

- [54] **PROCESSING OF CROSSLINKED
NITROCELLULOSE PROPELLANTS**
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[57] **ABSTRACT**

This invention relates to an improved process for crosslinking of nitrocellulose with an isocyanate to form a polymeric binder for a solid propellant grain. Gassing of the propellant grain is prevented, and reproducible propellant grains, with substantially void free properties, and having improved mechanical properties, are prepared.

9 Claims, No Drawings

PROCESSING OF CROSSLINKED NITROCELLULOSE PROPELLANTS

BACKGROUND OF THE INVENTION

This invention is in the field of solid propellant processing.

Crosslinking of Nitrocellulose (NC) with toluene diisocyanate (TDI) has been done for many years by different researchers. A problem which has always been prevalent is directly related to the presence of moisture on the ingredients going into the propellant mix. During the mixing of the propellant of reaction between the isocyanate and the moisture forms carbon dioxide. When the propellant is cast, especially into shapes wherein the propellant webs are not thin, the carbon dioxide or other gaseous products are not allowed to escape, and as a direct result thereof, cracks and voids are formed from the evolution of the gas within the highly viscous propellant mixture. The term gassing is generally applied to formation and evolution of gaseous products within the curing propellant grain. A grain which has undergone gassing is generally an inferior grain with poor mechanical properties. The burning of a grain having voids or tracks takes place unevenly, and reproducibility of results is difficult to obtain.

Stringent moisture controls on all ingredients has been necessary to produce good propellant, void free, and with reproducible mechanical properties. Many of the propellant ingredients have a tendency to attract moisture during storage and processing, and as a result, the processing of propellant grains has resulted in the production of more than the desired quantity of grains with inconsistent properties.

Therefore, an object of this invention is to provide a process for crosslinking nitrocellulose propellants which process yields a grain having improved mechanical properties.

A further object of this invention is to provide a process for crosslinking nitrocellulose propellants which process yields a grain substantially free of voids and a grain wherein gassing during curing of the grain is prevented.

Another object of this invention is to provide a process for crosslinking nitrocellulose propellants which process yields reproducible grains from batch to batch.

SUMMARY OF THE INVENTION

The process of this invention produces propellant grains which are substantially void free. The propellant grains have improved mechanical properties and the grains are consistently made with reproducible properties.

The process of this invention directly relates to the crosslinking of nitrocellulose propellant when the nitrocellulose source is double-base powder, single-base powder, or plastisol grade nitrocellulose. The specified nitrocellulose sources have a common characteristic of being a stabilized homogeneous product which is easily blended with many propellant ingredients.

The process of this invention involves reacting a portion of the isocyanate crosslinking agent (0.1-0.2 percent by weight) with propellant mixture at an elevated temperature, exclusive of the second and major portion

of the nitrocellulose source ingredient, to form carbon dioxide which is expelled as a gas from the propellant mixture. After combining the second portion of the nitrocellulose source ingredient and a second portion of an isocyanate crosslinking agent (suitable amount 0.2-3 percent by weight) with the propellant mixture and mixing to obtain a homogeneous propellant blend, the temperature of the blend is reduced to obtain a substantially constant viscosity after which the blend is cast into a suitable mold or rocket motor and cured to form a substantially void free propellant grain having improved mechanical properties and a grain which is reproducible from batch to batch.

A prepolymer such as polyglycol adipate-toluene diisocyanate (PGA-TDI) may be substituted for the nitrocellulose source ingredient and the second portion of toluene diisocyanate or (crosslinker). Hexamethylene diisocyanate (HMDI) may be used in prepolymer in place of TDI. When the prepolymer is used it is added last as in the case when the nitrocellulose and the balance of the isocyanate is added last. Nitrocellulose may be used with the prepolymer; however, because the concentration of nitrocellulose is usually low when PGA-TDI is used, the nitrocellulose may be added with the other ingredients and the 0.1-0.2 weight percent isocyanate. The prepolymer contains a suitable amount of an isocyanate crosslinker to provide from about 0.5 to about 3 percent isocyanate crosslinker in the propellant composition and grain.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The process of this invention works equally well when the nitrocellulose source ingredient (for first and minor portion and second and major portion of a nitrocellulose source ingredient) is double-base powder (e.g., contains nitrocellulose, nitroglycerine, and stabilizer), single-base powder (e.g., contains only nitrocellulose and optional stabilizer), or plastisol grade nitrocellulose, all of which are commercially available and well known in the processing art.

