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(54) **Molded gas generating compositions containing a quick cure hydroxyl-terminated binder system and process for producing the same**

Schnellhärtendes Bindemittelsystem mit Hydroxylendgruppen enthaltende, geformte, gaserzeugende Zusammensetzungen und Verfahren zur Herstellung

Compositions génératrices de gaz moulées contenant un système de liaison à terminaison hydroxyle, durcissement rapide et procédé de production associé

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DescriptionTechnical Field

5 **[0001]** The present invention relates to inflators for devices such as protective passive restraints or "air bags" used in motor vehicles, escape slide chutes, life rafts, and the like. More particularly, the present invention relates to molded gas-generating compositions according to claim 8 which are used in inflators and a method according to claim 1.

Background Art

10 **[0002]** Many devices, such as protective passive restraints or "air bags" used in motor vehicles, escape slide chutes, life rafts, and the like, are normally stored in a deflated state and are inflated with gas at the time of need. Such devices are generally stored and used in close proximity to humans and, therefore must be designed with a high safety factor which is effective at all times.

15 **[0003]** Inflation is generally accomplished by means of a gas, such as air, nitrogen, carbon dioxide, helium, and the like which is stored under pressure and further pressurized and supplemented at the time of use by the addition of high temperature combustion gas products produced by the burning of a gas-generating composition. In some cases, the inflation gases are solely produced by gas-generating compositions.

20 **[0004]** The components of gas-generating compositions are incorporated into mechanical inflator devices in the form of powders, grains, pellets, or the like. A particular convenient manner to incorporate gas-generating compositions into inflator devices is to form or mold the compositions into solid structures.

25 **[0005]** One concern with molded gas-generating components is that in order to be moldable they generally include binder components, some of which are suspected to produce hazardous combustion products. For example, polyvinyl chloride (PVC) is suspected of producing polychlorinated biphenyls (PCB's) when it is combusted at elevated temperatures.

[0006] The present invention is directed to the use in the method of claim 1 of moldable gas-generating compositions which do not include binder components which are suspected of producing harmful combustion products. More particularly, the present invention is directed to the use in the method of claim 1 of moldable gas-generating compositions which avoid the use of polyvinyl chloride (PVC) binders.

30 **[0007]** Gas-generating compositions containing hydroxyl terminated polybutadiene are known from EP 0194180 for use in gun propellant, from US4184031 for use in vorket propellants and from EP 0685368 (prior art as defined in Ar 54(3) EPC) for use in hydrid air bag inflation systems.

Disclosure of the Invention

35 **[0008]** It is accordingly an object of the present invention to use gas-generating compositions which can be molded into solid structures.

[0009] Another object of the present invention is to use gas-generating compositions which can be injection molded or extruded.

40 **[0010]** It is another object of the present invention to use moldable gas-generating compositions which do not include binder components which produce harmful combustion products.

[0011] A further object of the present invention is to use moldable gas-generating compositions which do not include polyvinyl chloride binder components.

45 **[0012]** A still further object of the present invention is to use moldable gas-generating compositions which include hydroxyl terminated polybutadiene (HTPB) binder systems.

[0013] A still further object of the present invention is to use moldable gas-generating compositions which can be quick cured.

[0014] A still further object of the present invention is to use moldable gas-generating compositions which can be cured in approximately 7 minutes or less.

50 **[0015]** A yet further object of the present invention is to provide a method of molding gas-generating compositions according to claim 1.

[0016] A yet further object of the present invention is to provide a method of molding gas-generating compositions which include hydroxyl terminated polybutadiene (HTPB) binder systems which can be quick cured.

55 **[0017]** According to these and further objects of the present invention which will become apparent as the description thereof proceeds, the present invention provides a molded gas-generating composition according to claim 8 which includes:

an oxidizer component;

a hydroxyl-terminated polybutadiene binder component;
 a curing agent for curing the hydroxyl-terminated polybutadiene binder component; and
 a cure catalyst for accelerating the curing rate of the hydroxyl-terminated polybutadiene component.

[0018] The present invention further provides a method of forming a molded gas-generating according to claim 1 which comprises:

forming a moldable gas-generating composition which includes an oxidizer component, a hydroxyl-terminated polybutadiene binder component, a curing agent for curing the hydroxyl-terminated polybutadiene binder component, and a cure catalyst for accelerating the curing rate of the hydroxyl-terminated polybutadiene component;
 shaping the moldable gas-generating composition; and
 curing the shaped gas-generating composition.

