

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
21 April 2005 (21.04.2005)

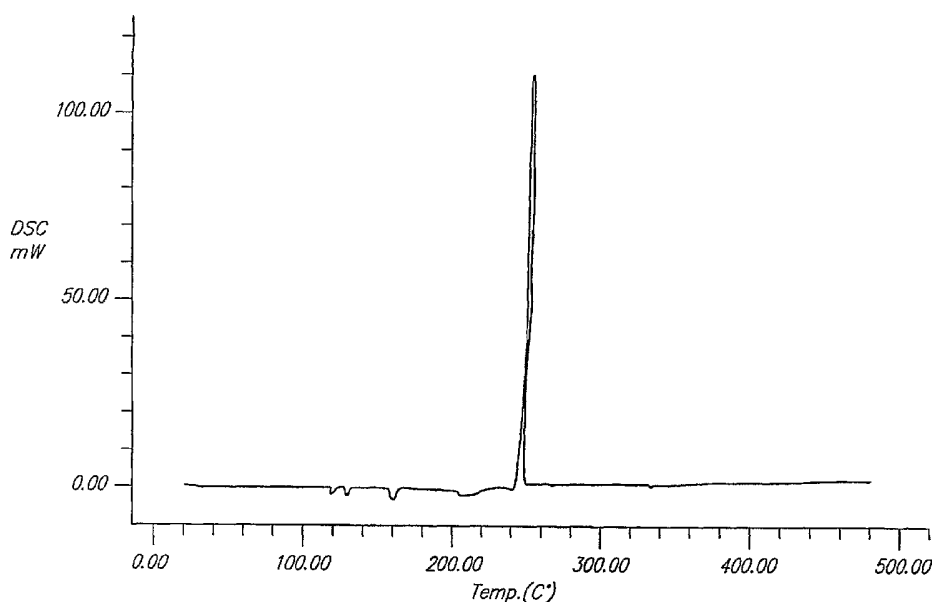
PCT

(10) International Publication Number
WO 2005/035466 A2

- (51) International Patent Classification⁷: **C06D**
- (21) International Application Number:
PCT/US2004/033783
- (22) International Filing Date: 12 October 2004 (12.10.2004)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
60/510,056 9 October 2003 (09.10.2003) US
- (71) Applicant (for all designated States except US): **AUTO-MOTIVE SYSTEMS LABORATORY, INC.** [US/US];
69700 Powell Road, Armada, MI 48005 (US).
- (72) Inventors: **WILLIAMS, Graylon, K.**; 30704 Lund Court, Warren, MI 48043 (US). **BURNS, Sean, P.**; 5640 Bella Villa Drive, Almont, MI 48003 (US). **MISHRA, Indu, B.**; 5424 Morning Glory Court, Columbia, MD 21044 (US).
- (74) Agents: **BEGIN, Laurence** et al.; L.C Begin & Associates, PLLC, 510 Highland Avenue, PMB 403, Milford, MI 48381 (US).
- (81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- Published:
— without international search report and to be republished upon receipt of that report

[Continued on next page]

(54) Title: GAS GENERATING COMPOSITIONS



Example 16

(57) Abstract: 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.



For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

GAS GENERATING COMPOSITIONS

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims the benefit of U.S. Provisional Application

5 Serial No. 60/510,056 filed on October 9, 2003.

TECHNICAL FIELD

The present invention relates generally to gas generating systems, and to gas generant compositions employed in gas generator devices

10 for automotive restraint systems, for example.

BACKGROUND OF THE INVENTION

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.

20

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.

25

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

30

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.

5 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
10 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.

 The use of phase stabilized ammonium nitrate as an oxidizer, for
15 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
20 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.

25 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,
30 which in turn reduces design flexibility of the inflator.

 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.

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.

5

SUMMARY OF THE INVENTION

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.

The fuel is selected from the group of polyvinyltetrazoles, polyvinyltriazoles, polyvinyl diazoles 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 NH_3 linkages and carbon/hydrogen content are generally useful, preferred compositions will not contain NH_3 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.

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.

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.

5 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.

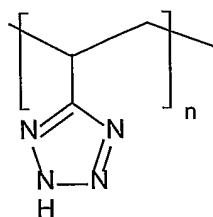
10 DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT(S)

The present invention generally relates to gas generant compositions for inflators of occupant restraint systems. In accordance with
15 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 oxidizers include nonmetal oxidizers such as ammonium nitrate and
20 ammonium perchlorate. Other oxidizers include alkali and alkaline earth metal nitrates.

