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POLYURETHANE PROPELLANT COMPOSITIONS PREPARED WITH HYDROXY-TERMINATED POLYESTERS

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No Drawing. Continuation of application Ser. No. 151,138, Nov. 1, 1961. This application Dec. 29, 1966, Ser. No. 607,133

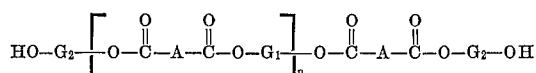
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9 Claims

ABSTRACT OF THE DISCLOSURE

An improved solid propellant having from 5 to about 40 percent of a binder, the binder being prepared from the reaction of an isocyanate or isothiocyanate with a polyester prepolymer having the formula:



wherein n is an integer ranging from 2 to about 50, A is selected from the group consisting of aliphatic and alicyclic radicals having from 0 to about 34 carbon atoms, G_1 and G_2 are selected from the group consisting of aliphatic and oxyaliphatic radicals, at least one of said radicals A, G_1 , and G_2 containing branched side chains.

This application is a continuation of our copending application Ser. No. 151,138, now abandoned, filed Nov. 1, 1961.

This invention relates to novel solid propellant compositions and a method for their manufacture. In particular, this invention relates to novel solid propellant compositions capable of holding large quantities of solid oxidizer materials, which compositions are readily made by employing a polyester component in the propellant binder which imparts low viscosity to the propellant mixture in its uncured state.

Various solid propellant compositions are known which employ a polyester component in the propellant binder. Although such propellant compositions have been used in the past, they all have fairly serious shortcomings which have inhibited their usefulness. Generally, such propellant compositions have been found difficult to mix and to load with the high percentage of solid ingredients which are necessary in a solid propellant. Secondly, these prior art propellant compositions have been difficult to form because the propellant mixture has had a poor pot life. Pot life is defined as the length of time between the mixing of the binder components with the polymerization catalyst and the time when the propellant composition becomes too viscous to cast. The short pot life of prior propellant compositions has made their processing very difficult since a slight delay in processing could result in setting-up of the propellant within the mixing vessel.

A further deficiency of prior art propellants has been their tendency to deteriorate rapidly when stored under adverse conditions. Although the deterioration mechanism is not known precisely, it apparently involves depolymerization of the binder or reaction of the binder with other components employed in the propellant formulation. On deterioration, the propellant is not only weakened but undesirable byproducts may be produced within the propellant itself. Typical of such undesirable byproducts are entrapped gases which may form voids or fissures within the propellant grain which can cause uneven burning or explosion when the propellant is burned. The propensity of prior art propellants toward deteriora-

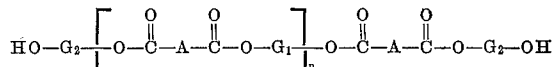
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tion has seriously limited their usefulness since military demands require a propellant formulation which can be stored under adverse conditions—such as in the tropics or the arctic—for long periods of time without impairing the properties of the propellant.

An object of this invention is to provide a propellant composition having the ability to hold large quantities of solid materials within the propellant grain. A further object of this invention is to provide a method for formulating such propellants by the use of a polyester ingredient which imparts a low viscosity and long pot life to the propellant formulation in its uncured state. An additional object is to provide propellant compositions which have high thermal stability such that they can be stored for long periods of time under adverse climatic conditions. Additional objects will appear from the specification and claims which follow.

The propellant compositions of our invention contain from about 5 to about 40 percent of a polymeric binder material and about 50 to about 95 percent of an oxidizer or mixture of oxidizers. In addition to the oxidizer and binder our propellants can contain such other ingredients as high energy fuels, powdered metals, resonance suppressants, burning rate modifiers, plasticizers, antioxidants, antifoaming agents, and the like. These additional propellant ingredients are present in lesser amounts than the binder or oxidizer as defined later in this specification.

As stated above, our propellant compositions employ a polyester as an ingredient in the propellant binder. Applicable materials are the hydroxy-terminated polyesters having the formula:



in which n is an integer ranging from about 2 to about 50, A is a divalent aliphatic or alicyclic radical having from 0 to 34 carbon atoms, and G_1 and G_2 are divalent aliphatic or oxyaliphatic radicals. In accord with our invention, one or all of the radicals A, G_1 , and G_2 contain branching side chains. Although not precisely understood, it is believed that the branching of A, G_1 , or G_2 is responsible for the improved viscosity of our propellants in their uncured state which permits the blending of large percentages of solid ingredients such as inorganic oxidizers within the propellant composition.

