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(54) **GAS GENERANT AND MANUFACTURING METHOD THEREOF**

(52) **U.S. Cl. 149/36**

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(57) **ABSTRACT**

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The present invention generally relates to gas generant compositions for inflators of occupant restraint systems, for example. An extrudable pyrotechnic composition includes polyvinylazoles for use within an airbag gas generator. The fuel may be selected from exemplary polyvinylazoles including 5-amino-1-vinyltetrazole, poly(5-vinyltetrazole), poly(2-methyl-5-vinyl tetrazole), poly(1-vinyl) tetrazole, poly(3-vinyl) 1,2,5 oxadiazole, and poly(3-vinyl) 1,2,4-triazole. An oxidizer is combined with the fuel and preferably contains phase stabilized ammonium nitrate. A novel method of forming the compositions is also presented wherein the various constituents are wetted and/or dissolved, and then cured within the polyvinylazole matrix thereby forming a more intimate combination within the gas generant composition. A vehicle occupant protection system 180, and other gas generating systems, incorporate the compositions of the present invention.

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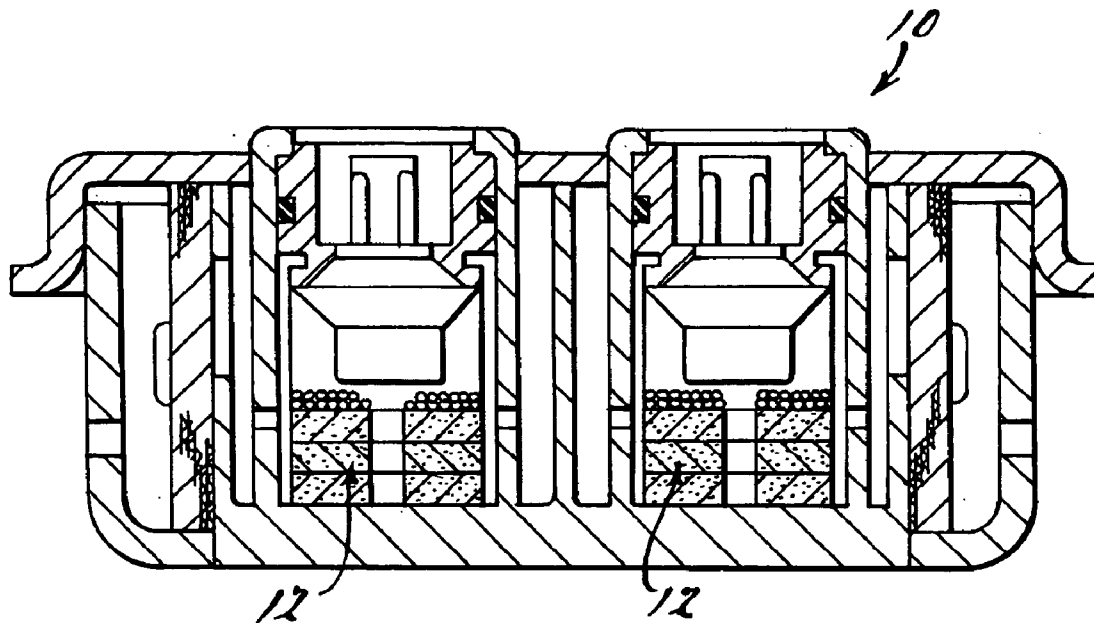
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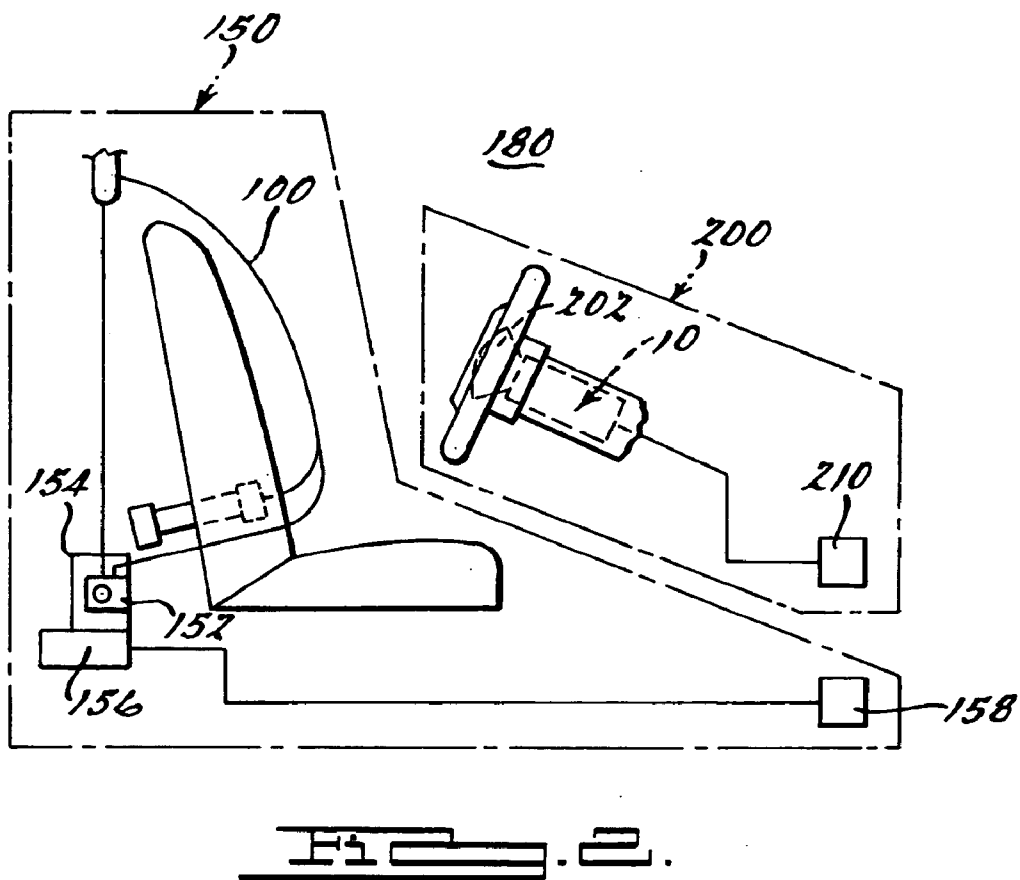
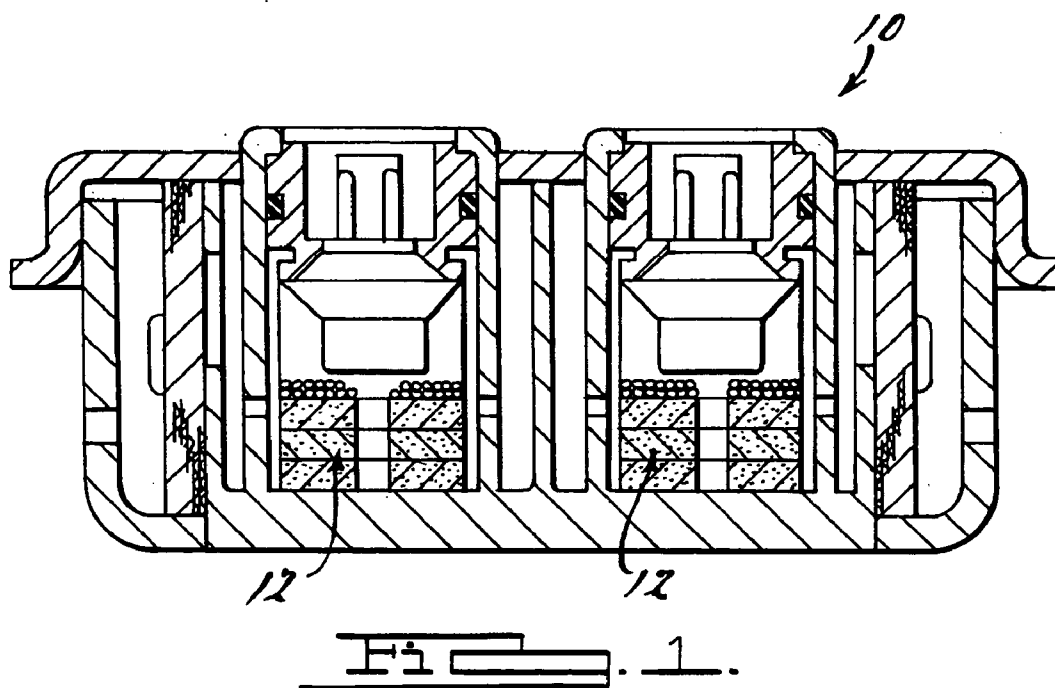
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(60) **Provisional application No. 60/557,279, filed on Mar. 29, 2004.**