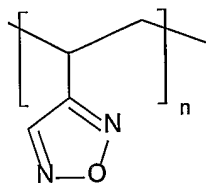
The fuel is selected from the group of polyvinyltetrazoles, polyvinyltriazoles, polyvinyl diazoles or polyvinylfurazans, and mixtures thereof.

A preferred group of fuels includes polymeric tetrazoles, triazoles, and
25 oxadiazoles (furazans), having functional groups on the azole pendants. Although compositions containing NH_3 linkages and carbon/hydrogen content are generally useful, preferred compositions will not contain NH_3 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
30 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

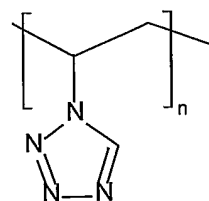
exemplified by, but not limited to, the structures shown below.



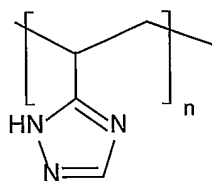
Poly(5-vinyl) tetrazole



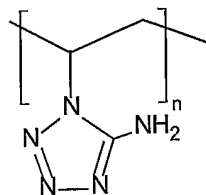
Poly(3-vinyl) 1,2,5-oxadiazole



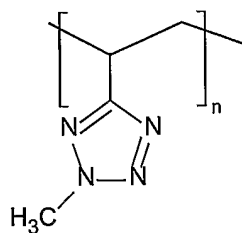
Poly(1-vinyl) tetrazole



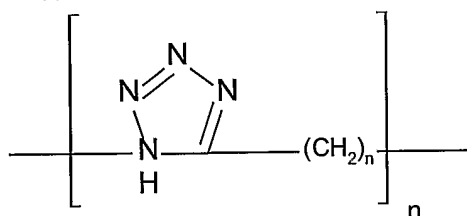
Poly(3-vinyl) 1,2,4-triazole



Poly(5-amino-1-vinyl) tetrazole



Poly(2-methyl-5-vinyl) tetrazole



Other possible tetrazole polymers:

5

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.

10 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

15 the same benefit. The polyvinylazole fuel preferably constitutes 5-40% by weight of the gas generant composition.

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

20 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.

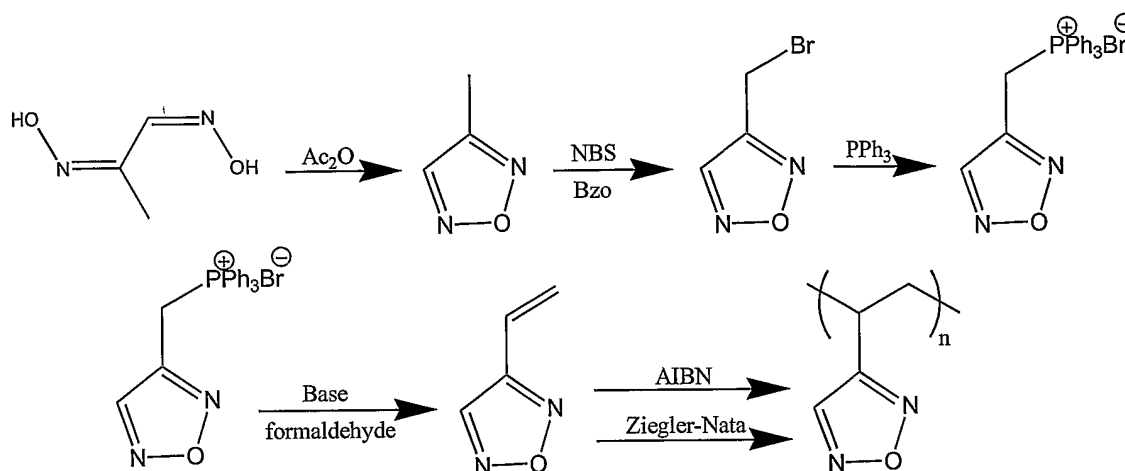
Other gas generant constituents known for their utility in air bag gas generant compositions may be employed in effective amounts in the compositions of the present invention. These include, but are not limited to, 5 coolants, slag formers, and ballistic modifiers known in the art.

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 10 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 15 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 20 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.