The term "plastisol nitrocellulose" (PNC) propellant is used to describe double-base propellant made by slurry mixing and pouring into casting molds or rocket motors. PNC propellants are made using ball powder (single or double-base) or plastisol grade nitrocellulose. PNC propellants are fluid and free-flowing usually less than one kilopoise in viscosity at room temperature.

Processing of crosslinked nitrocellulose propellants and crosslinked plastisol nitrocellulose (XL-PNC) propellants in accordance with the process of this invention involves preparing and heating the selected propellant ingredients (all ingredients except the second and major portion of the nitrocellulose source ingredient or prepolymer, and a suitable amount of crosslinker), during mixing and after mixing, so that any residual moisture will react with a first portion of an isocyanate. Heating above 85°F and within range of temperature from about 85°F to about 140°F is preferred. Water and isocyanates react to release carbon dioxide which in turn causes cracks and voids in the cured propellant unless the carbon dioxide is removed from the propellant before casting. The

process of this invention allows the carbon dioxide to escape during the continued mixing which yields a first homogeneous propellant blend. A predetermined amount of a prepolymer ingredient such as PGA-TDI or a second and major portion of a nitrocellulose source ingredient along with a second portion of an isocyanate crosslinker is combined with the homogeneous propellant blend and mixing is continued until a second homogeneous blend is achieved. The temperature of the blend is reduced to below about 70°F prior to casting into a suitable mold or rocket motor case. Combining the prepolymer or nitrocellulose is accomplished last to prevent any crosslinking of the nitrocellulose or prepolymer ingredients before a homogeneous mix is obtained. Also, by adding the major amount of nitrocellulose last, excessive swelling of the nitrocellulose during mixing at the elevated temperature is prevented.

The propellant mixing viscosity can be controlled by reducing the temperature to about 70°F or lower where the viscosity remains essentially constant. This procedure permits as much pot life as needed to load motor cases or molds. It has been found that the pot life extends to several days if the temperature is held below 70°F. The viscosity of the homogeneous blend remains essentially unchanged which offers a great advantage for the casting procedure. After casting the propellant into a motor case or mold, curing of the propellant grain is accomplished by standard procedures employed in the art.

In addition to the nitrocellulose, the other ingredients of a basic propellant mix which can be processed by the process of this invention includes a plasticizer, stabilizer, and crosslinker. Metal fuel and organic or inorganic oxidizers may be used. The propellant mix may contain one plasticizer compound or the mix may contain two or more plasticizer compounds as disclosed hereinbelow.

Composition of propellant blends for grains which can be produced by the process of this invention can vary greatly, but generally, the ranges of ingredients in the final propellant composition, in percent by weight, are as set forth in Table I below.

TABLE I

Ingredient	Composition Percent by Weight
Nitrocellulose	5-25
Plasticizers	20-60
Metal Fuel	0-30
Oxidizer	0-70
Stabilizer	1-2
Crosslinker	0.2-3

As earlier herein indicated a prepolymer, PGA-TDI, may be substituted for the second and major portion of the nitrocellulose source ingredient. The first and minor portion of the nitrocellulose ingredient in the range from about 3 to about 10 percent by weight of the propellant composition is preferred. Up to about 22 percent by weight of the propellant composition can be comprised of the prepolymer which may be substituted for a portion of all of the second and major portion of the nitrocellulose. When only the nitrocellulose source ingredient is used, an amount is used to provide up to about 25 percent by weight of the propellant composition.

Most of the conventional propellant ingredients can be used in crosslinked propellants. Oxidizers such as ammonium perchlorate, ammonium nitrate, potassium perchlorate, nitronium perchlorate, cyclotetramethylenetetranitramine (HMX), and cyclotrimethylenetrinitramine (RDX) can be used. Metal fuels such as aluminum, zirconium, boron, beryllium, and magnesium can be used.

Plasticizers which can be used are of two types: the energetic or explosive type such as nitroglycerin, butane trioltrinitrate (BTTN), diethylene glycol dinitrate (DEGDN), triethylene glycol dinitrate (TEGDN), trimethylol trinitrate (TMETN), and tetraethylene glycol dinitrate (4EGDN), and the inert or non-explosive type such as triacetin, diethyl phthalate, propyl adipate, and dibutyl sebacate.

Stabilizers are used to stabilize the nitrocellulose and nitrate ester plasticizers during cure and storage. Resorcinol and 2-nitrodiphenylamine may be used as stabilizers. Resorcinol, a good stabilizer, is also a colloid agent for nitrocellulose which help improve the mechanical properties in XL-PNC propellants.