As stated above, G_1 and G_2 are divalent aliphatic or oxyaliphatic radicals. When G_1 and G_2 are oxyaliphatic radicals, the radical may be a repeating one containing a plurality of aliphatic radicals interspersed by oxy groups such as in polyoxyalkylene compounds. The aliphatic portions of G_1 and G_2 contain from 2 to about 10 carbon atoms. In the case where G_1 and G_2 are aliphatic radicals rather than oxyaliphatic radicals, the aliphatic portion of G_1 and G_2 obviously constitutes the entire radical which is then an aliphatic radical containing from 2 to about 10 carbon atoms.

Preferably, G_1 contains branching aliphatic side chains which are situated within two carbon atoms of the terminal valences of G_1 . In the case where the side chains are attached to the terminal carbon atoms of G_1 , the terminal carbon atom may have either one or two side chains attached to it. In the case where the side chains are attached to the carbon atom which is adjacent to the terminal carbon atom, there are preferably two side chains attached to that carbon atom. To illustrate, when G_1 is 1,5-pentylene there may be any of:

- (1) One or two alkyl side chains attached to both the one and five carbon atoms,
- (2) Two alkyl side chains attached to both the two and four carbon atoms,

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(3) One or two alkyl side chains attached to the one carbon atom and two alkyl side chains attached to the four carbon atom,

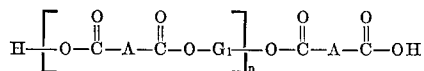
(4) One or two alkyl side chains attached to the five carbon atom and two alkyl side chains attached to the two carbon atom.

A still further preferred form of our invention is a propellant composition in which the binder composition contains a polyester as set forth above in which A is a divalent aliphatic radical having from about 0 to about 10 carbon atoms and G_1 and G_2 are divalent aliphatic radicals which contain from about 2 to about 10 carbon atoms. The aliphatic radicals A, G_1 and G_2 can be saturated or unsaturated and at least one of A, G_1 or G_2 contains branching aliphatic side chains. Preferably, G_1 contains branching aliphatic side chains which are located on the terminal carbon atoms or the carbon atoms adjacent to the terminal carbon atoms. As set forth above, when the branching on G_1 is on the terminal carbon atoms, the terminal carbon atoms can contain either one or two such branching side chains. When the branching is on the carbon atoms adjacent to the terminal carbon atoms, the adjacent carbon atoms contain at least two such branching alkyl side chains.

Preferably, the hydroxy-terminated polyester prepolymer employed in our invention is that described in our copending application Ser. No. 151,138, filed Nov. 1, 1961. As set forth in that application, A is an aliphatic radical having from 0 to about 10 carbon atoms and G_2 is an aliphatic radical having from 3 to about 10 carbon atoms which is bonded to the terminal hydroxy radical through a secondary carbon atom. G_1 is a divalent radical as set forth above having from 5 to about 10 carbon atoms.

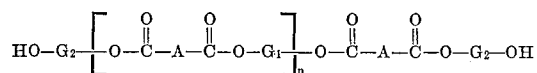
As more specifically pointed out in our copending application, A is preferably an alkylene radical containing from 5 to 9 carbon atoms in a straight chain and more preferably A contains 5, 7, or 9 carbon atoms in a straight chain. G_2 , as stated above, is preferably an alkylene radical containing from about 3 to about 10 carbon atoms and having at least one alkylene bond from a secondary carbon atom to the terminal hydroxy radical. Preferably, G_1 is an alkylene radical having from 5 to about 10 carbon atoms and branched as defined above. Polyesters having this composition are most effective in imparting a low viscosity and a slow curing rate to our propellant compositions. Further, by virtue of the branching in G_1 , as defined above, the cured propellant has a high thermal stability such that it can be stored for long periods under adverse climatic conditions.

The hydroxy-terminated polyesters employed in our propellants are prepared according to the general processes described in our copending application Ser. No. 151,138. In general, one such procedure involves heating a diol, $HO-G_2-OH$, with an acid-terminating polyester



to an elevated temperature under an inert atmosphere or vacuum. The polyesters can also be prepared by transesterification or by use of an acyl halide reactant as described in our copending application. While our copending application describes only the preparation of our most preferred polyester prepolymers, the methods described apply generally to the preparation of all the hydroxy-terminated prepolymers as used in our invention.

Preferably, the propellant compositions of our invention will be prepared using hydroxy-terminated polyesters having the formula:



wherein G_1 , G_2 , A, and n are as defined above. However, it may be desirable in some instances to use, in addition,

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other hydroxy-terminated polyesters in the binder in order to obtain desired properties. Thus, our invention includes the use of various polyester mixtures as long as a portion of the polyester material has the formula as set forth previously.