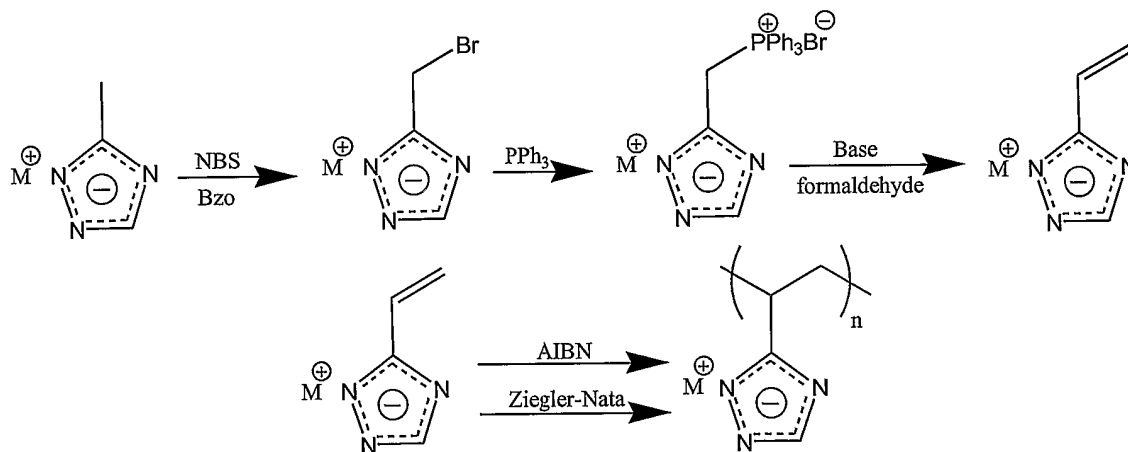
The polymeric fuels may be manufactured by known processes. For 25 example, vinylation of a tetrazole with vinyl acetate, followed by polymerization is described in Vereshchagin, et al., J. Org. Chem. USSR (Engl. Transl.) 22(9), 1777-83, (1987). The synthesis of various vinyltetrazoles is also described in Russian Chemical Reviews 72(2), pages 143-164 (2003), herein incorporated by reference. The methyl-group of the starting tetrazole 30 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 polyvinyl diazoles and polyvinyl triazoles of the

present invention. Exemplary reactions given below illustrate how various polyvinyl diazoles, polyvinyl triazoles and polyvinyl tetrazoles may be formed. Reaction 1 illustrates how polyvinyl diazoles may be formed. Reaction 2 illustrates how polyvinyl triazoles may be formed. Reaction 3 exemplifies how

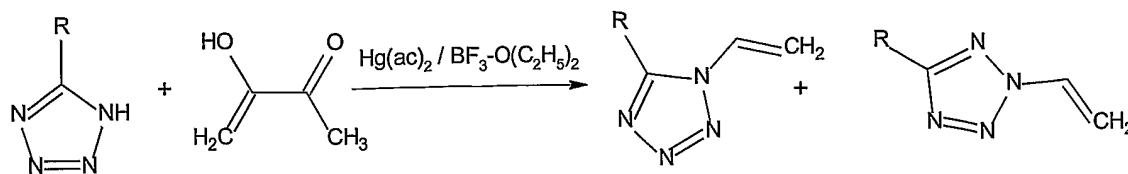
5 polyvinyl tetrazoles may be formed.



10 Reaction 1: This synthesis is for a poly(vinyl-1,2,5-oxadiazole) and exemplifies or blueprints a general method of forming polyvinyl diazoles.



15 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 polyvinyl triazoles.



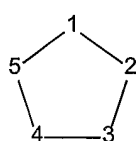
where R = CH₃, NH₂, etc.

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

5

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,

10



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

15

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.

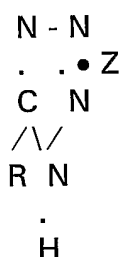
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The gas generant compositions of the present invention may also contain a secondary fuel formed from amine salts of tetrazoles and triazoles. These are described and exemplified in coowned U.S. Patent Nos. 5,872,329, 6,074,502, 6,210,505, and 6,306,232, 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.

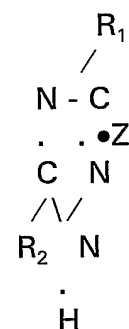
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More specifically, nonmetal salts of tetrazoles include in particular, amine, amino, and amide salts of tetrazole and triazole selected from the group including monoguanidinium salt of 5,5'-Bis-1H-tetrazole (BHT·1GAD), diguanidinium salt of 5,5'-Bis-1H-tetrazole (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).

