(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 333 941 B1**

(12) # EUROPEAN PATENT SPECIFICATION

(45) Date of publication of patent specification: **24.06.92**

(51) Int. Cl.[5]: **C06B 45/10**, C06B 21/00

(21) Application number: **88302462.2**

(22) Date of filing: **21.03.88**

(54) **High-energy compositions having castable thermoplastic binders.**

(43) Date of publication of application:
27.09.89 Bulletin 89/39

(45) Publication of the grant of the patent:
24.06.92 Bulletin 92/26

(84) Designated Contracting States:
DE FR GB IT SE

(56) References cited:
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Description

The present invention is directed to castable thermoplastic binders for high-energy compositions, particularly composite solid rocket propellants.

Conventional solid composite propellants utilize chemically cross-linked elastomers in which prepolymers are cross-linked by chemical curing agents. As outlined in detail in U.S. Patent No. 4,361,526, there are important disadvantages to cross-linked elastomers. Cross-linked elastomers must be cast within a short period of time after addition of the curative, which time period is known as the "pot life". Disposal of a cast cross-linked propellant composition is difficult except by burning which poses environmental problems.

As an alternative to cross-linked binders, U.S. Patent No. 4,361,526 proposes to use a thermoplastic elastomeric binder which is a block copolymer of a diene and styrene, the styrene blocks providing a meltable crystal structure and the diene blocks imparting rubbery or elastomeric properties to the copolymer. In order to prepare a propellant composition using the copolymer, the copolymer is dissolved in an organic solvent, such as toluene, and the solids and other propellant formulations are added. The solvent is then evaporated, leaving a rubbery solid which may be divided into pellets suitable for casting or other processing.

A disadvantage of formulating a propellant composition using a thermoplastic elastomeric binder which must be dissolved in a solvent is that the propellant formulation cannot be cast in a conventional manner, e.g., into a rocket motor casing. Furthermore, solvent-based processing presents problems with respect to solvent removal and recovery. Organic solvents, such as toluene, present certain hazards both to the immediate work area and to the larger environment, necessitating various precautions to be taken with respect to processing such propellant formulations.

It would be desirable to have propellants and other high-energy solid compositions which include thermoplastic elastomeric binders which can be melted and cast without the need for solvent processing.

In accordance with a first aspect of the invention, there is provided a melt-cast high energy composition comprising energetic particulate solids dispersed in and spatially immobilized in a binder system having between 25 and 50 weight percent of 1,2 syndiotactic polybutadiene and between 50 and 75 weight percent of a plasticizer miscible with said polybutadiene. The polybutadiene binder system is useful for spatially immobilizing solid particulates, such as fuel material particulates and oxidizer particulates, in a high-energy formulation such as a propellant. The polybutadiene binder is meltable, allowing it to be mixed with other components of the propellant formulation, including the solid particulates and the plasticizer, and is castable, e.g., into a rocket motor shell. No organic solvent is required to prepare or cast the propellant formulation.

Thus, according to a further aspect of the invention there is provided a method of preparing a high-energy composition comprising mixing energetic particulate solids with 1,2 syndiotactic polybutadiene plus a plasticizer that is miscible with said polybutadiene at a temperature whereat said polybutadiene is molten, melt-casting said molten mixture into a mould, and allowing said molten mixture to cool to a solid high-energy composition with said solid particulates dispersed in plasticized polybutadiene.

High molecular weight syndiotactic 1,2 polybutadiene in combination with a suitable plasticizer, is found to provide a suitable elastomeric binder system for solid propellant compositions or the like. The polymer is a thermoplastic elastomer which generally melts in the temperature range of from 70 °C to 100 °C and therefore can be melted in the presence of fuel particulates and oxidizers to form a solvent-free propellant formulation melt. The melt is directly castable as a propellant charge into a rocket motor casing or the like.