[0019] The present invention further provides an inflator for inflating emergency devices which inflator includes a molded gas-generating composition according to claim 8 that consists essentially of an oxidizer component and a hydroxyl-terminated polybutadiene binder component.

Best Mode for Carrying out the Invention

[0020] The present invention is directed to the use in the method of claim 1 of gas-generating compositions which, upon ignition, rapidly generate large amounts of gaseous reaction products. The gas-generating compositions used in the present invention are moldable. In this regard, they can be prepared so as to have a suitable viscosity for injection molding, extrusion, or the like. After molding the composition can be cured to form solid structures

[0021] In use, the gas-generating compositions are molded into solid shapes which are incorporated into mechanical inflator devices such as protective passive restraints or "air bags" used in motor vehicles, escape slide chutes, life rafts, or the like. The present gas-generating compositions can be used in conjunction with inflator devices which primarily rely upon stored pressurized gas, and combustible gas-generating compositions to supplement the pressure of the stored gas at the time of use. Alternatively, the present gas-generating compositions can be used as the primary source of gas used to inflate an inflation device.

[0022] When incorporated into mechanical inflator devices, the molded gas-generating compositions of the present invention can be ignited by a conventional initiator or ignitor. For example, when used in conjunction with protective passive restraints or "air bags" used in motor vehicles, electric squibs which are activated upon a sensed impact of the motor vehicle can be used to ignite the gas-generating compositions.

[0023] The gas-generating compositions used in the present invention according to claim 8 include an oxidizer component, a binder component which serves as a fuel, a curing agent for the binder component, and a cure catalyst. For purposes of gas generation, the essential components include the oxidizer component and the binder component. For purposes of molding and curing the gas-generating composition, the curing agent and cure catalyst can be considered essential components. However, it is to be understood that the cure catalyst is only necessary when one desired to quicken the curing rate of the compositions.

[0024] Suitable oxidizers which can be used in the gas-generating compositions include alkali metal chlorates, alkali metal perchlorates, and mixtures thereof. Examples of these oxidizers include sodium chlorate, potassium chlorate, lithium chlorate, sodium perchlorate, potassium perchlorate, and lithium perchlorate. Other oxidizers which can be used include alkaline earth metal perchlorates and ammonium perchlorate.

[0025] One oxidizer which has been found to be particularly useful for purposes of the present invention is potassium perchlorate.

[0026] The binder component used in the gas-generating compositions is a hydroxyl-terminated polybutadiene (HTPB). This binder functions as both a binder and a fuel component in the composition. Hydroxyl-terminated polybutadiene has been found to be a desirable binder component since it does not produce hazardous compounds upon combustion.

[0027] A curing agent for the binder component is included in the gas-generating composition. The curing agent causes the binder component to cure during the molding process.

[0028] Curing agents include isocyanates and diisocyanates, particularly di-polyfunctional diisocyanates. Exemplary curing agents include hexamethylene diisocyanate, poly phenylmethylene isocyanate, isophorone diisocyanate, dimeryl diisocyanate, and the like.

[0029] In addition to the curing agent, a cure catalyst is included in the gas-generating compositions. The cure catalyst accelerates the curing speed of the gas-generating compositions so that they can be quick cured after molding.

[0030] The curing catalysts are selected from the group consisting of triphenylbismuth, dibutyltin dilaurate, and mixtures thereof. The curing catalyst accelerates the curing of the gas-generating compositions so that they can be molded

quickly.

[0031] In preferred embodiments the oxidizer component comprises about 83 to 95 weight percent of the gas-generating compositions, the binder component and the curing agent together comprise about 5 to 17 weight percent of the composition, and the cure catalyst comprises about 0.025 to 0.5 weight percent of the composition.

[0032] In more preferred embodiments the oxidizer component comprises about 85 to 90 weight percent of the gas-generating compositions, the binder component and the curing agent together comprise about 10 to 15 weight percent of the composition, and the cure catalyst comprises about 0.025 to 0.5 weight percent of the composition.

[0033] In even more preferred embodiments the oxidizer component comprises about 88 weight percent of the gas-generating compositions, the binder component and the curing agent together comprise about 11.8 to 11.9 weight percent of the composition, and the cure catalyst comprises about 0.1 to 0.2 weight percent of the composition.

[0034] The gas-generating compositions used in the present invention have a cure rate of less than 7 minutes and more typically between about 3 to 5 minutes, over a temperature range of about 93.3 to 190.6°C (200 to 375°F). The curing rate of the gas-generating compositions used in the present invention is dependent upon the curing temperature, as one would expect. The fastest curing times are obtained at higher curing temperatures. The upper limit of the curing temperature is just below the decomposition temperature of the composition. Therefore, for purposes of the present invention, the upper cure temperature should be limited to about 190.6°C (375°F).