The hydroxy-terminated polyesters employed in this invention can be present in an amount from as low as 40 percent up to about 95 percent by weight of the propellant binder. Preferably, these polyesters will be used in an amount varying from 60 percent to 80 percent by weight of the propellant binder.

Various other ingredients are employed in the preparation of the binder for our propellant compositions. These ingredients include isocyanate and cross-linking monomers.

Isocyanate or isothiocyanate compounds are condensed with our polyester prepolymers to produce the polyurethane binder for our solid propellants. Isocyanates or isothiocyanates used for this purpose will preferably be diisocyanates or diisothiocyanates. However, it is within the scope of our invention to use other isocyanates such as trisocyanates or polyisothiocyanate if desired. The nature of the organic radical which carries the isothiocyanate or isocyanate group is not critical so long as it is compatible with the other ingredients employed in the composite propellant. Thus, the isocyanate materials can contain, for example, aliphatic, alicyclic, aryl, heterocyclic radicals, and nitro derivatives.

Where it is desired to produce a cross-linked binder and only bifunctional reactants have been employed to produce the major part of the binder, it is necessary to employ a cross-linking agent. Suitable cross-linking reactants have more than two functional groups such as triols and triisocyanate compounds. Suitable cross-linking agents include glycerol, glycerol monoricinoleate, glycerol triricinoleate, 1,2,6-hexanetriol, methylenebis-(orthochloroaniline), triethanolamine, trimethylolpropane, N,N,N',N'-tetrakis - (2-hydroxypropyl) ethylenediamine, toluene-2,4,6-trisocyanate, and diethylenetriamine.

The nature of the cross-linking agent is not critical so long as it provides functional groups which will react to form bridges between the linear chains of the main components of the binder. Mixtures of cross-linking agents can be employed if desired. The cross-linking agents can be present in amounts varying from about 0.5% to about 3.0% by weight of the total propellant composition.

Various additives can be incorporated in the propellant compositions of this invention. Such additives include plasticizers, combustion regulators, high energy fuels, burning rate catalysts, antioxidants, curing catalysts, solvents, wetting agents, antifoaming agents, resonance suppressants, etc. The total aggregate of these additives can amount to from a trace to about 15% by weight of the total propellant composition.

Powdered metals can also be incorporated in our propellant composition. Such metals include aluminum, magnesium, lithium, titanium, tungsten, zirconium, or their alloys. These metals can be incorporated in an amount from trace percentages up to about 30 percent by weight of the total propellant composition. The use of powdered aluminum is described in assignee's application Ser. No. 33,054, filed May 31, 1960.

The propellant compositions of this invention are prepared by mixing the binder ingredients with the other additives of the propellant and casting the composite mixture in the form of a propellant grain. Usually, the composite mixture is cast in situ in a rocket motor. The propellant composition can, however, be cast outside of the rocket motor and inserted therein after curing is complete.

Mixing is usually accomplished in a mixer equipped with facilities for heating, cooling, and subjecting the propellant batches to vacuum during mixing. If powdered metals are employed it is preferable to add these pow-

dered metals to one or more of the liquid binder components prior to incorporating the oxidizer and other ingredients therein. This avoids the fire hazard created by mixing oxidizer and powdered metals in a dry state. The liquid binder components can be added all at one time or in any sequence desired. The various ingredients of the propellant composition can be added all at the same stage of processing or in any sequence desired.

After the propellant batch has been mixed to substantial uniformity it is cast, extruded, or compressed to the desired shape and cured at an elevated temperature.

In the following examples the term "rex hardness" is used. Rex hardness is the measure of resistance of a solid material to the penetration of a calibrated tapered probe applied to the surface of the solid material at constant force (registered by an arbitrary scale known as the rex hardness scale). The higher the rex hardness number the harder the material.

In the following examples various quantities of monomers and prepolymers are provided. Upon curing, the functional groups of these monomers and prepolymers will react with one another to form the propellant binder. The ratio of the concentrations of the various types of functional groups to one another is defined as the "chemical equivalent ratio." For example, the concentration of the hydroxy groups in one-third mole of a triol would be one, or the product of the number of groups per molecule (3) times the number of moles (one-third). The concentration of the isocyanate groups in one mole of diisocyanate would be two or the product of one and two. Thus, the chemically equivalent ratio of diisocyanate to triol would be, in the above case, two to one.