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 dinitrobitriazole (DNBTR·2NH₃), diguanidinium salt of dinitrobitriazole (DNBTR·2GAD), and monoammonium salt of 3,5-dinitro-1,2,4-triazole (DNTR·1NH₃).



Formula I



Formula II

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, carbohydrazide, 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:

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:

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
5 synthesis of poly(vinyl-1,2,4-triazole) is described.

Example 3:

A gas generant composition of the present invention is formed by first synthesizing a polyvinyl diazole. An alkenol containing two -OH groups is
10 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
15 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
20 complex. Reaction 1 exemplifies the process described above wherein the synthesis of poly(vinyl-1,2,5-oxadiazole) is described.

Examples 4--9:

Examples 4-9 are tabulated below and provide a comparative view of the
25 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. Patent No. 5,035,757 herein incorporated by reference. Example 5 is a
30 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. Patent 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. Patent 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. Patent 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. Patent 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).

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.

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

Table 1

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:

5 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
10 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
15 equivalent heat sink design.

	Example	Constituents (wt% of 100g)	Flame Temp. (K)	Exhaust Temp. (K)	Gas
					Products (mol)
20	10	15% APV 85% PSAN10	2222	857	2.25 H ₂ O 1.33 N ₂
					0.39 CO ₂
25	11	16% APV 40% PSAN10	2057	900	2.25 H ₂ O 1.33 N ₂
		10% Strontium Nitrate 05% Clay			0.39 CO ₂
30	12	22% APV 73% Strontium Nitrate 05% Clay	2054	1225	0.64 H ₂ O 0.83 N ₂ 0.52 CO ₂
35	13	08% APV 64.60% PSAN10 10% Strontium Nitrate 05% Clay 12.40% BHT.2NH ₃	2036	874	1.86 H ₂ O 1.34 N ₂ 0.35 CO ₂
40	14	08% APV 80.60% PSAN10 11.40% BHT.2NH ₃	2206	835	2.20 H ₂ O 1.45 N ₂ 0.34 CO ₂
45	CO ₂				

Table 2

Example 10 has been found to be thermally stable at 105 degrees Celsius for 400 hours with only a .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.

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.

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.

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 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:

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

5 35% BHT.2NH₃. As shown in Figure 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

10 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.

In yet another aspect of the invention, the present compositions may be employed within a gas generating system. For example, as

15 schematically shown in Figure 3, 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

20 gas generating system. More specifically, each gas generator employed in the automotive gas generating system may contain a gas generating composition as described herein.

The present description is for illustrative purposes only, and should not be construed to limit the breadth of the present invention in any way. Thus, those skilled in the art will appreciate that various modifications could be made to the presently disclosed embodiments without departing from the scope of the present invention as defined in the appended claims.

5

WE CLAIM:

1. A gas generating system comprising a composition, the composition comprising:

an aromatic fuel component consisting of one or more aromatic fuels,
said fuel comprising a member of the group consisting of
polyvinyltetrazoles, polyvinyltriazoles, and polyvinyl diazoles; and
an oxidizer,

wherein said polymeric azole comprises about 5 – 40%, and said
oxidizer comprises about 60-95%, said percentages stated by
weight of said composition, and said composition extrudable
upon combination of said fuel and said oxidizer.

2. The gas generating system of claim 1 wherein said composition further comprises:

a secondary fuel selected from the group consisting 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), 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 dinitrobitriazole (DNBTR·2NH₃), diguanidinium salt of dinitrobitriazole (DNBTR·2GAD), and monoammonium salt of 3,5-dinitro-1,2,4-triazole (DNTR·1NH₃).

3. A gas generating system comprising a composition, the composition comprising:

a fuel component comprising a member of the group consisting of

polyvinyltetrazoles, polyvinyltriazoles, and polyvinyl diazoles; and phase stabilized ammonium nitrate,

35 wherein said polymeric azole comprises about 5 – 40%, and said phase stabilized ammonium nitrate comprises about 60-95%, said percentages stated by weight of said composition.

4. The gas generating system of claim 1 wherein said oxidizer is selected from the group consisting of transitional metal nitrates, alkali metal
40 nitrates, alkaline earth metal nitrates, and combinations thereof.