[0035] In preferred embodiments, a composition which included about 88 weight percent of the oxidizer component, about 11.8 to 11.9 weight percent of the binder component, and about 0.1 to 0.2 weight percent of the cure catalyst was found to have a curing rate of between about 3 to 5 minutes at 176.7°C (350°F).

[0036] The gas-generating compositions used in the present invention are prepared by mixing the individual components together. In preparing the composition, the binder component and oxidizer component can be premixed together. It is preferred to add the curing agent and cure catalyst to the binder component and oxidizer component just prior to molding or extruding the composition so that the composition does not begin to cure prematurely.

[0037] The components can be mixed together utilizing conventional mixers, blenders, mills, etc. which are known to be useful for mixing pyrotechnic compositions.

[0038] During a typical extrusion process, an extrudable mass of the composition is prepared by mixing the components together. The extrudable mass is then fed into an extruder, extruded and blocked as desired. Next the extrudable mass is extruded, cut free and cured.

[0039] The viscosity of the mixed composition can be adjusted as necessary by incorporating a removable solvent such as ethyl acetate, acetone, ethyl alcohol, or mixtures thereof. The necessary viscosity for extrusion (or injection molding) can easily be determined based upon the specifications of the processing equipment used.

[0040] In addition to the above-discussed components, other components such as conventional stabilizers, colorants, opacifiers, and the like can be included as desired. A preferred stabilizer used in the examples which follow includes Triphenylbismuth, Maleic Anhydride, and Magnesium Oxide used together in substantially equal proportions or about 2:1:1.

[0041] Features and characteristics of the present invention will be further understood from the following non-limiting examples which are included for exemplary purposes. In these examples and throughout the specification, percentages are given as weight percents unless otherwise indicated.

Example 1

[0042] In this example four gas-generating compositions having the following formulations were prepared:

TABLE 1

Component	Parts by Weight			
Hydroxyl-terminated Polybutadiene	15.63	10.85	9.61	2.54
Isophorone Diisocyanate	1.37	0.95	0.84	0.39
Potassium Perchlorate	83	88	89.5	94
Triphenylbismuth Maleic Anhydride Magnesium Oxide	0.2	0.2	0.2	0.2

[0043] The above formulations were mixed, mold cured for 3 minutes at 176.7°C (350°F) and found to have the following properties.

TABLE 2

Performance Properties				
Viscosity (K _p)	2.5	5.5	5.3	5.3
Burning rates @ 6.9 mPa (1000 psi) 2.54 cm/s (in/sec)	2.0 (0.80)	2.2 (0.87) - 2.3 (0.90)	~2.4 (~0.95)	4.4 (1.73)
Sensitivity - Impact, friction, ESO and auto ignition	Low	Low	Low	Low
Mechanical Properties				
Stress mPa (psi)	0.81 (118)	1.04 (151)	1.46 (212)	0.26 (38)
Strain (%)	26	18	8	6.4
Modulus mPa (psi)	10.7 (1550)	12.4 (1800)	21.6 (4584)	8.6 (1250)

[0044] This data indicates that the formulations meet the requirements for air bag generator (inflator) applications.

Claims

1. A method of forming a molded gas-generating composition suitable for inflators which comprises:

forming a moldable gas-generating composition which includes an oxidizer component selected from the group consisting of alkali metal chlorates, alkali metal perchlorates, alkaline earth metal chlorates, alkaline earth metal perchlorates, ammonium perchlorate, and mixtures thereof, a hydroxyl-terminated polybutadiene binder component, a curing agent selected from the group consisting of isocyanates, diisocyanates, and mixtures thereof for curing said hydroxyl-terminated polybutadiene binder component, and a cure catalyst selected from the group consisting of triphenylbismuth, dibutyltin dilaurate, and mixtures thereof for accelerating the curing rate of said hydroxyl-terminated polybutadiene component;
shaping said moldable gas-generating composition by injection molding or extrusion thereof; and
curing said shaped gas-generating composition.

2. A method of forming a molded gas-generating composition according to Claim 1, wherein said gas-generating composition has a cure rate of 5 minutes or less at a temperature of 93.3 to 190.6°C (200 to 375°F)

3. A method of forming a molded gas-generating composition according to Claim 1, wherein said gas-generating composition further includes a removable solvent.

