the restricter in place with good adhesion of restricter to grain surface, but have inexplicably been inadequate after undergoing the extreme temperature changes because of the appearance of fissures, which as mentioned above, give rise to an uncontrolled gas production.

An improved process for the production of polyurethane restricted propellant has now been discovered. Grains produced by this improved process have met with nearly complete success in their ability to withstand repeated changes of temperature extremes without developing fissures.

Very briefly, the process of the present is described as follows: A propellant composition containing ammonium nitrate as the principal oxidizing agent is molded under pressure. The propellant grain is then placed in a mold adapted to accommodate the application of restricter; and fluid polyurethane is forced into the mold around said grain and allowed to cure. The restricted grain is then heated and placed in a repress mold and compressed. The restricted propellant grain is heated to a temperature and for a time sufficient to cause softening of the surface of the propellant. The heated grain is then subjected to a pressure of at least 2,000 p.s.i. This additional critical step of repressing has been found to be the difference between failure of a large number of grains and nearly complete acceptance. It has been found that the process of the present invention has the unexpected result of creating a grain capable of withstand the temperature cycling test much more effectively than polyurethane restricted grains of the past, i.e., fewer failures have been found after temperature cycling the grain produced by the process of this invention.

More specifically, it is advantageous that the restricted grain be heated to a temperature of between about 200° F. to 225° F. for a period of between about 4 to 6 minutes.

Heating the grain to this temperature will not only soften the surface of the grain, but have the additional advantage of catalytically curing the restricter. It is preferred to heat the grain to a temperature of between 210° F. to 160° F. The grain may then be subjected to a high pressure in the mold in which it is heated or may then be put into a hot mold and subsequently subjected to pressure. The pressure which may be used to obtain the beneficial results of this process must be at least 2,000 p.s.i. and may be exerted for a time from several seconds until the grain is cooled. The upper limit of the pressure depends, for practical purposes, upon the economics of production. A suitable pressure range would be between 2,000 p.s.i. and 20,000 p.s.i. for a period of between 2 to 4 minutes. It is preferred that the pressure be between 3,000 and 8,000 p.s.i.

If a liner or insulator, such as an asbestos sleeve, is to be used with the propellant, it may be incorporated during the potting procedure. This may be accomplished by placing the asbestos sleeve within the potting mold, and forcing the fluid polyurethane between the liner and the grain and thereby bonding the restricter to both the grain and the liner. It may also be desirable during the potting procedure to isolate the restricted grain from the repress mold. This may be accomplished by applying a metal coated polyester film (Mylar) to the restricted portion of the grain. Aluminized polyester film is preferable. In addition to protecting the restricter, such film has the added advantage of facilitating removal from the mold.

Under certain conditions it is desirable to provide an undercoating adhering to the body portion of ammonium nitrate propellant in order to seal the body portion so that the restricter coating adhered to the undercoating cannot contact ammonium nitrate.

The undercoating is a material capable of adhering firmly to the surface of the ammonium nitrate body portion and also capable of forming an adhesion bond with the restricter coating material. Also, the undercoating must be sufficiently impervious to seal the surface and
bar access of the restrictor coat to said surface. In those cases where the restrictor coating is applied by potting the undercoated grain using a liquid reaction mixture to provide the restrictor coating, the undercoating must be essentially insoluble in the liquid reaction mixture. The undercoating is generally in itself not capable for use in the restrictor material and therefore there is applied in a thickness just enough to provide the necessary sealing effect. The thickness is dependent upon the particular undercoat forming material and may be from \( \frac{1}{1000} \) inch to the order of \( \frac{1}{8} \) inch. In those cases where the undercoat material is sufficiently flexible to act as a restrictor a thicker coating may be used.

The solid propellant of the invention comprises a shaped body portion formed of ammonium nitrate as the major component, and an oxidizer binder therefor. This body portion may be any of the configurations commonly used for gas generator purposes, for 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 polyurethane restrictor is 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 surfaces. In other instances 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 and yet immediately after ignition pressure surges must be avoided. This is done by restricting only a small portion of the body control burning for perhaps one-half second and at the end of that time the restrictor coating will be removed by the combustion gases.

Many polyurethane materials are known in the art for use as combustion restrictors. A number of polyurethane restrictors and the preparation thereof are found in U.S. 3,012,508, see also Dombrow, Polyeurethanes (Reinhold 2nd ed. 1965).