The term "Crawford bomb burning rate" employed in the examples refers to a standard burning rate test. In this test, confined propellant strands (coated with a low burning acrylate polymer) are burned under controlled nitrogen pressure. The burning rate is determined by placing low melting wires within the propellant strands at right angles to the longitudinal axis of the strand. The wires, which are connected to a source of electrical current, are melted through burning of the strand. This causes discontinuity of the electrical circuit which included the wires. By timing the interval between the melting of adjacent wires, the burning rate is determined.

In the following examples all parts and percentages are by weight unless otherwise specified.

EXAMPLE I

The following propellant composition was prepared by blending to a uniform consistency the following ingredients in the relative specified proportions.

Ingredient:	Wt. percent
Ammonium perchlorate	60.00
Aluminum powder	20.00
Carbon black	0.10
Cuprous oxide powder	0.10
-phenylnaphthyl amine	0.20
Lecithin	0.20
Ferric acetylacetonate	0.03
Diocetylazelate (plasticizer)	1.95
Neopentyl glycol azelate	8.32
Tripropylene glycol azelate	5.82
Glycerol monoricinoleate	0.97
Triethanolamine	0.17
Tolylene diisocyanate	2.14
	100.00

The chemical equivalent ratio of Diols:Triols:Tolylene diisocyanate was 60:40:107. After being mixed, the com-

position was cast in situ in a rocket motor and cured for three days at 110° F. The cured propellant composition has the following physical properties:

Rex hardness (ambient temperature)	65
Density (lbs./cu. in.)	0.064
Tensile strength at maximum stress (lbs./sq. in.):	
0° F.	1050
40° F.	280
80° F.	120
Elongation at maximum stress (percent of initial length):	
0° F.	20
40° F.	42
80° F.	60

The propellant composition was easily cast because the viscosity of the liquid binder components was below 4000 centipoises (cps.), at 77° F. The cured propellant was found to possess superior thermal stability.

EXAMPLE II

The following propellant composition was prepared by uniformly mixing the following ingredients:

Ingredient:	Wt. percent
Ammonium perchlorate	60.00
Aluminum powder	20.00
Carbon black	0.10
Cuprous oxide powder	0.10
-phenylnaphthyl amine	0.20
Sorbitan trioleate	0.20
Ferric acetylacetonate	0.03
Diocetyl azelate (plasticizer)	1.95
Neopentyl glycol sebacate	7.07
Tripropylene glycol azelate	7.07
Glycerol monoricinoleate	0.97
Triethanolamine	0.17
Tolylene diisocyanate	2.14
	100.00

The chemical equivalent ratio of Diols:Triols:Tolylene diisocyanate was 60:40:107. The composition was cast in situ in a rocket motor and cured for three days at 110° F. The cured propellant composition had the following physical properties:

Rex hardness (ambient temperature)	65
Density (lbs./cu. in.)	0.064
Tensile strength at maximum stress (lbs./sq. in.):	
0° F.	820
40° F.	260
80° F.	118
Elongation at maximum stress (percent of initial length):	
0° F.	18
40° F.	44
80° F.	62

The viscosity of the liquid binder components was below 4000 cps., at 77° F. and the cured propellant possessed superior thermal stability.

Example II is repeated using the reaction product of acid-terminated neopentyl glycol azelate and 1,2-propylene glycol in place of the neopentyl sebacate and tripropylene glycol azelate. The preparation and casting of the propellant composition is easily accomplished due to the low viscosity and the long pot life of the propellant composition. The cured propellant composition is found to possess high thermal stability.

7 EXAMPLE III

The following propellant composition was prepared by mixing to uniformity the following ingredients in their stated percentages:

Ingredient:	Wt. percent
Ammonium perchlorate	60.00
Aluminum powder	20.00
Carbon black	0.10
Cuprous oxide powder	0.10
-phenylnaphthyl amine	0.20
Sorbitan trioleate	0.20
Ferric acetylacetonate	0.03
Diocetyl azelate (plasticizer)	1.95
Neopentyl glycol azelate	9.85
Triethylene glycol azelate	4.93
Hexane triol	0.16
Triethanolamine	0.30
Hexamethylene diisocyanate	2.18
	100.00

The chemical equivalent ratio of Diol:Triol:Hexamethylene diisocyanate was 60:40:107. The composition was cast in situ in a rocket motor and cured for three days at 110° F. The cured propellant had the following physical properties:

Rex hardness (ambient temperature)	80
Density (lbs./cu. in.)	0.063
Tensile strength at maximum stress (lbs./sq. in.):	
0° F.	1210
40° F.	380
80° F.	140
Elongation at maximum stress (percent of initial length):	
0° F.	9
40° F.	33
80° F.	35

Example III is repeated using the reaction product of acid-terminated 2,2,4,4-tetramethyl-1,5-pentyleneoxalate and 1,2-butylene glycol in place of the neopentyl glycol azelate and triethylene glycol azelate. The above procedure is repeated again using the reaction product of polyethylene glycol isosebacate and ethylene glycol in place of the neopentyl glycol azelate and triethylene glycol azelate. The resulting propellant compositions are readily processible due to their low viscosity and ability to hold a high percentage of solid ingredients.