4. A method of forming a molded gas-generating composition according to Claim 1, wherein said moldable gas-generating composition comprises about 85 to 95 weight percent of said gas-generating composition, said hydroxyl-terminated polybutadiene binder component and the curing agent together comprise about 5 to 15 weight percent of said gas-generating composition, and said cure catalyst comprises about 0.025 to 0.5 weight percent of said gas-generating composition.

5. A method of forming a molded gas-generating composition according to Claim 4, wherein said moldable gas-generating composition comprises about 85 to 90 weight percent of said gas-generating composition, said hydroxyl-terminated polybutadiene binder component and the curing agent together comprise about 10 to 15 weight percent of said gas-generating composition, and said cure catalyst comprises about 0.025 to 0.5 weight percent of said gas-generating composition.

6. A method of forming a molded gas-generating composition according to Claim 5, wherein said moldable gas-generating composition comprises about 88 weight percent of said gas-generating composition, said hydroxyl-terminated polybutadiene binder component and the curing agent together comprise about 11.8 to 11.9 weight percent of said gas-generating composition, and said cure catalyst comprises about 0.01 to 0.2 weight percent of said gas-generating composition.

7. A method of forming a molded gas-generating composition according to Claim 6, wherein said gas-generating composition has a cure time of about 3 minutes at a temperature of about 176.7°C (350°F).
8. A molded gas-generating composition obtainable by the method according to Claim 1.

Patentansprüche

1. Verfahren zum Bilden einer geformten gaserzeugenden Zusammensetzung, geeignet zur Verwendung in Aufblasseinrichtungen, umfassend:

Bilden einer formbaren gaserzeugenden Zusammensetzung, die einen Oxidationsmittelbestandteil enthält, ausgewählt aus der Gruppe, bestehend aus Alkalimetallchloraten, Alkalimetallperchloraten, Erdalkalimetallchloraten, Erdalkalimetallperchloraten, Ammoniumperchlorat und Gemischen davon, einem Hydroxyl-terminierten Polybutadienbindemittelbestandteil, einem Härter, ausgewählt aus der Gruppe, bestehend aus Isocyanaten, Diisocyanaten und Gemischen davon zu Härten des Hydroxyl-terminierten Polybutadienbindemittelbestandteils, und einen Härtungskatalysator, ausgewählt aus der Gruppe, bestehend aus Triphenylbismuth, Dibutylzinndilaurat und Gemischen davon zum Beschleunigen der Härtungsgeschwindigkeit des Hydroxyl-terminierten Polybutadienbindemittelbestandteils;

Formen der formbaren gaserzeugenden Zusammensetzung durch Spritzgießen oder Extrudieren; und Härten der geformten gaserzeugenden Zusammensetzung.

2. Verfahren zum Bilden einer geformten gaserzeugenden Zusammensetzung nach Anspruch 1, wobei die gaserzeugende Zusammensetzung eine Härtungsgeschwindigkeit von 5 Minuten oder weniger bei einer Temperatur von 93,3 bis 190,6°C (200 bis 375°F) aufweist.

3. Verfahren zum Bilden einer geformten gaserzeugenden Zusammensetzung nach Anspruch 1, wobei die gaserzeugende Zusammensetzung weiterhin ein entfernbares Lösungsmittel aufweist.

4. Verfahren zum Bilden einer geformten gaserzeugenden Zusammensetzung nach Anspruch 1, wobei die formbare gaserzeugende Zusammensetzung ungefähr 85 bis 95 Gew.-% der gaserzeugenden Zusammensetzung ausmacht, der Hydroxylterminierte Polybutadienbindemittelbestandteil und das Härtungsmittel zusammen ungefähr 5 bis 15 Gew.-% der gaserzeugenden Zusammensetzung ausmachen, und der Härtungskatalysator etwa 0,025 bis 0,5 Gew.-% der gaserzeugenden Zusammensetzung ausmacht.

5. Verfahren zum Bilden einer geformten gaserzeugenden Zusammensetzung nach Anspruch 4, wobei die formbare gaserzeugende Zusammensetzung ungefähr 85 bis 90 Gew.-% der gaserzeugenden Zusammensetzung ausmacht, der Hydroxylterminierte Polybutadienbindemittelbestandteil und das Härtungsmittel zusammen ungefähr 10 bis 15 Gew.-% der gaserzeugenden Zusammensetzung ausmachen, und der Härtungskatalysator etwa 0,025 bis 0,5 Gew.-% der gaserzeugenden Zusammensetzung ausmacht.