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GAS GENERANT AND MANUFACTURING METHOD THEREOF

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Application Ser. No. 60/557,279 filed on Mar. 29, 2004.

TECHNICAL FIELD

[0002] The present invention relates generally to gas generating systems, and to gas generant compositions employed in gas generator devices for automotive restraint systems, for example.

BACKGROUND OF THE INVENTION

[0003] The present invention relates to nontoxic gas generating compositions that upon combustion rapidly generate gases that are useful for inflating occupant safety restraints in motor vehicles and specifically, the invention relates to thermally stable nonazide gas generants having not only acceptable burn rates, but that also, upon combustion, exhibit a relatively high gas volume to solid particulate ratio at acceptable flame temperatures.

[0004] The evolution from azide-based gas generants to nonazide gas generants is well-documented in the prior art. The advantages of nonazide gas generant compositions in comparison with azide gas generants have been extensively described in the patent literature, for example, U.S. Pat. Nos. 4,370,181; 4,909,549; 4,948,439; 5,084,118; 5,139,588 and 5,035,757, the discussions of which are hereby incorporated by reference.

[0005] In addition to a fuel constituent, pyrotechnic nonazide gas generants contain ingredients such as oxidizers to provide the required oxygen for rapid combustion and reduce the quantity of toxic gases generated, a catalyst to promote the conversion of toxic oxides of carbon and nitrogen to innocuous gases, and a slag forming constituent to cause the solid and liquid products formed during and immediately after combustion to agglomerate into filterable clinker-like particulates. Other optional additives, such as burning rate enhancers or ballistic modifiers and ignition aids, are used to control the ignitability and combustion properties of the gas generant.

[0006] One of the disadvantages of known nonazide gas generant compositions is the amount and physical nature of the solid residues formed during combustion. When employed in a vehicle occupant protection system, the solids produced as a result of combustion must be filtered and otherwise kept away from contact with the occupants of the vehicle. It is therefore highly desirable to develop compositions that produce a minimum of solid particulates while still providing adequate quantities of a nontoxic gas to inflate the safety device at a high rate.

[0007] The use of phase stabilized ammonium nitrate as an oxidizer, for example, is desirable because it generates abundant nontoxic gases and minimal solids upon combustion. To be useful, however, gas generants for automotive applications must be thermally stable when aged for 400 hours or more at 107.degree. C. The compositions must also retain structural integrity when cycled between -40.degree.

C. and 107.degree. C. Further, gas generant compositions incorporating phase stabilized or pure ammonium nitrate sometimes exhibit poor thermal stability, and produce unacceptably high levels of toxic gases, CO and NO.sub.x for example, depending on the composition of the associated additives such as plasticizers and binders.

[0008] Yet another problem that must be addressed is that the U.S. Department of Transportation (DOT) regulations require "cap testing" for gas generants. Because of the sensitivity to detonation of fuels often used in conjunction with ammonium nitrate, many propellants incorporating ammonium nitrate do not pass the cap test unless shaped into large disks, which in turn reduces design flexibility of the inflator.

[0009] Yet another concern includes slower cold start ignitions of typical smokeless gas generant compositions, that is gas generant compositions that result in less than 10% of solid combustion products.

[0010] Yet another concern regards the environmental impact of manufacturing gas generant compositions. In many manufacturing processes, the gas generant is formed in a solvent-based process. As such, the organic solvent remnant must be disposed of with the attendant environmental concerns.

[0011] Accordingly, ongoing efforts in the design of automotive gas generating systems, for example, include other initiatives that desirably produce more gas and less solids without the drawbacks mentioned above.

SUMMARY OF THE INVENTION

[0012] The above-referenced concerns are resolved by gas generating systems including a gas generant composition containing an extrudable polyvinylazole fuel such as a polyvinyltetrazole, polyvinyltriazole, or polyvinyl diazole. Preferred oxidizers include nonmetal oxidizers such as ammonium nitrate and ammonium perchlorate. Other oxidizers include alkali and alkaline earth metal nitrates.

[0013] The fuel is selected from the group of polyvinyltetrazoles, polyvinyltriazoles, polyvinyl diazoles or polyvinyl furazans, and mixtures thereof. A preferred group of fuels includes polymeric tetrazoles, triazoles, and oxadiazoles (furazans), having functional groups on the azole pendants. Although compositions containing NH₃ linkages and carbon/hydrogen content are generally useful, preferred compositions will not contain NH₃ linkages due to handling concerns, and the carbon and hydrogen content will be minimized to inhibit the formation of carbon dioxide and water. Preferred vinyl tetrazoles include 5-Amino-1-vinyltetrazole and poly(5-vinyltetrazole), both exhibiting self-propagating thermolysis or thermal decomposition. Other fuels include poly(2-methyl-5-vinyl) tetrazole, poly(1-vinyl) tetrazole, poly(3-vinyl) 1,2,5-oxadiazole, and poly(3-vinyl) 1,2,4-triazole. These and other possible fuels are structurally illustrated in the figures included herewith. The fuel preferably constitutes 10-40% by weight of the gas generant composition.