EXAMPLE IV

The following propellant composition was prepared by uniformly mixing the stated percentages of the following ingredients:

Ingredient:	Wt. percent
Ammonium perchlorate	60.00
Aluminum powder	20.00
Carbon black	0.10
Cuprous oxide	0.10
-phenylnaphthyl amine	0.2
Sorbitan monoleate	0.15
Dodecyl benzene sulfonic acid	0.05
Silicone oil	0.005
Ferric acetyl acetate	0.03
Neopentyl glycol dimer acid polyester	15.41
Glycerol monoricinoleate	1.50
Tolyene diisocyanate	2.455
	100.000

The chemical equivalent ratio of Diol:Triol:Tolyene diisocyanate was 65:35:107. This composition was mixed in a 60-lb. mixer and cast in situ in a rocket motor and cured for four days at 110° F. The physical properties of the cured propellant were as follows:

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Rex hardness (ambient temperature)	65
Density (lbs./cu. in.)	0.064
Crawford bomb burning rate at 1000 lbs./sq.in. (inches per second)	0.29
Tensile strength at maximum stress (lbs./sq. in.):	
0° F.	1050
40° F.	341
80° F.	121
Elongation at maximum stress (percent of initial length):	
0° F.	9
40° F.	18
80° F.	35

The propellant was maintained at a constant strain of 20 percent elongation for 14 days at 80° F. Upon release the propellant regained 48 percent of the 20 percent elongation. The sample was found to have a tensile strength at maximum stress of 86 p.s.i. at 80° F., and an elongation at maximum stress at 80° F. of 35 percent.

Example IV is repeated using the reaction product of acid-terminated 2,2-diethyl-1,3-propylene hydromuconate and 2,2,4-trimethyl-3-ethyl-1,5-pentane diol in place of the neopentyl glycol dimer acid polyester. The resulting propellant composition is readily processible due to its low viscosity. The above procedure is repeated again using the reaction product of acid-terminated 2,2,5,5-tetramethyl-3-hexene pimelate and 1-methyl-2-butene glycol in place of the neopentyl dimer acid polyester. The resulting propellant composition is readily processible due to its low viscosity and long pot life.

EXAMPLE V

The following propellant composition was prepared by uniformly mixing the following ingredients:

Ingredient:	Wt. percent
Ammonium perchlorate	60.00
Aluminum powder	20.00
Cuprous oxide	0.10
-phenylnaphthyl amine	0.20
Carbon black	0.10
Ferric acetyl acetate	0.03
Lecithin	0.20
Tricresylphosphate	1.94
Neopentyl glycol dimer acid polyester (molecular weight—1800) (M.W.)	13.88
Glycerol monoricinoleate	1.38
Tolyene diisocyanate	2.17
	100.00

The chemical equivalent ratio of Diol:Triol:Toluene diisocyanate was 65:35:110. This propellant composition was prepared in a 60-lb. mixer and was cast in situ in a rocket motor. After curing for four days at 110° F. the physical properties of this propellant were:

Rex hardness (ambient temperature)	65
Density (lbs./cu. in.)	0.064
Crawford bomb burning rate at 1000 p.s.i. (in./sec.)	0.295
Tensile strength at maximum stress (lbs./sq. in.):	
0° F.	337
40° F.	104
80° F.	94
Elongation at maximum stress (percent of initial length):	
0° F.	9
40° F.	21
80° F.	30

A sample of the propellant was kept at 25 percent elongation for 14 days at 50° F. and allowed to recover for 24 hours. The extent of recovery was found to be 70 percent of the initial 25 percent elongation. The specimen was tested for tensile strength and elongation and it was found that the tensile strength at maximum stress at 80° F. was 102 p.s.i. The elongation at maximum stress at 80° F. was 30 percent.

The above procedure is repeated using the reaction product of acid-terminated ethylenephthalate and triisobutylene glycol in place of the neopentyl glycol dimer acid polyester. The resulting propellant composition is readily processible due to its low viscosity and ability to hold high percentages of solid ingredients.