Polybutadienes in accordance with the present invention preferably have weight average molecular weight of between 100,000 and 200,000. The crystallinities typically range from 10 percent to 35 percent and preferably between 15 and 30%. Densities typically range from 0.90 to 0.91. By 1,2 butadiene is meant that substantially all, i.e., greater than 90% of monomer addition is by 1,2 polymerization. By syndiotactic is meant that at least 90% of the 1,2 additions result in the pendant vinyl group extending from the side opposite that of the two flanking pendant vinyl groups. Syndiotactic 1,2-polybutadiene polymers suitable for use as binders are sold, for example, by the Japanese Synthetic Rubber Company under the trade designations JSR RB-810, JSR RB-820 and JSR RB-830.

Polybutadienes used in accordance with the present invention have thermal properties which make them especially suitable as propellant binders, the range from the brittle point (glass transition temperature (T_g)) to the softening point generally encompassing the ordinary ambient temperature range. Viscat softening points of these compounds range from 35 °C to 70 °C; melting points range from 70 °C to 100 °C and brittle points range from -35 °C to -40 °C. Thus while the thermoplastics are elastomers at ambient temperatures, they can be processed as molten plastics at temperatures far below the temperatures where high-energy solids become unstable. The low processing temperatures of 1,2 syndiotactic butadienes is

considered an important advantage relative to other thermoplastic elastomers which have been considered for use as propellant binders.

The polybutadienes have good tensile properties for binders. 300% moduli range from 40 to 80 kg/cm^2; Tensile strengths range from 60 to 140 kg/cm^2 and elongation ranges from 650 to 800 %. Shore D hardnesses range from 30 to 50.

To provide the polymer with suitable elastomeric properties to serve as a binder, the complete binder system includes a plasticizer with which the polymer is miscible. Suitable plasticizers include dioctyl adipate (DOA) and dioctyl phthalate (DOP); however, other miscible plasticizers known in the art are also suitable. Mixtures of plasticizers, such as DOA/DOP mixtures are also suitable. Particularly suitable plasticizers are naphthenic oils, such as those sold under the trademark Tufflo by Arco, particularly Tufflo-500. The plasticizer comprises between 50 and 75 percent by weight of the binder system (binder plus plasticizer) and preferably between 50 and 67 percent by weight.

The binder system may also include a minor amount of a wetting agent or lubricant, such as lecithin. The wetting agent or lubricant enables a higher solids loading. The lubricant typically comprises up to 4 weight percent of the total weight of the polybutadiene plus plasticizer. A presently preferred lubricant is a coating agent sold under the trade designation FC-430 by 3M.

A complete propellant formulation includes a high percentage of energetic solid particulates, including fuel material particulates, such as aluminum, and oxidizer particulates, such as ammonium perchlorate (AP), cyclotetramethylene tetranitramine (HMX) and cyclotrimethylene trinitramine (RDX), the solid particulates typically comprising between 70 and 90 wt. percent of the propellant composition and the balance being substantially all binder system. In addition, the propellant may include minor amounts of additional components, such as a bonding agent and burn rate modifiers.

Because the thermoplastic elastomer does not have a "pot life" in the sense of cross-linked elastomers, the order of mixing propellant formulation ingredients is not considered to be critical. However, for ease of mixing, it is generally preferred that the binder system, including the binder, plasticizer, and any lubricant, be blended under binder melting conditions prior to adding the solids. After the binder system is melted and blended, the solids are added, and mixing is continued to provide a uniform dispersion of solids in binder system. To provide a uniform cast, it is preferred to deaerate the molten formulation and then to cast the melt.

Cast propellant may be remelted after solidifying. Thus, there is no need to cast the propellant immediately after mixing, although from an energy efficiency standpoint this is generally desirable.

An important advantage of having a propellant which is meltable is that the propellant from an outdated missile can be melted down and reused. At the time of such remelting, the propellant might be reformulated, e.g., by addition of additional fuel or oxidizer particulates. Accordingly, the thermoplastic of the propellant composition provides for its eventual recycle, as opposed to the burning required for disposal of thermoset propellant compositions. Because the thermoplastic propellant does not have a "pot life", there are no limitations to the time of casting, and if any problems develop during casting, the process can be delayed as long as necessary merely by maintaining the propellant formulation in molten form.