[0014] An oxidizer is preferably selected from the group of nonmetal, and alkali and alkaline earth metal nitrates, and mixtures thereof. Nonmetal nitrates include ammonium nitrate and phase stabilized ammonium nitrate, stabilized as known in the art. Alkali and alkaline earth metal nitrates

include potassium nitrate and strontium nitrate. Other oxidizers known for their utility in air bag gas generating compositions are also contemplated. The oxidizer preferably constitutes 60-90% by weight of the gas generant composition.

[0015] Other gas generant constituents known for their utility in air bag gas generant compositions may be employed in effective amounts in the compositions of the present invention. These include, but are not limited to, coolants, slag formers, and ballistic modifiers known in the art.

[0016] In sum, the present invention includes gas generant compositions that maximize gas combustion products and minimize solid combustion products while retaining other design requirements such as thermal stability. These and other advantages will be apparent upon a review of the detailed description.

[0017] In yet another aspect of the invention, a method of manufacturing a gas generant composition incorporating a polyvinylazole is described. A vinyl azole is first added to a vessel. If necessary, an aqueous, organic, or aqueous/organic solvent is provided in an amount effective to dissolve all constituents to be added to the vessel. In preferred embodiments, a liquid vinyl azole will complete wet and/or facilitate the solubility of the other gas generant constituents without the use of a solvent. An oxidizer, preferably non-metallic, is next added. Other constituents/solutes such as a secondary fuel(s), a secondary oxidizer(s), slag former(s), processing aid(s), coolant(s), and/or burn rate modifier(s) may be added to the slurry and stirred to a substantially uniform or homogeneous mixture. Next, an initiator is added to facilitate the curing or polymerization of the mixture. The mixture is then cured either statically, or without stirring, wherein a solid is then formed, or, while stirring wherein granules may then be formed. If cured statically, the mixture may be poured within molds, for example, to form the desired propellant shape(s). If cured while stirring, crushing and formation of the granules is not necessary given the inherent formation of the granules. Thermoplastic polymers facilitate melt processing for further shaping of the propellant if desired.

BRIEF DESCRIPTION OF THE DRAWINGS

[0018] FIG. 1 is an exemplary airbag inflator containing a gas generant composition formed in accordance with the present invention.

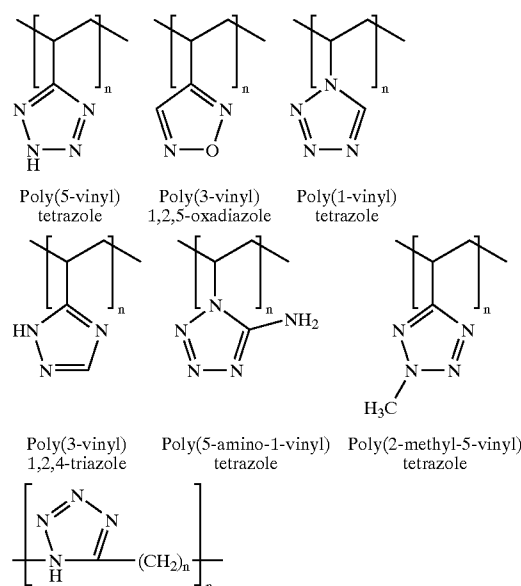
[0019] FIG. 2 is a schematic representation of an exemplary vehicle occupant restraint system incorporating the inflator of FIG. 1 and a gas generant in accordance with the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT(S)

[0020] The present invention generally relates to gas generant compositions for inflators of occupant restraint systems. In accordance with the present invention, a pyrotechnic composition includes extrudable fuels such as polyvinyltetrazoles (PVT) for use within a gas generating system, such as that exemplified by a high gas yield automotive airbag propellant in a vehicle occupant protection system. The fuel also functions as a binder. Preferred ox-

idizers include nonmetal oxidizers such as ammonium nitrate and ammonium perchlorate. Other oxidizers include alkali and alkaline earth metal nitrates.

[0021] The fuel is selected from the group of polyvinyltetrazoles, polyvinyltriazoles, polyvinlyldiazoles or polyvinylfurazans, and mixtures thereof. A preferred group of fuels includes polymeric tetrazoles, triazoles, and oxadiazoles (furazans), having functional groups on the azole pendants. Although compositions containing HN_3 linkages and carbon/hydrogen content are generally useful, preferred compositions will not contain HN_3 linkages due to handling concerns, and the carbon and hydrogen content will be minimized to inhibit the formation of carbon monoxide, carbon dioxide, and water. In general, the consumption of oxygen from the oxidizer is preferentially inhibited with regard to the formation of these gaseous or vapor products. Preferred vinyl tetrazoles include 5-Amino-1-vinyltetrazole and poly(5-vinyltetrazole), both exhibiting self-propagating thermolysis or thermal decomposition. Other fuels include poly(2-methyl-5-vinyl) tetrazole, poly(1-vinyl) tetrazole, poly(3-vinyl) 1,2,5-oxadiazole, and poly(3-vinyl) 1,2,4-triazole. These and other possible fuels are exemplified by, but not limited to, the structures shown below.



[0022] Other Possible Tetrazole Polymers:

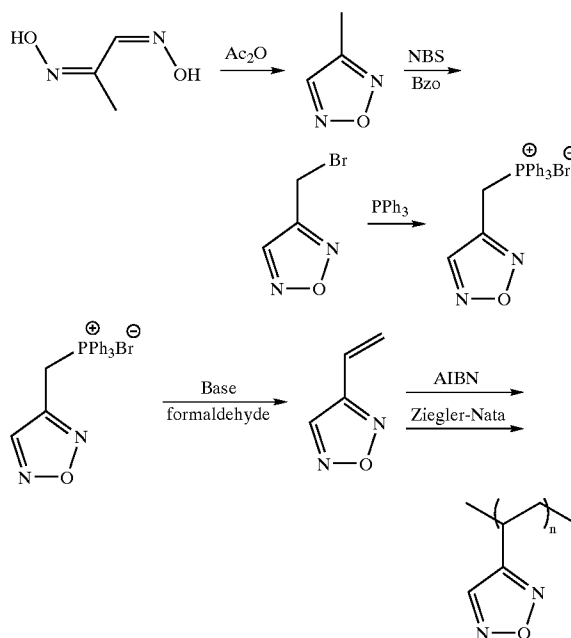
[0023] As such, it has been discovered that an additional benefit with the present fuels is that compositions resulting in difficult cold-start ignitions that necessitate more powerful ignition trains and boosters, are avoided. Poly(5-amino-1-vinyl) tetrazole, for example, has no endothermic process before exothermic decomposition begins. Therefore, the heat-consuming step normally attendant prior to the energy releasing steps of combustion (that acts as an energy barrier) is not present in the present compositions. It is believed that other polymeric azoles functioning as fuels in the present invention have the same benefit. The polyvinylazole fuel preferably constitutes 5-40% by weight of the gas generant composition.