The diisocyanates (crosslinkers) used have included toluene diisocyanate (TDI), hexamethylene diisocyanate (HMDI), and a prepolymer of polyglycol adipate-toluene diisocyanate (PGA-TDI).

Table II sets forth two compositions used in crosslinking accomplished in accordance with the process of this invention.

TABLE II

Ingredient	Composition Percent by Weight	
	I	II
Double-base powder	12.0	16.0
TEGDN	28.0	35.0
BTTN	16.0	0.0
HMX	40.0	0.0
Aluminum	0.0	15.0
Ammonium perchlorate	0.0	30.0
Resorcinol	1.0	1.0
EDI (added)	1.0	1.0
Ballistic modifier	3.0	3.0
Totals:	101.0	101.0

Table III and Table IV set forth typical mechanical properties of propellant before and after crosslinking (only difference in crosslinked and non-crosslinked is the addition of toluene diisocyanate, TDI).

TABLE III
COMPOSITION I

Temperature °F	Crosslinked		Non-Crosslinked	
	Stress	Strain	Stress	Strain
-40	536 psi	25%	336 psi	11%
75	165 psi	35%	52 psi	26%
140	113 psi	35%	40 psi	30%

Table IV
Composition II

Temperature °F	Crosslinked		Non-Crosslinked	
	Stress	Strain	Stress	Strain
75	554 psi	27%	330 psi	17%
140	138 psi	34%	58 psi	20%
	88 psi	38%	41 psi	22%

Table III and IV illustrate the reproducible physical properties which are most essential for a useable propellant grain. In addition, the substantially void free grains, illustrated in Tables III and IV, burn smoothly and do not break up during the burning of the grain, an essential requirement for satisfactory performance.

The equipment normally used in the mixing and processing of solid propellants work well with the process procedures of this invention. For example, a mixer equipped with heating and cooling means and facilities for remote operation under vacuum or inert gas pressurized system to ensure safety of operation and to assist in gaseous product removal, purging of systems, and preventing entrapment of gaseous products during mixing. Casting and curing of propellant are accomplished by procedures and with equipment and facilities which are standard for the art and which are suitable for forming and curing the size grains desired.

The propellants which can be processed by the process of this invention include high energy conventional propellants as well as smokeless propellants.

The process of this invention offer the following benefits and attractive results:

1. Elimination of porous propellant grains, caused by gassing of nitrocellulose-isocyanate crosslinked propellant, by elevating the temperature during mixing to react the isocyanate with moisture thus eliminating evolution of carbon dioxide during cure cycle.

2. Control viscosity of the propellant mix by elevating the temperature to gain the desired viscosity and then reducing the temperature to 70°F or lower where the viscosity essentially remains constant.

3. Homogeneous mixing and dispersion of oxidizers that tend to agglomerate and yield poor quality propellant.

4. Good dispersion of the ballistic modifiers without resorting to ball milling, surfactants, or some other more sophisticated method.

5. Elimination of stringent drying and propellant ingredients prior to mixing.

A savings can achieve in processing costs which is directly related to features set forth above, particularly, with respect to the benefit and/or results noted under items 2, 4, and 5. The qualities of the propellants made by the process of this invention are enhanced by the results achieved when the problems associated with prior art processes are eliminated, particularly, the problems associated with all items set forth above.

I claim:

1. A process for the preparation of crosslinked nitrocellulose propellant grains comprising:

- a. preparing a first homogeneous blend of selected propellant ingredients which includes blending together a predetermined amount of plasticizer, a stabilizer, a first portion of a diisocyanate crosslinker, and a first and minor portion of a nitrocellulose source ingredient selected from the group consisting of double-base powder, single-base powder, and plastisol grade nitrocellulose;

- b. heating said blend to about 85°F to achieve viscosity control and to allow said first portion of a diisocyanate crosslinker to react and to effect removal of gaseous products including carbon dioxide formed from said reaction;

- c. combining with said first homogeneous blend a predetermined amount of an ingredient selected from a prepolymer ingredient having a suitable amount of said first portion of a diisocyanate crosslinker mixed therein and a second and major portion of a nitrocellulose source ingredient along with a suitable amount of a second portion of a diisocyanate crosslinker;

- d. mixing combined ingredients to achieve a second homogeneous blend and thereafter reducing temperature of said second homogeneous blend to below about 70°F where the viscosity of the said second homogeneous blend remains essentially constant;

- e. casting said second homogeneous blend into a suitable mold; and, thereafter,

- f. curing said second homogeneous blend to form a crosslinked nitrocellulose propellant grain, said propellant grain being characterized by having substantially void free properties and having improved mechanical properties which are reproducible from batch to batch processing as determined by a comparison of measurable mechanical properties of grains formed from different batches processed by said process.