5. The gas generating system of claim 1 wherein said fuel is selected from the group consisting of 5-amino-1-vinyltetrazole, poly(5-vinyltetrazole), poly(2-methyl-5-vinyl) tetrazole, poly(1-vinyl) tetrazole, poly(3-vinyl) 1,2,5
45 oxadiazole, and poly(3-vinyl) 1,2,4-triazole.

6. The gas generating system of claim 1 wherein said oxidizer is selected from the group consisting of metal and nonmetal nitrates, perchlorates, and chlorates, and metal and nonmetal organic and inorganic oxides, and
5 combinations thereof.

7. The gas generating system of claim 1 wherein said composition comprises:

a fuel selected from the group consisting of poly(2-methyl-5-vinyl)
10 tetrazole, 5-amino-1-vinyltetrazole, poly(5-vinyltetrazole), poly(1-vinyl) tetrazole, poly(3-vinyl) 1,2,5-oxadiazole, and poly(3-vinyl) 1,2,4-triazole, and mixtures thereof; and

an oxidizer selected from the group consisting of strontium nitrate,
potassium nitrate, and phase stabilized ammonium nitrate.

8. The gas generating system of claim 1 wherein said composition comprises 5-amino-1-vinyltetrazole and phase stabilized ammonium nitrate.

9. The gas generating system of claim 1 wherein said composition comprises poly(2-methyl-5-vinyl) tetrazole and phase stabilized ammonium
5 nitrate.

10. The gas generating system of claim 1 wherein said composition comprises poly(5-vinyltetrazole) and phase stabilized ammonium nitrate.

11. The gas generating system of claim 1 wherein said composition comprises poly(1-vinyl) tetrazole and phase stabilized ammonium nitrate.

10 12. The gas generating system of claim 1 wherein said composition comprises poly(3-vinyl) 1,2,5 oxadiazole and phase stabilized ammonium nitrate.

13. The gas generating system of claim 1 wherein said composition comprises poly(3-vinyl) 1,2,5 triazole and phase stabilized ammonium nitrate.

14. A method of forming a gas generating composition comprising a
5 polymeric azole fuel and an oxidizer, the method comprising the steps of:

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

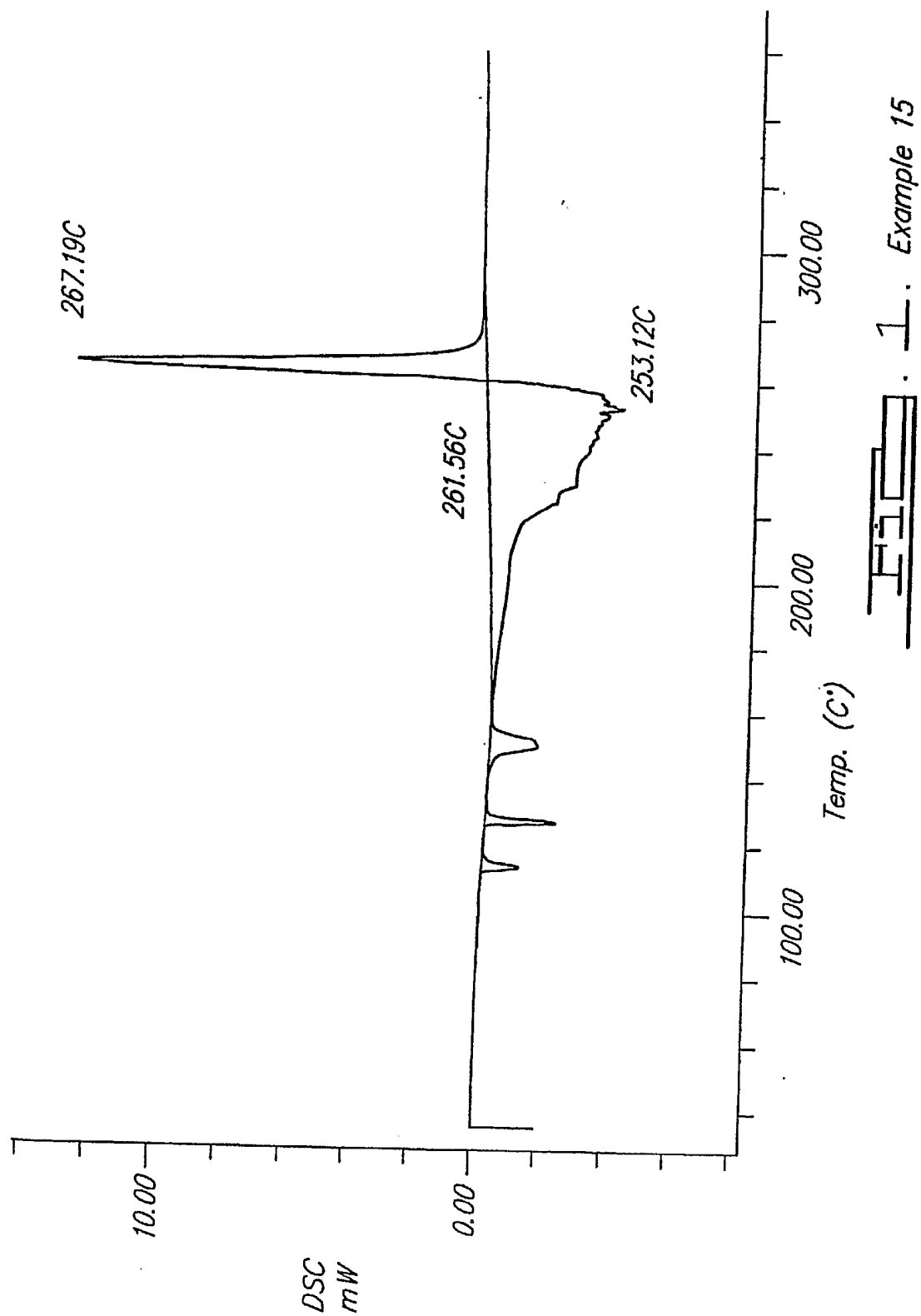
heating the solvent below boiling and below the autoignition temperature
of any constituents to be added to the vessel;