[0024] An oxidizer is preferably selected from the group of nonmetal, and alkali and alkaline earth metal nitrates, and mixtures thereof. Nonmetal nitrates include ammonium nitrate and phase stabilized ammonium nitrate, stabilized as known in the art. Alkali and alkaline earth metal nitrates include potassium nitrate and strontium nitrate. Other oxidizers known for their utility in air bag gas generating compositions are also contemplated. The oxidizer preferably constitutes 60-95% by weight of the gas generant composition.

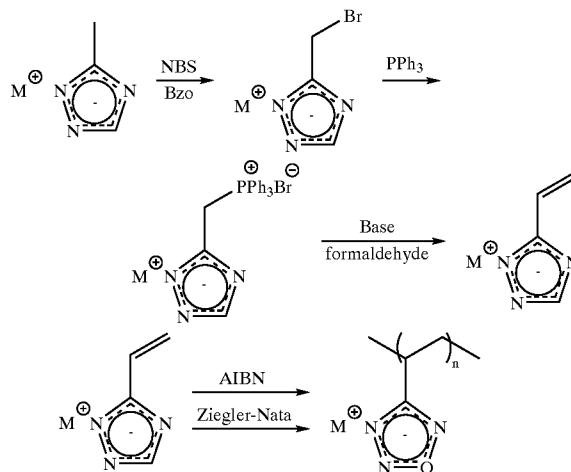
[0025] Other gas generant constituents known for their utility in air bag gas generant compositions may be employed in effective amounts in the compositions of the present invention. These include, but are not limited to, coolants, slag formers, and ballistic modifiers known in the art.

[0026] The gas generant constituents of the present invention are supplied by suppliers known in the art and are preferably blended by a wet method. A solvent chosen with regard to the group(s) substituted on the polymeric fuel is heated to a temperature sufficient to dissolve the fuel but below boiling, for example just below 100° C., but low enough to prevent autoignition of any of the constituents as they are added and then later precipitate. Hydrophilic groups, for example, may be more efficiently dissolved by the use of water as a solvent. Other groups may be more efficiently dissolved in an acidic solution, nitric acid for example. Other solvents include alcohols and plasticizers such as polyethylene glycol. Once a suitable solvent is chosen and heated, the fuel is slowly added and dissolved. The oxidizer is then slowly added and also dissolved. Any other desirable constituents are likewise dissolved. The solution is heated and continually stirred. As the solvent is cooked off over time, the fuel and oxidizer, and any other constituents, are co-precipitated in a homogeneous solid solution. The precipitate is removed from the heat once the solvent has been at least substantially volatilized, but more preferably completely volatilized. The composition may then be extruded into pellets or any other useful shape.

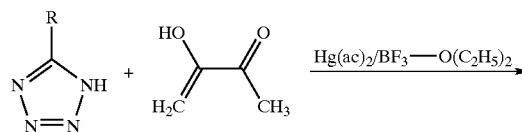
[0027] The polymeric fuels may be manufactured by known processes. For example, vinylation of a tetrazole with vinyl acetate, followed by polymerization is described in Vereshchagin, et al., J. Org. Chem. USSR (Engl. Transl.) 22(9), 1777-83, (1987). The synthesis of various vinyltetrazoles is also described in Russian Chemical Reviews 72(2), pages 143-164 (2003), herein incorporated by reference. The methyl-group of the starting tetrazole can be exchanged for an amino group. The vinyltetrazoles are then polymerized using a common polymerization initiator such as azoisobutyronitrile (AIBN). It is believed that similar vinylation of furazans and triazoles will also yield the polyvinylidiazoles and polyvinyltriazoles of the present invention. Exemplary reactions given below illustrate how various polyvinylidiazoles, polyvinyltriazoles and polyvinyltetrazoles may be formed. Reaction 1 illustrates how polyvinylidiazoles may be formed. Reaction 2 illustrates how polyvinyltriazoles may be formed. Reaction 3 exemplifies how polyvinyltetrazoles may be formed.

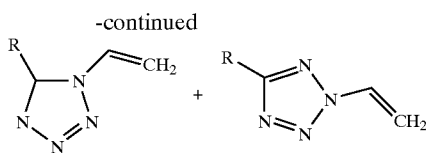


[0028] Reaction 1: This synthesis is for a poly(vinyl-1,2,5-oxadiazole) and exemplifies or blueprints a general method of forming polyvinylidiazoles.



[0029] Reaction 2: This synthesis is for an ionic polymer version of poly(vinyl-1,2,4-triazole) and exemplifies or blueprints a method of forming other polyvinyltriazoles.





where R = CH₃, NH₂, etc.

[0030] Reaction 3: This synthesis is for a substituted polyvinyltetrazole and exemplifies or blueprints a method of forming other polyvinyltetrazoles.

[0031] A generic polyvinylazole, or a structure that generically represents the polyvinyltetrazoles, polyvinyltriazoles, and polyvinyl diazoles of the present invention, may be represented by an aromatic ring having five sites that contains,



At any numbered position: $\left\{ \begin{array}{l} \text{at least 2 nitrogen atoms} \\ \text{no more than 1 oxygen atom} \\ \text{at least 2 carbon atom} \end{array} \right\}$

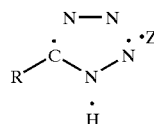
[0032] Stated another way, the aromatic ring will contain from zero to a single oxygen atom, will contain at least two nitrogen atoms, and will contain at least one carbon atom. More preferably, a gas generant composition of the present invention will contain a polymeric azole and phase stabilized ammonium nitrate. The advantages are high gas yield and low solids production, a high energy fuel/binder, and a low-cost oxidizer thereby obviating the need for filtration of the gas given that little if any solids are produced upon combustion. The compositions of the present invention may be extruded given the pliant nature of the polymeric fuels.

[0033] The gas generant compositions of the present invention may also contain a secondary fuel formed from amine salts of tetrazoles and triazoles. These are described and exemplified in co-owned U.S. Pat. Nos. 5,872,329, 6,074,502, 6,210,505, and 6,306,232, each herein incorporated by reference. The total weight percent of both the first and second fuels, or the fuel component of the present compositions, is about 10 to 40 weight % of the total gas generant composition.