2. The process of claim 1 wherein said predetermined amount of plasticizer is from about 20 to about 60 percent by weight; said predetermined amount of stabilizer is from about 1 to about 2 percent by weight; said predetermined amount of a first portion of a diisocyanate crosslinker is from about 0.1 to about 0.2 percent by weight; said predetermined amount of a first and minor portion of a nitrocellulose source ingredient is from about 3 to about 10 percent by weight, said percent by weight being based on the total weight of the propellant composition; a second and major portion of a nitrocellulose source ingredient is the ingredient selected for combining with said first homogeneous blend, said second and major portion of nitrocellulose being used in an amount to provide up to about 25 percent by weight of the propellant grain; and said second portion of a diisocyanate crosslinker being selected in an amount from about 0.3 to about 3 percent by weight of said propellant grain.

3. The process of claim 2 wherein said plasticizer is selected from the plasticizers consisting of nitroglycerin, butane trioltrinitrate, diethylene glycol dinitrate, trimethylol ethane trinitrate, tetraethylene glycol dinitrate, triacetin, diethyl phthalate, propyl adipate, and dibutyl sebacate; said first portion of a diisocyanate crosslinker and said second portion of a diisocyanate crosslinker is selected from the diisocyanates consisting of toluene diisocyanate and hexamethylene diisocyanate; and said stabilizer is selected from the stabilizers consisting of resorcinol and 2-nitrodiphenylamine.

4. The process of claim 3 wherein said heating is accomplished within a range of temperature from about 85°F to about 140°F.

5. The process of claim 4 wherein said selected propellant ingredients for preparing said first homogeneous blend additionally includes a metal fuel selected from the metal fuels consisting of aluminum, zirconium, boron, beryllium, and magnesium in amounts up to about 30 percent by weight of said

propellant grain; and an oxidizer selected from the oxidizers consisting of ammonium perchlorate, ammonium nitrate, potassium perchlorate, nitronium perchlorate, cyclotetramethylenetetranitramine, and cyclotrimethylenetrinitramine in amounts up to about 70 percent by weight of said propellant grain.

6. The process of claim 1 wherein said predetermined amount of plasticizer is from about 20 to about 60 percent by weight; said predetermined amount of stabilizer is from about 1 to about 2 percent by weight; said predetermined amount of a first portion of an isocyanate crosslinker is from about 0.1 to about 0.2 percent by weight; said predetermined amount of a first and major portion of a nitrocellulose source ingredient is from about 3 to about 10 percent by weight, said percent by weight being based on the total weight of the propellant composition; said ingredient selected for combining with said first homogeneous blend is a prepolymer ingredient which is used in amounts up to about 22 percent by weight of the propellant grain, said prepolymer ingredient being polyglycol adipate having a suitable amount of a diisocyanate crosslinker mixed therein, said suitable amount of a diisocyanate crosslinker being a second portion of a diisocyanate crosslinker sufficient to provide from about 0.5 to about 3 percent diisocyanate crosslinker in said propellant grain.

7. The process of claim 6 wherein said plasticizer is

selected from the plasticizers consisting of nitroglycerin, butane trioltrinitrate, diethylene glycol dinitrate, trimethylol ethane trinitrate, tetraethylene glycol dinitrate, triacetin, diethyl phthalate, propyl adipate, and dibutyl sebacate; said first portion of a diisocyanate crosslinker and said second portion of a diisocyanate crosslinker is selected from the diisocyanates consisting of toluene diisocyanate and hexamethylene diisocyanate; and said stabilizer is selected from the stabilizers consisting of resorcinol and 2-nitrodiphenylamine.

8. The process of claim 7 wherein said heating is accomplished within a range of temperature from about 85°F to about 140°F.

9. The process of claim 8 wherein said selected propellant ingredients for preparing said first homogeneous blend additionally includes a metal fuel selected from the metal fuels consisting of aluminum, zirconium, boron, beryllium, and magnesium in amounts up to about 30 percent by weight of said propellant grain; and an oxidizer selected from the oxidizers consisting of ammonium perchlorate, ammonium nitrate, potassium perchlorate, nitronium perchlorate, cyclotetramethylenetetranitramine, and cyclotrimethylenetrinitramine in amounts up to about 70 percent by weight of said propellant grain.

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