In preparing propellants in accordance with the present invention, no solvents or other highly volatile substances are required. Accordingly, no special measures or special apparatus are required to contain solvent vapors, to remove solvent from the formulation or to recover solvent for reuse. Propellant formulations in accordance with the present invention may be prepared by conventional mixing apparatus without requiring extrusion, although extrusion may be used to prepare certain forms of propellants, such as propellant pellets.

An important advantage of syndiotactic butadienes for use in propellant binders is their low melting temperatures, and propellant formulations using syndiotactic butadienes are processable in the range of to 120 °C. Low processing temperatures help to ensure safety in processing high-energy compounds. Syndiotactic butadienes also have excellent low-temperature properties, typically having glass transition temperatures in the range of -40 °F (-40 °C). Low-temperature properties are important for propellant systems which might be used at very low temperatures or even exposed to very low temperatures prior to use.

The invention will now be described in greater detail by way of specific examples.

Example 1

A pilot scale mix of a composite propellant with a thermoplastic elastomeric binder is described in this example. 240 grams of a composite propellant were made from the following ingredients:

Ingredient	Weight Percent
Syndiotactic Polybutadiene RB-810	8.3
Dioctyl Adipate	15.9
Lecithin	0.8
Unground Ammonium Perchlorate (AP) 200μ	50.0
Ground Ammonium Perchlorate (AP) 18μ	25.0

The ingredients were mixed in a Baker Perkins twin blade vertical mixer with a working capacity of approximately 0.5 liters. First the polybutadiene, dioctyl adipate, and lecithin were added to the mix bowl and mixed for a total of 70 minutes with stops after 10, 20, 40 and 60 minutes for scrape down of the mixer blades. A water/ethylene glycol mixture at 99 °C (210 °F) was circulated through the mixer jacket in order to heat the mixture. After 70 minutes of mix time, the mix temperature had climbed to 71 °C (160 °F) and the polybutadiene was partially melted. At this point, one half of the unground AP was added to the mix bowl and mixed for 20 minutes. After 130 minutes total of mix time, the mixing was complete and the batch was uniform in appearance. The mix temperature was 80.6 °C (177 °F) and its viscosity was 8 Kp. The mix was then deaerated and cast into a rectangular mold by letting it drop through a funnel and slit plate into a vacuum bell.

After the mold had cooled, the propellant was removed from it and cut into 6.35 mm ($\frac{1}{4}$″) diameter by 10.2 cm (4″) long cylindrical stands for testing of burn rate. Four strands were prepared and inhibited on all but one circular face with black enamel paint. These strands were then burned in a pressurized bomb to determine propellant burn rate. Two strands were burned at an average pressure of 6.998 MPa (1015 psig) and had an average burn rate of 6.27 mm/sec (0.247 in/sec). The other two were burned at a pressure of 3.516 MPa (510 psig) and had an average burn rate of 4.65 mm/sec (0.183 in/sec).

Example 2

Nine more pilot scale batches of composite propellants using the thermoplastic elastomer binder were made and cast substantially the same manner as described in Example 1. The level of AP oxidizer was varied from 75% to 85% of the total mixture by weight. Both RB-810 and RB-820 grades of JSR syndiotactic polybutadiene were used and plasticizer to polymer ratio was varied between 2 to 1 and 1 to 1. The table below indicates the batch numbers, formulation and processing results for these batches. JANNAF Class C uniaxial tensiles were prepared from the finished batches and tested at a constant strain rate of 5.08 cm/min (2.0 in/min) at a temperature of 25 °C (77 °F). Maximum stress, strain at maximum stress and elastic modulus were calculated from these tests and are presented in the table.