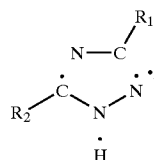
[0034] More specifically, nonmetal salts of tetrazoles include in particular, amine, amino, and amide salts of tetrazole and triazole selected from the group including monoguanidinium salt of 5,5'-Bis-1H-tetrazole (BHT.1GAD), diguanidinium salt of 5,5'-Bis-1H-tetrazole (BHT.2GAD), monoaminoguanidinium salt of 5,5'-Bis-1H-tetrazole (BHT.1AGAD), diaminoguanidinium salt of 5,5'-Bis-1H-tetrazole (BHT.2AGAD), monohydrazinium salt of 5,5'-Bis-1H-tetrazole (BHT.1HH), dihydrazinium salt of 5,5'-Bis-1H-tetrazole (BHT.2HH), monoammonium salt of 5,5'-bis-1H-tetrazole (BHT.1NH₃), diammonium salt of 5,5'-bis-1H-tetrazole (BHT.2NH₃), mono-3-amino-1,2,4-triazolium salt of 5,5'-bis-1H-tetrazole (BHT.1ATAZ), di-3-

amino-1,2,4-triazolium salt of 5,5'-bis-1H-tetrazole (BHT.2ATAZ), and diguanidinium salt of 5,5'-Azobis-1H-tetrazole (ABHT.2GAD).

[0035] Amine salts of triazoles include monoammonium salt of 3-nitro-1,2,4-triazole (NTA.1NH₃), monoguanidinium salt of 3-nitro-1,2,4-triazole (NTA.1GAD), diammonium salt of dinitrotriazole (DNBTR.2NH₃), diguanidinium salt of dinitrotriazole (DNBTR.2GAD), and monoammonium salt of 3,5-dinitro-1,2,4-triazole (DNTR.1NH₃).



Formula I



Formula II

[0036] A generic nonmetal salt of tetrazole as shown in Formula I includes a cationic nitrogen containing component, Z, and an anionic component comprising a tetrazole ring and an R group substituted on the 5-position of the tetrazole ring. A generic nonmetal salt of triazole as shown in Formula II includes a cationic nitrogen containing component, Z, and an anionic component comprising a triazole ring and two R groups substituted on the 3- and 5-positions of the triazole ring, wherein R₁ may or may not be structurally synonymous with R₂. An R component is selected from a group including hydrogen or any nitrogen-containing compound such as an amino, nitro, nitramino, or a tetrazolyl or triazolyl group as shown in Formula I or II, respectively, substituted directly or via amine, diazo, or triazo groups. The compound Z is substituted at the 1-position of either formula, and is formed from a member of the group comprising amines, aminos, and amides including ammonia, carbonylhydrazide, oxamic hydrazide, and hydrazine; guanidine compounds such as guanidine, aminoguanidine, diaminoguanidine, triaminoguanidine, dicyandiamide and nitroguanidine; nitrogen substituted carbonyl compounds or amides such as urea, oxamide, bis-(carbonamide) amine, azodicarbonamide, and hydrazodicarbonamide; and, amino azoles such as 3-amino-1,2,4-triazole, 3-amino-5-nitro-1,2,4-triazole, 5-aminotetrazole, 3-nitramino-1,2,4-triazole, 5-nitraminotetrazole, and melamine.

EXAMPLE 1

[0037] A gas generant composition of the present invention is formed by first synthesizing a polyvinyltetrazole. A generic substituted tetrazole and vinyl acetate are combined to vinylate the tetrazole. The vinylated tetrazole is added to a molar equivalent of mercury acetate and boron trifluoride-etherate for polymerization thereof. The resulting products may then be separated by oil distillation for example. The polyvinyltetrazoles illustrated in the drawings may be formed in the same way. Reaction 3 exemplifies the process described above.

EXAMPLE 2

[0038] A gas generant composition of the present invention is formed by first synthesizing a polyvinyltriazole. A generic substituted triazole metal or nonmetal salt is added to a molar equivalent amount of a free radical brominating reagent such as n-bromo-succinamide and to a benzoyl-peroxide free radical initiator to form a brominated triazole. The brominated triazole is then added to triphenyl phosphine to form a Wittig salt group on the substituted triazole salt. The triazole salt is then added to a metal or nonmetal organic or inorganic base, and also to formaldehyde to form a vinylated triazole salt. The vinylated triazole salt is next added to a free radical polymerization reagent such as azoisobutyronitrile and a catalytic amount of a cationic polymerizer or Ziegler-Natta catalyst such as a metal or titanium complex. Reaction 2 exemplifies the process described above wherein the synthesis of poly(vinyl-1,2,4-triazole) is described.

EXAMPLE 3

[0039] A gas generant composition of the present invention is formed by first synthesizing a polyvinyl diazole. An alkenol containing two —OH groups is added to acetic anhydride to form a substituted diazole. The substituted diazole is then added to a molar equivalent amount of a free radical brominating reagent such as n-bromo-succinamide and to a free radical initiator such as benzoyl-peroxide to form a brominated diazole. The substituted diazole is then added to triphenyl phosphine to form a Wittig salt group on the substituted diazole salt. The diazole salt is then added to a metal or nonmetal organic or inorganic base, and also to formaldehyde to form a vinylated diazole salt. The vinylated diazole salt is next added to a free radical polymerization reagent such as azoisobutyronitrile and a catalytic amount of a cationic polymerizer or Ziegler-Natta reagent such as a metal complex. Reaction 1 exemplifies the process described above wherein the synthesis of poly(vinyl-1,2,5-oxadiazole) is described.

Examples 4-9

[0040] Examples 4-9 are tabulated below and provide a comparative view of the different types and amounts of gas produced with regard to several known gas generant compositions and a gas generant formed in accordance with the present invention. Example 4 is a representative gas generant composition formed from 5-aminotetrazole and strontium nitrate, in accordance with U.S. Pat. No. 5,035,757 herein incorporated by reference. Example 5 is a representative gas generant composition formed from an amine salt of tetrazole such as diammonium salt of 5,5'-bi-1H-tetrazole, phase stabilized ammonium nitrate, strontium nitrate, and clay in accordance with U.S. Pat. No. 6,210,505 herein incorporated by reference. Example 6 is a representative gas generant composition formed from an amine salt of tetrazole such as diammonium salt of 5,5'-bi-1H-tetrazole and phase stabilized ammonium nitrate in accordance with U.S. Pat. No. 5,872,329 herein incorporated by reference. Example 7 is a representative gas generant composition formed from ammonium nitramine tetrazole and phase stabilized ammonium nitrate in accordance with U.S. Pat. No. 5,872,329 herein incorporated by reference. Example 8 is a representative gas generant composition formed from ammonium nitramine tetrazole, phase stabilized ammonium nitrate, and

a slag former in accordance with U.S. Pat. No. 5,872,329 herein incorporated by reference. Example 9 is a representative composition formed in accordance with the present invention containing ammonium polyvinyl tetrazole and phase stabilized ammonium nitrate (ammonium nitrate coprecipitated with 10% potassium nitrate).