By way of example, a particular polyurethane restrictor coating may be produced by a slow setting reaction involving an aromatic diisocyanate, a saturated polyester having terminal hydroxyl groups and a molecular weight between about 600 and 3,000, and a catalyst. The restrictor must be free of holes and thin spots, therefore, precautions should be taken to keep the reaction mixture essentially free of foam by reaction with the isocyanate group. For this reason, it is preferred to use a polyester which is essentially free of carboxyl groups. The isocyanate groups are present in an amount of at least theoretical equivalent 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 reaction 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, the restrictor surface over which the reaction is produced in costs as thin as \( \frac{1}{8} \) inch. It is usual to use a thicker restrictor coat and in general the coat will be between about \( \frac{1}{8} \) and \( \frac{1}{8} \) inch thick, circumstances may require costing \( \frac{1}{8} \) 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 un-economical costs and added weight. 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 1,700 with 10 grams of toluene diisocyanate (80:20 commercial mixture) and 1 gram of catalyst intermingled at 70-80° F. be at least about 30 minutes; the timing 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 thin void space may require a far slower setting mixture than a short wide void space. In general, for ease in operation, the catalyst type used and speed will be determined to give a setting time of 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-ecocomorphillines, pyridines, quinolines, isoquinolines, and ethoxylated amines. In addition to pyridine, quinolines and isoquinoline per se various substituted members of these compounds are useful as catalysts in the process. 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 .25 part and 3 parts by weight.

The propellant body of the invention contains ammonium nitrate as the major component. Ammonium nitrate compositions consist essentially of ammonium nitrate particles in an oxidizable organic material (binder) and various other additives such as catalyst for the promotion of combustion, carbon, chemical stabilizer to reduce decomposition, etc. To improve the burning quality, and to utilize the excess free oxygen made available by the decomposition of the ammonium nitrate, oxidizable organic material, which also may function as binder material for the shaping of the ammonium nitrate into grans... are admixed with ammonium nitrate. These oxidizable organic materials may be any thermoplastic known to the art for use in propellant compositions.

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 aliphatic acids containing from 2-4 carbon atoms such as cellulose acetate, cellulose butyrate and cellulose propionate.

The polyvinyl resins such as polyvinyl chloride and polyvinyl acetate also are good bases; styrene acrylonitrile is an example of a copolymer which forms a good base material; polyacrylonitrile is another suitable base material; as are polyamide resins (such as nylon).

The plasticizer component of the binder also, preferably, contains combined oxygen. The oxygen may be present in the plasticizer as an ether linkage and/or hydroxyl or and/or carbonyl; also the oxygen may be present as an inorganic substituent, particularly a nitro group.

In general, any plasticizer which is adapted to plasticize the particular polymer may be used. A single plasticizing compound may be used; more usually 2 or more compounds are used in conjunction; for example, acetyl triethyl citrate and triethyl citrate, etc.

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. The precise amount of plasticizer is dependent upon the type of material forming the binder as well as the requirements for the particular grain.

Example

Several temperature shock-cycling tests (hereinafter described) were performed on an ammonium nitrate composition of the following formulation: 62.3% ammonium nitrate, 11.4% cellulose acetate, 21.1% plasticizers, 3.0% carbon black, 1.0% sodium barbiturate, 1.2% stabilizers.

After mixing, the above formulation was heated to 100-110° C. and molded under pressure. An undercoating
We claim:

1. A process for the preparation of a propellant grain comprising a propellant composition containing ammonium nitrate as the primary oxidant, which process comprises molding said composition under pressure to form a grain, applying a polyurethane combustion restrictor to the surface of said grain to be restricted, at least partially curing said restrictor, heating said restricted composition to a temperature sufficient to cause softening of the surface of said grain, and subjecting said heated restricted grain to a repressing step at a pressure of at least 2,000 p.s.i.

3. The process of claim 1 wherein said pressure applied to said restricted grain is in the range of 2,000 to 20,000 p.s.i.

4. The process of claim 1 wherein said restricted composition is heated to a temperature in the range of 100 to 230° F.

5. The process of claim 1 wherein said restricted composition is heated to a temperature in the range of 140 to 160° F.

6. In a process for the production of a polyurethane restricted propellant grain comprising a propellant composition containing ammonium nitrate as the primary oxidant, which process comprises molding said composition under pressure to form a grain, applying a polyurethane combustion restrictor to the surface of said grain to be restricted, at least partially curing said restrictor, the improvement which comprises heating said grain to a temperature sufficient to cause softening of the surface of said grain, and subjecting said heated restricted grain to a repressing step at a pressure of at least 2,000 p.s.i.

7. The process of claim 6 wherein said restricted grain has applied to the restricted portion of said grain, an aluminumized polyurethane film prior to being subjected to said pressure.