6. Verfahren zum Bilden einer geformten gaserzeugenden Zusammensetzung nach Anspruch 5, wobei die formbare gaserzeugende Zusammensetzung ungefähr 88 Gew.-% der gaserzeugenden Zusammensetzung ausmacht, der Hydroxylterminierte Polybutadienbindemittelbestandteil und das Härtungsmittel zusammen ungefähr 11,8 bis 11,9 Gew.-% der gaserzeugenden Zusammensetzung ausmachen, und der Härtungskatalysator etwa 0,01 bis 0,2 Gew.-% der gaserzeugenden Zusammensetzung ausmacht.

7. Verfahren zum Bilden einer geformten gaserzeugenden Zusammensetzung nach Anspruch 6, wobei die gaserzeugende Zusammensetzung eine Härtungszeit von etwa 3 Minuten bei einer Temperatur von etwa 176,7°C (350°F) aufweist.

8. Geformte gaserzeugende Zusammensetzung, erhältlich durch das Verfahren gemäß Anspruch 1.

Revendications

1. Procédé de formation d'une composition génératrice de gaz moulée adaptée pour les gonfleurs, qui comprend :

la formation d'une composition génératrice de gaz moulable qui comprend un composant oxydant choisi dans le groupe comprenant les chlorates de métal alcalin, les perchlorates de métal alcalin, les chlorates alcalino-terreux, les perchlorates alcalino-terreux, le perchlorate d'ammonium et leurs mélanges, un composant liant polybutadiène terminé par un hydroxyle, un agent durcissant choisi dans le groupe comprenant les isocyanates, les diisocyanates, et leurs mélanges, pour durcir ledit composant liant polybutadiène terminé par un hydroxyle, et un catalyseur de durcissement choisi dans le groupe comprenant le triphénylbismuth, le dilaurate de dibutylétain, et leurs mélanges, pour accélérer la vitesse de durcissement dudit composant polybutadiène terminé par un hydroxyle ;

la formation de ladite composition génératrice de gaz moulable par son moulage par injection ou extrusion ; et le durcissement de ladite composition génératrice de gaz formée.

2. Procédé de formation d'une composition génératrice de gaz moulée selon la revendication 1, dans lequel ladite composition génératrice de gaz a une vitesse de durcissement de 5 minutes ou inférieur à une température de 93,3 à 190,6°C (200 à 375°F).
3. Procédé de formation d'une composition génératrice de gaz moulée selon la revendication 1, dans lequel ladite composition génératrice de gaz comprend en outre un solvant amovible.
4. Procédé de formation d'une composition génératrice de gaz moulée selon la revendication 1, dans lequel ladite composition génératrice de gaz comprend environ 85 à 95 pour cent en poids de ladite composition génératrice de gaz, ledit composant liant polybutadiène terminé par un hydroxyle et l'agent durcissant ensemble comprennent environ 5 à 15 pour cent en poids de ladite composition génératrice de gaz, et ledit catalyseur de durcissement comprend environ 0,025 à 0,5 pour cent en poids de ladite composition génératrice de gaz.
5. Procédé de formation d'une composition génératrice de gaz moulée selon la revendication 4, dans lequel ladite composition génératrice de gaz moulable comprend environ 85 à 90 pour cent en poids de ladite composition génératrice de gaz, ledit composant liant polybutadiène terminé par un hydroxyle et l'agent durcissant ensemble comprennent environ 10 à 15 pour cent en poids de ladite composition génératrice de gaz, et ledit catalyseur de durcissement comprend environ 0,025 à 0,5 pour cent en poids de ladite composition génératrice de gaz.
6. Procédé de formation d'une composition génératrice de gaz moulée selon la revendication 5, dans lequel ladite composition génératrice de gaz comprend environ 88 pour cent en poids de ladite composition génératrice de gaz, ledit composant liant polybutadiène terminé par un hydroxyle et l'agent durcissant ensemble comprennent environ 11,8 à 11,9 pour cent en poids de ladite composition génératrice de gaz, et ledit catalyseur de durcissement comprend environ 0,01 à 0,2 pour cent en poids de ladite composition génératrice de gaz.
7. Procédé de formation d'une composition génératrice de gaz moulée selon la revendication 6, dans lequel ladite composition génératrice de gaz a un temps de durcissement d'environ 3 minutes à une température d'environ 176,7°C (350°F).
8. Composition génératrice de gaz moulée que l'on peut obtenir par le procédé selon la revendication 1.