[0041] Table 1 details the relative amounts produced (ppm) of carbon monoxide (CO), ammonia (NH₃), nitrogen monoxide (NO), and nitrogen dioxide (NO₂) with regard to each example and the amount of gas generant in grams (Gg). All examples were combusted in a gas generator of substantially the same design.

TABLE 1

Example	Gg	P _c	CO	NH ₃	NO	NO ₂
4	45	15	125	10	49	9
5	25	36	109	65	29	4
6	25	29	111	29	37	5
7	25	36	62	10	28	3
8	25	37	98	35	33	4
9	25	34	129	4	28	4

[0042] The data collected indicates that the composition of Example 9, formed in accordance with the present invention, results in far less ammonia than the other examples, well below the industry standard of 35 ppm. It has been discovered that compositions of the present invention result in substantially less amounts of ammonia as compared to other known gas generants. In many known gas generant compositions, it is often difficult to reduce the total amount of ammonia produced upon combustion, even though other performance criteria remain favorable.

Examples 10-14

[0043] Theoretical examples 10-14 are tabulated below and provide a comparative view of the different amounts and types of gas produced with regard to several gas generant compositions formed in accordance with the present invention. All phase stabilized ammonium nitrate (PSAN10) referred to in Table 2 has been stabilized with 10% by weight potassium nitrate of the total PSAN. All examples employ ammonium poly(C-vinyltetrazole) (APV) as the primary fuel. Certain examples employ nonmetal diammonium salt of 5,5'-Bis-1H-tetrazole (BHT.2NH₃) as a secondary fuel. All examples reflect results generated by combustion of the gas generant constituents (propellant composition) within a similarly designed inflator or gas generator with equivalent heat sink design.

TABLE 2

Example	Constituents (wt % of 100 g)	Flame Temp. (K)	Exhaust Temp. (K)	Gas Combustion Products (mol)
10	15% APV 85% PSAN10	2222	857	2.25 H ₂ O 1.33 N ₂ 0.39 CO ₂
11	16% APV 40% PSAN10 10% Strontium Nitrate 05% Clay	2057	900	2.25 H ₂ O 1.33 N ₂ 0.39 CO ₂

TABLE 2-continued

Example	Constituents (wt % of 100 g)	Flame Temp. (K)	Exhaust Temp. (K)	Gas Combustion Products (mol)
12	22% APV	2054	1225	0.64 H ₂ O
	73% Strontium Nitrate			0.83 N ₂
	05% Clay			0.52 CO ₂
13	08% APV	2036	874	1.86 H ₂ O
	64.60% PSAN10			1.34 N ₂
	10% Strontium Nitrate			0.35 CO ₂
	05% Clay			
14	12.40% BHT.2NH ₃	2206	835	2.20 H ₂ O
	08% APV			1.45 N ₂
	80.60% PSAN10			0.34 CO ₂
	11.40% BHT.2NH ₃			

[0044] Example 10 has been found to be thermally stable at 105 degrees Celsius for 400 hours with only a 0.5% mass loss. Accordingly, Example 10 exemplifies the unexpected thermal stability of gas generant compositions of the present invention, particularly those incorporating a polyvinylazole as defined herein and phase stabilized ammonium nitrate (stabilized with 10% potassium nitrate). It should be emphasized that other phase stabilizers are also contemplated as known or recognized in the art.

[0045] Examples 11 through 13 exemplify the use of a polyvinylazole with metallic oxidizers. In certain applications, the use of a metallic oxidizer may be desired for optimization of ignitability, burn rate exponent, gas generant burn rate, and other design criteria. The examples illustrate that the more metallic oxidizer is used the less mols of gas produced upon combustion.

[0046] In contrast, Examples 10 and 14 illustrate that molar amounts of gas combustion products are maximized when nonmetal gas generant constituents are employed. Accordingly, preferred gas generant compositions of the present invention contain at least one polyvinylazole as a fuel component and a nonmetal oxidizer as an oxidizer component.

[0047] Finally, with regard to Example 14, it has been found that the gas generant burn rate may be enhanced by adding another nonmetal fuel, BHT.2NH₃, to APV and PSAN10, thereby optimizing the combustion profile of the gas generant composition. The burn rate of Example 14 is recorded at 1.2 inches per second at 5500 psi. It can be concluded therefore, that the addition of nonmetal amine salts of tetrazoles and/or nonmetal amine salts of triazoles as described in U.S. Pat. No. 5,872,329 may be advantageous with regard to burn rate and gas generation. Furthermore, the pliant nature of the APV provides extrudability of the propellant composition.

EXAMPLES 15 and 16

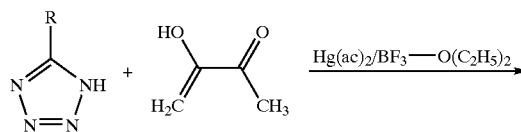
[0048] Examples 15 and 16 exemplify the cold start advantage of gas generant compositions containing a polyvinylazole. As shown by differential scanning calorimetry (DSR), typical smokeless or nonmetal compositions may exhibit an endothermic trend prior to exothermic combustion. As a result, relatively greater amounts of energy must be available to ignite the gas generant and sustain combustion of the same. Oftentimes, a more aggressive ignition

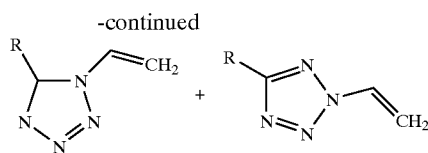
train, to include an aggressive booster composition perhaps, is required to attain the energy level necessary to ignite the gas generant and sustain combustion. Example 15 pertains to a composition containing 65% PSAN10 and about 35% BHT.2NH₃. As shown in FIG. 1, an endotherm is maximized at 253.12 degrees Celsius, thereby representing a recorded loss of about 508.30 joules/gram of gas generant. In comparison, Example 16 pertains to a composition containing about 15% poly(C-vinyltetrazole) and about 85% PSAN10. Most unexpectedly, there is no endothermic process and accordingly, combustion proceeds in an uninhibited manner. As a result, less energy is required to combust the gas generant composition thereby reducing the ignition train or ignition and booster requirements.