EXAMPLE VI

The following propellant composition was prepared by uniformly mixing the stated ingredients:

Ingredient:	Wt. percent
Ammonium perchlorate -----	70.00
Aluminum powder -----	10.00
Cuprous oxide -----	0.10
-phenyl-naphthyl amine -----	0.20
Ferric acetyl acetate -----	0.03
Carbon black -----	0.10
Sorbitol monoleate -----	0.10
Dodecyl benzene sulfonic acid -----	0.10
Dibutyl phthalate -----	1.94
Neopentyl glycol dimer acid polyester (M.W. 1600) -----	14.03
Glycerol monoricinoleate -----	1.00
Triethanolamine -----	0.11
Tolylene diisocyanate -----	2.29
	<hr/> 100.00

The chemical equivalent ratio of Diol:Triol:Tolylene diisocyanate was 65:35:115. This composition was mixed in a 60-lb. mixer and cast in situ in a rocket motor. The composition was cured for four days at 110° F. The physical properties of the cured propellant were:

Rex hardness (ambient temperature) -----	65
Density (lbs./cu. in.) -----	0.064
Crawford bomb burning rate at 1000 p.s.i. (in./sec.) -----	0.290
Tensile strength at maximum stress (lbs./sq. in.):	
0° F. -----	615
40° F. -----	242
80° F. -----	118
Elongation at maximum stress (percent of initial length):	
0° F. -----	14
40° F. -----	31
80° F. -----	44

A sample of the cured propellant was kept at 25 percent elongation for 14 days at 50° F. and allowed to recover for 24 hours. The sample recovered 70 percent of the initial 25 percent elongation. The residual tensile strength of the specimen at maximum stress and 85° F. was 120 p.s.i. The elongation of the specimen at maximum stress at 80° F. was 40 percent.

Example VI is repeated using 50% by weight of the total propellant of hydrazine perchlorate and 30% ammonium nitrate in place of the ammonium perchlorate. The powdered aluminum is omitted from the propellant composition. The propellant composition obtained is easily castable and capable of holding a high quantity of solid material. Similarly, when Examples I through V are repeated with the omission of the powdered aluminum, good propellant compositions are obtained.

Preferably, the polyester prepolymers used in this invention will have a viscosity below 10,000 centipoises (cps.) at 77° F. More preferably, the viscosity of the polyester prepolymers used will be lower than 4000 cps. at 77° F. It is permissible to obtain this low viscosity by employing mixtures of polyester materials. Different polyesters within the scope of the previous definition can be mixed with one another or polyesters within the scope of previous definition can be mixed with other polyester materials outside the scope of the definition.

As set forth above the aliphatic G₁ radicals used in our polyester prepolymer are preferably highly branched

compounds. Applicable G₁ radicals include the following:

- 3-oxy-1,5-pentylene,
- 1,4-butenylene-2,
- 4,4-dimethyl-1,5-pentenylene-2,
- 2,2,4,4-tetramethyl-1,5-pentylene, and the like.

Preferred G₁ alkylene radicals are:

- 2,2,4,4-tetramethyl-1,5-pentylene,
- 2,2-dimethyl-1,3-propylene,
- 2,2,3,3-tetramethyl-1,4-butenylene,
- 2,2,5,5-tetramethyl-1,6-hexylene,
- 2,2,5,6-tetramethyl-1,6-hexylene,
- 1,2,5,6-tetramethyl-1,6-hexylene, and the like.

As described previously, the difunctional organic radical A can be aliphatic or alicyclic. The radical A can, for example, include the following radicals:

- 1,4-butenylene-2,
- 1,4-cyclohexylene,
- 2,2-dimethyl-1,3-propylene,
- 2,3-dimethyl-1,4-butenylene,
- 2,2-diethyl-1,5-pentenylene-3,
- 1,4-cyclohexanediethylene, methylene,
- 1,2-ethylene, and the like.

The G₂ radical of the binder will preferably, as discussed above, contain at least one alkylene bond attached to a secondary carbon atom. This secondary alkylene bond will be attached to the terminal hydroxy group in the polyester prepolymer. This secondary bonding is thought to be responsible for considerably extending the period of time which is required to cure the propellant composition. Our preferred G₂ radicals are those containing this secondary alkyl bond and are described more particularly in our copending application Ser. No. 151,138. Other G₂ radicals which can be used in the binder of our propellant composition include the following:

- 2,2,4-trimethyl-1,3-pentylene,
- 4-oxy-1,8-octylene,
- 1,4-butadienylene-1,3,
- 1,3-propylene,
- 1,2-propylene,
- 1-methyl-1,3-propylene,
- 1,3-dimethyl-1,3-propylene,
- 2,2,4-trimethyl-1,4-butenylene, and the like.