Batch Number	725	726	736	737	738	741	742	743	744
TPE Type*	810	810	810	810	810	810	810	820	820
Bonding Agent Type**	HX-752	--	--	--	KR	KR	KR	KR	KR
Weight Percent									
TPE	8.3	8.3	6.7	8.0	6.5	7.3	4.9	4.9	4.9
Dioctyl adipate	15.8	16.7	13.3	12.0	13.1	7.3	9.7	9.7	9.7
Bonding Agent	0.4	--	--	--	0.4	0.4	0.4	0.4	0.4
AP, unground (200μ)	50.0	50.0	53.3	53.3	53.3	56.7	56.7	56.7	56.7
AP, ground (18μ)	25.0	25.0	26.7	26.7	26.7	28.3	28.3	28.3	28.3
Processing Results									
End of mix temp., (°C)		77.8	87.8	90.6	91.1	90.6	84.4	85.6	93.9
., (°F)	--	(172)	(190)	(195)	(196)	(195)	(184)	(186)	(201)
End of mix viscosity, Kp	--	16	22	40	24	216	60	100	68
Tensile Results									
Maximum stress, kPa (psi)	896(13)	62(9)	62(9)	82.7(12)	62(9)	117(17)	--	103(15)	103(15)
Strain at max stress, %	47	77	55	28	52	13	--	21	16
Elastic modulus, kPa (psi)	669(97)	262(38)	490(71)	772(112)	324(47)	1841(267)	--	841(122)	1145(165)

* 810 = JSR grade RB-810; 820 = JSR grade RB-820

**HX 742 = oxidizer bonding agent HX-752, 3M Company
KR = Titanate bonding agent KRP 380, Kenrich Chemical

Although the novel binder system according to the present invention has been described primarily in terms of its use in propellants, the binder system is applicable to other solid, high-energy compositions, such as explosives and gasifiers.

Claims

1. A melt-cast high energy composition comprising energetic particulate solids dispersed in and spatially immobilized in a binder system having between 25 and 50 weight percent of 1,2 syndiotactic polybutadiene and between 50 and 75 weight percent of a plasticizer miscible with said polybutadiene.

2. A composition in accordance with Claim 1 comprising between 70 and 90% energetic particulate solids, balance said binder system.

3. A composition in accordance with Claim 1 or Claim 2 wherein said 1,2 syndiotactic polybutadiene has a weight average molecular weight of between 100,000 and 200,000.

4. A composition in accordance with any preceding claim wherein said plasticizer is selected from dioctyl, adipate, dioctyl phthalate and mixtures thereof.

5. A composition according to any preceding claim wherein said binder system includes up to 4 wt. percent of a wetting agent based upon the total weight of plasticizer and polybutadiene in said binder system.

6. A method of preparing a high-energy composition comprising mixing energetic particulate solids with 1,2 syndiotactic polybutadiene plus a plasticizer that is miscible with said polybutadiene at a temperature whereat said polybutadiene is molten, melt-casting said molten mixture into a mould, and allowing said molten mixture to cool to a solid high-energy composition with said solid particulates dispersed in plasticized polybutadiene.

7. A method according to Claim 6 wherein said molten mixture is deaerated before cooling.

8. A method according to Claim 7 wherein said molten mixture is cast after deaeration and prior to cooling.

9. A method according to any one of Claims 6 to 8 wherein said temperature is at least 90 ° C.

10. A method according to any one of Claims 6 to 9 wherein said polybutadiene and said plasticizer are blended at said temperature and then said energetic solids are added.

Revendications

1. Composition de haute énergie à couler en masse fondue, cette composition comprenant des solides particulaires énergétiques dispersés dans, et spatialement immobilisés dans, un système liant comportant entre 25 et 50 % en poids de polybutadiène-1,2 syndiotactique et entre 50 et 75 % en poids d'un plastifiant miscible audit polybutadiène.

2. Composition selon la revendication 1 comprenant entre 70 et 90 % de solides particulaires énergétiques, le reste étant formé par ledit système liant.

3. Composition selon la revendication 1 ou la revendication 2, dans laquelle ledit polybutadiène-1,2 syndiotactique a un poids moléculaire moyen en poids compris entre 100 000 et 200 000.

4. Composition selon l'une quelconque des revendications précédentes, dans laquelle ledit plastifiant est choisi parmi de l'adipate de dioctyle, du phtalate de dioctyle et leurs mélanges.