[0049] In yet another aspect of the invention, the present compositions as exemplified herein may be employed within a gas generating system. For example, as schematically shown in FIG. 2, a vehicle occupant protection system made in a known way contains crash sensors in electrical communication with an airbag inflator in the steering wheel, and also with a seatbelt assembly. The gas generating compositions of the present invention may be employed in both subassemblies within the broader vehicle occupant protection system or gas generating system. More specifically, each gas generator employed in an automotive gas generating system may contain a gas generating composition as described herein.

[0050] In yet another aspect of the invention, a method of manufacturing a gas generant composition includes polymerizing a monomer component of a polymeric binder/fuel in the presence of at least an oxidizer thereby forming a homogeneous solid composite gas generant formulation. The polymeric binder/fuel is generally selected from a myriad of polymeric azoles including vinyl tetrazoles, vinyl triazoles, vinyl oxadiazoles (furazans), copolymers thereof, as described above for example. Functional groups may be present on the azole pendants, however, preferred compositions avoid HN₃ linkages due to sensitivity issues. Furthermore, preferred compositions will also have relatively lower amounts of carbon/hydrogen content thereby facilitating cooler formulations upon combustion believed attributable to the lower amounts of water and carbon dioxide formed. The polymeric binder/fuel is exemplified by any of several polyvinyl tetrazole compounds including poly(vinyl-5-amino)tetrazole, poly(vinyl-5-methyl)tetrazole, poly(5-amino-1-vinyltetrazole), poly(5-vinyltetrazole) and poly(vinyl-bitetrazolamine), or mixtures thereof. Other polymeric azole fuels are illustrated in the discussion given above. Other fuels contemplated as useful in the present invention include metal salts and complexes of the azole polymers described above.

[0051] The polymeric azoles may be purchased from suppliers known in the art. They may also be manufactured by vinylation of an azole with vinyl acetate. For example, the vinylation of a tetrazole with vinyl acetate, followed by polymerization, yields desirable poly vinyl tetrazoles.





where R = CH₃, NH₂, etc.

[0052] The procedure is detailed in Vereshchagin, et al., *J. Org. Chem. USSR (Engl. Transl.)*, 22(9), 177-83, (1987), herein incorporated by reference. The methyl-group of the starting tetrazole may be exchanged for an amino-group. The vinyltetrazoles are then polymerized using a common polymerization initiator such as azoisobutyronitrile (AIBN). Other syntheses may be employed. It is believed that vinylation of furazans and triazoles would similarly yield desirable polymers.

[0053] The oxidizer is preferably selected from exemplary compounds to include alkali metal, alkaline earth metal, transitional metal, and nonmetal nitrates and perchlorates. Specific oxidizers include ammonium nitrate, phase stabilized ammonium nitrate, potassium nitrate, strontium nitrate, potassium perchlorate, ammonium perchlorate, sodium nitrate, sodium perchlorate, and mixtures thereof.

[0054] When preparing the compositions, the monomer(s)/copolymer(s) and oxidizer(s) are added to an inorganic solvent such as water, or to an organic solvent such as dimethylformamide, depending on the chemistry of the monomer/copolymers. If water is used, a water-based polymerization initiator such as ammonium persulfate is employed in the aqueous slurry resulting in a relatively thinner or less rigid slurry. If an organic-based solvent is used, an organic solvent based initiator such as azobisisobutyronitrile (AIBN) is employed in the organic slurry resulting in relatively thicker or more viscous slurry.

[0055] Typically, the azole monomer or azole copolymer is solvated in an appropriate solvent, either water, a mixture of water and miscible solvent (ethanol, methanol, or other alcohols; acetone, tetrahydrofuran (THF), dimethylformamide (DMF), dimethylsulfoxide (DMSO), or a non-water miscible organic solvent selected from the group including ethers, such as dimethylether and diethylether, and also from the group including aromatics, such as toluene and benzene. Other known additives such as slag formers, coolants, burn rate modifiers, secondary fuels, and secondary oxidizers may be added to the solvent in known effective amounts to make a slurry in the solvent. The slag formers, processing aids, coolants, and/or burn rate modifiers include stearates such as magnesium stearate, graphite, clays, micas, talcs, silicates, aluminates, and other functionally similar constituents. The secondary fuels include tetrazoles, triazoles, imidazoles, pyrazoles, oxiadiazoles, guanidines such as nitroguanidine and guanidine nitrate, and other constituents functional as fuel components in the present invention. Secondary oxidizers include metal and nonmetal chlorates, perchlorates, nitrates, nitrites, oxides, and other compounds having an oxidizing function.

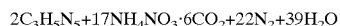
[0056] The polymerization initiator is then added after the addition of all of the other constituents, and is selected from known initiators. For example, a preferred free radical

initiator is 2,2'-azobisisobutyronitrile (AIBN) and may be employed in a known manner. Other types of initiators such as ammonium persulfate are also contemplated. In general, the polymerization initiator is provided at about 100-250 mg per batch. Nevertheless, all that is required is that is a relatively small amount as compared to the overall weight of the mix whereby the formation of free radicals is facilitated. After that, the polymerization reaction self propagates. Temperature may be increased or lowered to tailor the desired cure time. At room temperature, curing may take from three to twenty-four hours. A preferred temperature range is from 10-90° C. Although an apparently cured material may be obtained in a relatively short time, the curing process may continue for a number of hours. After mixing the constituents to form a substantially homogeneous slurry, curing in a static state produces a solid block of finished propellant while stirring during the curing process forms granules.

[0057] Depending on the monomer/copolymer and the solvent temperature, 10-50% propellant mixture per unit solvent weight is desirable. The solvent can be removed during or after the curing process by evaporation. Note that if the monomer/copolymer is a liquid, a solvent may not be necessary. In essence, the liquid monomer or copolymer must be in an amount effective to "wet" the solids to be added thereto. "Wet" as used herein is meant as at least partially solvating, and more preferably completely solvating, the constituents added to the fuel. The effective liquid monomer/copolymer amount can therefore be iteratively determined based on the weight percent desired relative to the fuel function and relative to the propensity of the fuel to wet the rest of the constituents. If a solvent is still required to wet the constituents, the solvent may be added to ensure wetting of the solid constituents within the vessel. In general, the various constituents may be added to the slurry at the following weight percents: 5-20% of the azole monomer/copolymer(s); 50-90% of the oxidizer(s); 0-25% additional fuels; and 0-10% processing aids, slag formers, and/or burning rate modifiers. Note that the weight percents represent the total weight prior to addition to the slurry, or prior to combination thereof.