Where a polyurethane binder is to be prepared as described above, the nature of the isocyanate monomer is not critical so long as it does not adversely affect the other components of the propellant composition. Isocyanate monomers which can be used in preparing the binder for the solid propellant compositions of this invention include the following:

(a) Alkane diisocyanates such as:

- ethylene diisocyanate;
- trimethylene diisocyanate;
- propylene-1,2-diisocyanate;
- tetramethylene diisocyanate;
- butylene-1,3-diisocyanate;
- decamethylene diisocyanate;
- octadecamethylene diisocyanate; etc.

(b) Alkene diisocyanates such as:

- 1-propylene-1,2-diisocyanate;
- 2-propylene-1,2-diisocyanate;
- 1-butenylene-1,2-diisocyanate;
- 3-butenylene-1,2-diisocyanate;
- 1-butenylene-1,3-diisocyanate;
- 1-butenylene-2,3-diisocyanate; etc.

(c) Alkylidene diisocyanates such as:

- ethylidene diisocyanate;
- propylidene-1,1-diisocyanate;
- propylidene-2,2-diisocyanate; etc.

(d) Cycloalkylene diisocyanates such as:

cyclopentylene-1,3-diisocyanate;
cyclohexylene-1,2-diisocyanate;
cyclohexylene-1,3-diisocyanate;
cyclohexylene-1,4-diisocyanate; etc.

(e) Cycloalkylidene diisocyanates such as:

cyclopentylidene diisocyanate;
cyclohexylidene diisocyanate; etc.

(f) Aromatic diisocyanates such as:

m-phenylene diisocyanate;
o-phenylene diisocyanate;
p-phenylene diisocyanate;
1-methyl-2,4-phenylene diisocyanate;
naphthylene-1,4-diisocyanate;
2,4-tolylene diisocyanate;
2,6-tolylene diisocyanate;
4,4'-diphenylmethane diisocyanate;
1,5-naphthalene diisocyanate;
methylene-bis-(4-phenylisocyanate);
2,2-propylene-bis-(4-phenylisocyanate);
diphenylene-4,4'-diisocyanate; etc.

(g) Aliphatic-aromatic diisocyanates such as:

xylylene-1,4-diisocyanate;
xylylene-1,3-diisocyanate;
4,4'-diphenylenemethane diisocyanate;
4,4'-diphenylene-propane diisocyanate; etc.

(h) Diisocyanates containing hetero-atoms such as:

$\text{OCN}-\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_2-\text{NCO}$;
2,3-pyridine diisocyanate; etc.

Oxidizers which can be employed in this invention include chromates, dichromates, permanganates, nitrates, chlorates, and perchlorates of the alkali or alkaline earth metals, ammonia, hydrazine, or guanidine, or mixtures thereof. Preferred oxidizer materials are the perchlorates and the nitrates.

The selection of the oxidizing salt depends upon the specific burning properties desired in the propellant grain. Thus, where a low smoke propellant is desired a non-metallic oxidizing salt such as ammonium perchlorate or ammonium nitrate should be employed rather than an oxidizing salt containing a metal such as sodium nitrate, potassium perchlorate, or calcium chlorate. Mixtures of suitable inorganic oxidizing salts can be used within the scope of this invention.

Typical plasticizers which can be used include isodecyl pelargonate; 4-nitrazapentanitrile; 2,2-dinitropropyl-4-nitrazapentanoate; dioctyl azelate; dibutylphthalate; tricresylphosphate; trinitrato pentaerythritol, bis-2,2-dinitropropyl acetal; and the like.

Polymerization catalysts which can be used to promote the formation of the binder include triethylamine and other tertiary amines; ferric acetylacetonate and other metal acetylacetonates; boron trifluoride; stannic chloride; dibutyltin laurate; N-methyl morpholine; ferric chloride; cobalt naphthanate; and the like.

Burning rate modifiers which can be employed in our solid propellant include copper chromite, finely divided carbon black, lithium carbonate, boron, nitroguanidine, and the like.

Resonance suppressants which can be used in our propellants include silicon dioxide, ferric oxide, calcium oxalate, and calcium carbonate. Wetting agents which can be employed in this invention include lecithin, sorbitan trioleate, sorbitan monooleate, polyoxyethylene esters of mixed acids, etc.