5. Composition selon l'une quelconque des revendications précédentes, dans laquelle le système liant comprend jusqu'à 4 % en poids d'un agent mouillant, sur la base du poids total du plastifiant et du polybutadiène dans ledit système liant.

6. Procédé pour préparer une composition de haute énergie (à grand pouvoir énergétique) comprenant le mélangeage de solides particulaires énergétiques avec du polybutadiène-1,2 syndiotactique, plus un plastifiant qui est miscible audit polybutadiène à une température à laquelle ledit polybutadiène est fondu, la coulée dudit mélange fondu dans un moule, et le fait de laisser ledit mélange fondu refroidir jusqu'à donner une composition solide à haute énergie, dans laquelle lesdits solides particulaires sont

dispersés dans le polybutadiène plastifié.

7. Procédé selon la revendication 6, dans lequel ledit mélange fondu est désaéré avant son refroidissement.

8. Procédé selon la revendication 7, dans lequel ledit mélange fondu est coulé après désaération et avant son refroidissement.

9. Procédé selon l'une quelconque des revendications 6 à 8, dans lequel ladite température est au moins égale à 90 °C.

10. Procédé selon l'une quelconque des revendications 6 à 9, dans lequel on mélange ledit polybutadiène et ledit plastifiant à ladite température, puis l'on ajoute lesdits solides énergétiques.

Patentansprüche

1. Schmelzgiessbare hochenergetische Zusammensetzung, **gekennzeichnet durch** energetische Feststoffpartikel dispergiert und räumlich immobilisiert in einem Binder-System enthaltend zwischen 25 und 50 Gewichts-% 1,2 syndioaktisches Polybutadien und zwischen 50 und 75 Gewichts-% eines mit dem Polybutadien mischbaren Plastifiziermittels.

2. Zusammensetzung nach Anspruch 1, **dadurch gekennzeichnet,** daß diese zwischen 70 und 90% energetische Feststoffpartikel enthält, ausgleichend dieses Binder-System.

3. Zusammensetzung nach Anspruch 1 oder 2, **dadurch gekennzeichnet,** daß das 1,2 syndioaktische Polybutadien ein durchschnittliches Molekulargewicht zwischen 100,000 und 200,000 hat.

4. Zusammensetzung nach einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet,** daß das Plastifiziermittel aus Dioktyl, Adipat, Dioktylphtalat und Gemischen derselben ausgewählt ist.

5. Zusammensetzung nach einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet,** daß das Binder-System bis zu 4 Gewichts-% eines Benetzungsmittels einschließt, basierend auf dem Gesamtgewicht des Plastifiziermittels und Polybutadiens in diesem Binder-System.

6. Verfahren zur Aufbereitung einer hochenergetischen Zusammensetzung, **gekennzeichnet durch** Mischen energetischer Feststoffpartikel mit 1,2 syndioaktischen Polybutadien plus einem Plastifiziermittel, das mit diesem Polybutadien bei einer Temperatur mischbar ist, bei der das Polybutadien im geschmolzenen Zustand ist, Schmelzgießen des geschmolzenen Gemischs in eine Form, und danach abkühlen lassen dieses geschmolzenen Gemischs zu einer festen hochenergetischen Zusammensetzung mit den Feststoffpartikeln in dem plastifizierten Polybutadien dispergiert.

7. Verfahren nach Anspruch 6, **dadurch gekennzeichnet,** daß das geschmolzene Gemisch vor dem Abkühlen entlüftet wird.

8. Verfahren nach Anspruch 7, **dadurch gekennzeichnet,** daß das geschmolzene Gemisch nach dem Entlüften und vor dem Abkühlen gegossen wird.

9. Verfahren nach einem der Ansprüche 6 bis 8, **dadurch gekennzeichnet,** daß die Temperatur mindestens 90° beträgt.

10. Verfahren nach einem der Ansprüche 6 bis 9, **dadurch gekennzeichnet,** daß das Polybutadien und das Plastifiziermittel bei dieser Temperatur vermengt und danach die energetischen Feststoffe hinzugegeben werden