[0058] Compositions formed in this manner result in consistent repeatable performance based on the intimate combination of the constituents resulting from the mixing and curing process. Furthermore, the manufacturing process of the gas generant is simplified as compared to other gas generant syntheses thereby reducing the associated costs. In addition to the advantages stated above, other advantages include the ability to melt form many of the compositions when the monomer/copolymer employed is thermoplastic in nature. Furthermore, the pliant nature of the compositions facilitates containment flexibility with many of the present compositions whereby the propellant or gas generant 12 may be compressively stored in cavities within the inflator thereby optimizing the use of available space. As a result, the size of the inflator may be effectively reduced while still retaining the same effective amount of gas generation, thereby retaining the same inflation pressure profile that would typically be represented by a relatively larger inflator.

[0059] Stoichiometric amounts of fuel and oxidizer are preferably combined in the slurry thereby resulting in a balanced combustion reaction. An exemplary balanced combustion reaction of poly(5-amino-1-vinyl) tetrazole with ammonium nitrate is shown below:



[0060] The weight percents of the fuel and oxidizer are about 14% PV5AT and about 86% AN. Other oxidizers including strontium nitrate, potassium perchlorate, ammonium perchlorate, and so forth may also be employed depending on application design criteria. In general, the fuel/oxidizer weight percent ratio ranges from 45/50 to 5/90, respectively.

[0061] The polymerization process may be accelerated by the amount of initiator employed and also by the application of heat, for example. Other acceleration methods are contemplated.

[0062] It is also contemplated that the present compositions be employed in an airbag device to include airbag modules, airbag inflators, seatbelt pretensioners, or, vehicle occupant restraint systems, all schematically represented in FIG. 2 and all built or designed as well known in the art. Furthermore, the present compositions may more generally be provided in gas generating systems designed for a variety of applications such as inflatable flotation devices, inflatable aircraft slides, fire extinguishers, and vehicle occupant protection systems that include airbag devices and/or seatbelt assemblies with pretensioners, for example.

[0063] As shown in FIG. 1, an exemplary inflator incorporates a dual chamber design to tailor the force of deployment an associated airbag. In general, an inflator containing a gas generant 12 formed as described herein may be manufactured as known in the art. U.S. Pat. Nos. 6,422,601, 6,805,377, 6,659,500, 6,749,219, and 6,752,421 exemplify typical airbag inflator designs and are each incorporated herein by reference in their entirety.

[0064] Referring now to FIG. 2, the exemplary inflator 10 described above may also be incorporated into an airbag system 200. Airbag system 200 includes at least one airbag 202 and an inflator 10 containing a gas generant composition 12 in accordance with the present invention, coupled to airbag 202 so as to enable fluid communication with an interior of the airbag. Airbag system 200 may also include (or be in communication with) a crash event sensor 210. Crash event sensor 210 includes a known crash sensor algorithm that signals actuation of airbag system 200 via, for example, activation of airbag inflator 10 in the event of a collision.

[0065] Referring again to FIG. 2, airbag system 200 may also be incorporated into a broader, more comprehensive vehicle occupant restraint system 180 including additional elements such as a safety belt assembly 150. FIG. 2 shows a schematic diagram of one exemplary embodiment of such a restraint system. Safety belt assembly 150 includes a safety belt housing 152 and a safety belt 100 extending from housing 152. A safety belt retractor mechanism 154 (for example, a spring-loaded mechanism) may be coupled to an end portion of the belt. In addition, a safety belt pretensioner 156 containing propellant 12 may be coupled to belt retractor mechanism 154 to actuate the retractor mechanism in the event of a collision. Typical seat belt retractor mechanisms which may be used in conjunction with the safety belt embodiments of the present invention are described in U.S. Pat. Nos. 5,743,480, 5,553,803, 5,667,161, 5,451,008, 4,558,832 and 4,597,546, incorporated herein by reference. Illustrative examples of typical pretensioners with which the safety belt embodiments of the present invention may be combined are described in U.S. Pat. Nos. 6,505,790 and 6,419,177, incorporated herein by reference.

[0066] Safety belt assembly 150 may also include (or be in communication with) a crash event sensor 158 (for example, an inertia sensor or an accelerometer) including a known crash sensor algorithm that signals actuation of belt pretensioner 156 via, for example, activation of a pyrotechnic igniter (not shown) incorporated into the pretensioner. U.S. Pat. Nos. 6,505,790 and 6,419,177, previously incorporated herein by reference, provide illustrative examples of pretensioners actuated in such a manner.

[0067] It should be appreciated that safety belt assembly 150, airbag system 200, and more broadly, vehicle occupant protection system 180 exemplify but do not limit gas generating systems contemplated in accordance with the present invention.

[0068] It will be understood that the foregoing descriptions of various embodiments of the present invention are for illustrative purposes only, and should not be construed to limit the breadth of the present invention in any way. As such, the various structural and operational features disclosed herein are susceptible to a number of modifications, none of which departs from the scope of the present invention as defined in the appended claims.

We claim:

1. A method of forming a gas generating composition comprising the steps of:

providing a solvent effective to dissolve a fuel comprising a polymeric azole selected from the group consisting of vinyl tetrazoles, vinyl triazoles and vinyl furazans, the solvent selected with regard to the solvability of the functional group(s) that may be present on the polymeric azole, the solvent placed in a mixing vessel;

adding the fuel to the mixing vessel;

adding an oxidizer to the mixing vessel;

stirring the mixture;

adding an initiator to the mixing vessel to initiate polymerization of the slurry; and

curing the mixture.

2. The method of claim 1 further comprising the step of adding an additive to the mixing vessel prior to adding the initiator.

3. The method of claim 1 further comprising the step of heating the mixing vessel below boiling.

4. The method of claim 1 wherein adding the solvent and adding the fuel to the mixing vessel comprises the same step whereby the fuel also functions as the solvent.

5. A gas generating system containing a gas generant produced by the method of claim 1.

6. A gas generating system containing a gas generant formed by the method comprising the steps of:

providing a solvent effective to dissolve a fuel comprising a polymeric azole selected from the group consisting of vinyl tetrazoles, vinyl triazoles and vinyl furazans, the solvent selected with regard to the solvability of the functional group(s) that may be present on the polymeric azole, the solvent placed in a mixing vessel;

adding the fuel to the mixing vessel;
adding an oxidizer to the mixing vessel;
stirring the mixture;
adding an initiator to the mixing vessel to initiate polymerization of the slurry; and
curing the mixture.

7. The gas generating system of claim 6 wherein said system is a vehicle occupant protection system.

8. The gas generating system of claim 6 wherein said system is an airbag system.

9. The gas generating system of claim 6 wherein said system is a seatbelt assembly system.

10. The gas generating system of claim 6 wherein said system activates an inflatable floatable device.

11. The gas generating system of claim 6 wherein said system is a fire extinguishing system.

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