adding the fuel to the solvent and dissolving the same while stirring the mixture;

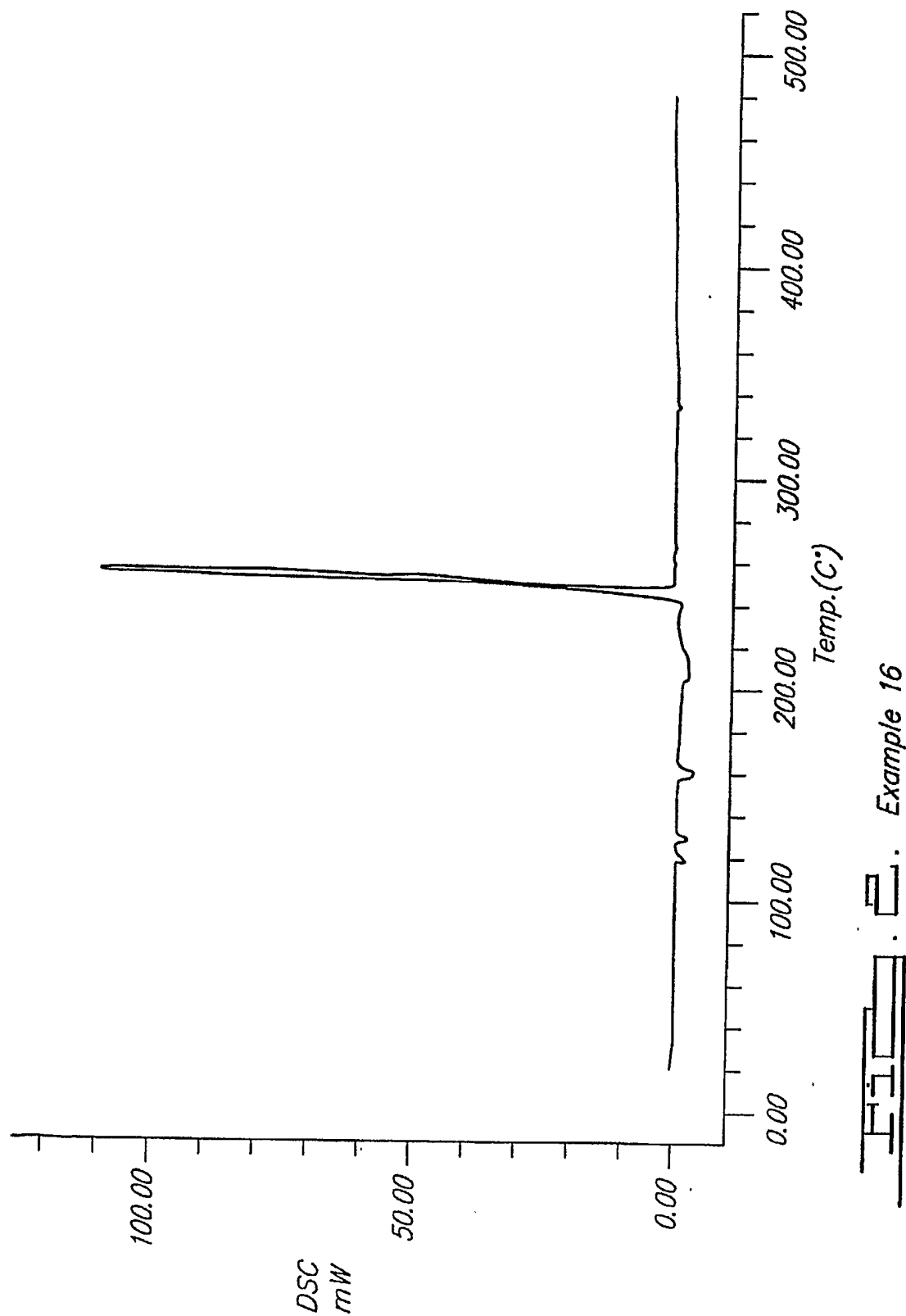
adding the oxidizer to the solvent and dissolving the same while stirring the mixture;