Various antioxidants may be employed as follows: N, N'-diphenyl - p - phenylenediamine; N,N'-di-naphthyl-p-phenylene-diamine; phenylnaphthylamine; etc.

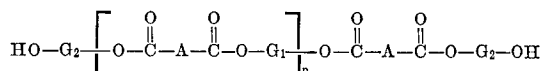
The solid propellants of this invention can be conveniently ignited by a conventional igniter as, for example,

the igniter disclosed in U.S. Pat. 3,000,312, issued Sept. 19, 1961. The propellant is preferably cast directly into a rocket chamber which is attached to a conventional venturi rocket nozzle. Upon ignition large quantities of gases are produced and exhausted through the nozzle creating propulsive force.

Our preferred propellants can be stored for long periods of time without danger of thermal deterioration. Thermally stable propellants are required where the properties of the propellant must remain substantially constant over long periods of time and under adverse conditions. Such adverse conditions are found in tropical or desert climates where it is often necessary to stockpile rockets. Thus, our new thermally stable propellants make feasible the stockpiling of weapons in critical areas where previous solid propellants could not be stored due to excessive thermal deterioration. All of our propellant compositions can be loaded with a high amount of solids.

We claim:

1. A cured solid propellant composition comprising from about 50 to about 95 percent of an oxidizer and from 5 to about 40 percent of a binder, said binder being prepared by reaction of a polyester prepolymer having the formula:



wherein n is an integer ranging from 2 to about 50, A is selected from the group consisting of aliphatic and alicyclic radicals having from 0 to about 34 carbon atoms, G_1 and G_2 are selected from the group consisting of aliphatic and oxyaliphatic radicals, at least one of said radicals A, G_1 , and G_2 containing branched side chains, with a compound selected from the group consisting of isocyanates and isothiocyanates, said polyester prepolymer comprising from about 40 to about 95 percent of the binder.

2. The cured solid propellant composition of claim 1, wherein G_1 contains branching aliphatic side chains within two carbon atoms of the terminal carbon atom.

3. The cured propellant composition of claim 1, wherein A is an aliphatic radical having from 0 to about 10 carbon atoms, and G_1 and G_2 are aliphatic radicals containing from 2 to about 10 carbon atoms.

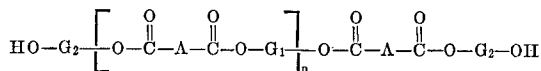
4. The cured propellant composition of claim 3, wherein G_1 contains branching aliphatic side chains located within two carbon atoms of the terminal carbon atoms.

5. The cured propellant composition of claim 1, wherein A is an aliphatic radical having 0 to about 10 carbon atoms, G_1 is an aliphatic radical having from 5 to about 10 carbon atoms containing branching aliphatic side chains located within two carbon atoms of the terminal carbon atoms, and G_2 is an aliphatic radical having from 3 to about 10 carbon atoms which is bonded to the terminal hydroxy radical through a secondary carbon atom.

6. The cured propellant composition of claim 5, wherein A is an alkylene radical containing from 5 to 9 carbon atoms, and G_1 and G_2 are alkylene radicals.

7. The cured propellant composition of claim 6, wherein A contains an odd number of carbon atoms.

8. A cured propellant composition comprising from about 50 to about 95 percent of an oxidizer, and from about 5 to about 40 percent of a binder, said binder formed from the reaction of a diisocyanate and a polyester prepolymer having the formula:

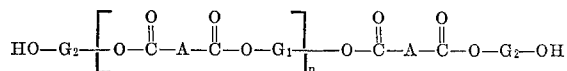


wherein n is an integer ranging from 2 to about 50, A is selected from the group consisting of aliphatic and alicyclic radicals having from 0 to about 34 carbon atoms, G_1 and G_2 are selected from the group consisting of aliphatic and oxyaliphatic radicals, at least one of said radicals A, G_1 , and G_2 containing branched side chains,

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said polyester prepolymer comprising from about 40 to about 95 percent by weight of the binder.

9. The method of preparing a cured propellant composition which comprises mixing from about 50 to about 95 percent of an oxidizer with from about 5 to about 40 percent of a binder, said binder comprising from 40 to about 95 percent by weight of a polyester prepolymer having the formula:



wherein n is an integer ranging from 2 to about 50, A is selected from the group consisting of aliphatic and alicyclic radicals having from 0 to about 34 carbon atoms, G_1 and G_2 are selected from the group consisting of ali-

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phatic and oxyaliphatic radicals, at least one of said radicals A, G_1 , and G_2 containing branched side chains, and a compound selected from the group consisting of isocyanates and isothiocyanates, and curing said binder.

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