5 at least partly cooking off the solvent by maintaining a steady heat and stirring of the slurry; and
coprecipitating a homogenous solution containing the fuel and the oxidizer.

10 15. A gas generating system containing a gas generant produced by the method of claim 14.



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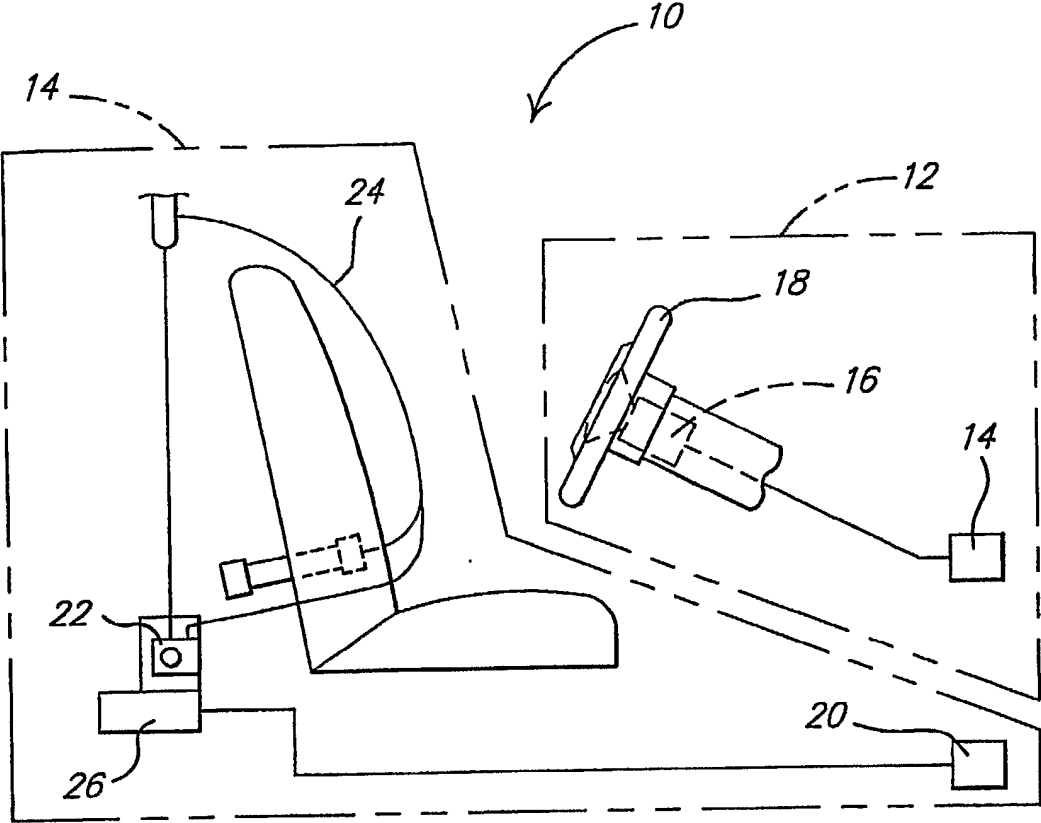


FIG. 3.