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(54) GAS GENERATING SYSTEM

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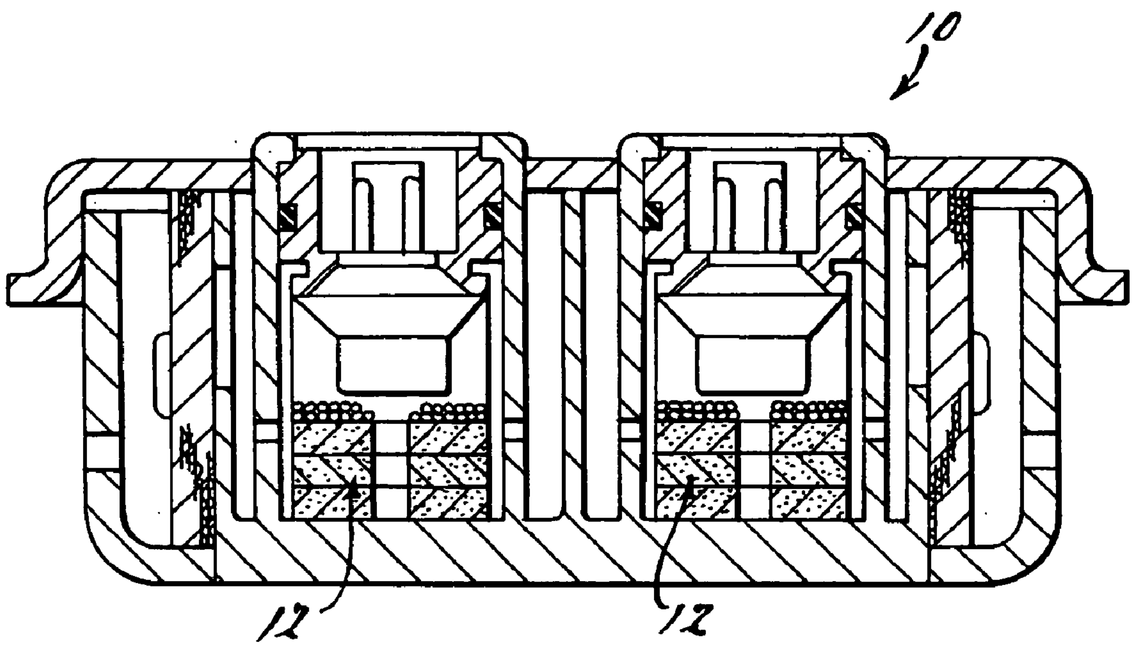
(57) **ABSTRACT**

The present invention generally relates to gas generant compositions for inflators of occupant restraint systems, for example. A gas generating composition **12** formed in accordance with the present invention includes an alkyl cellulosic fuel/binder, an oxidizer, and a burn inhibitor or ignition catalyst. A vehicle occupant protection system **180**, and other gas generating systems, incorporate the compositions of the present invention.



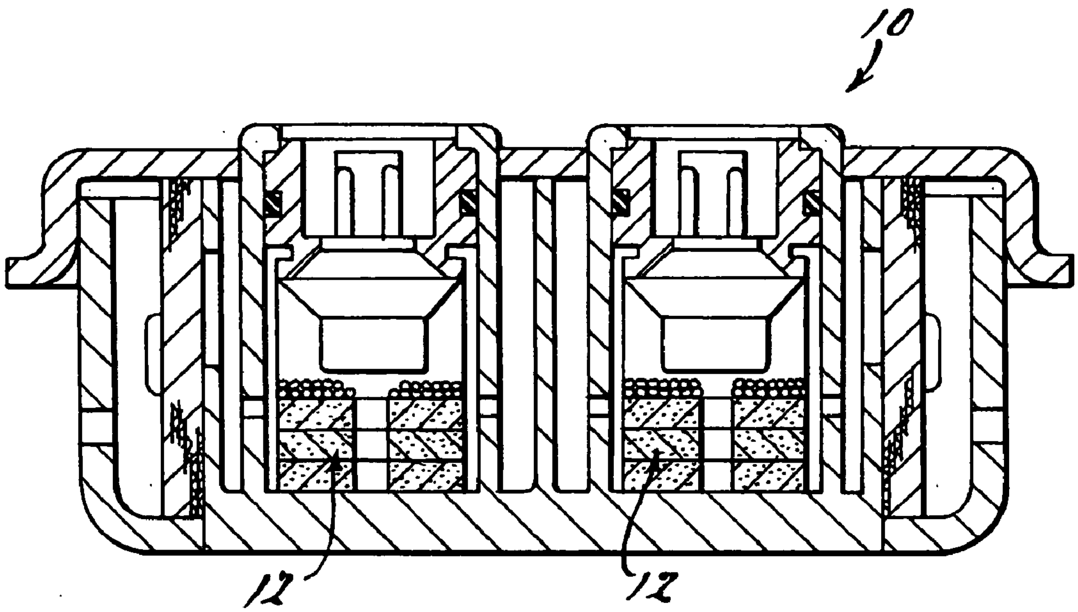



FIG. 1.

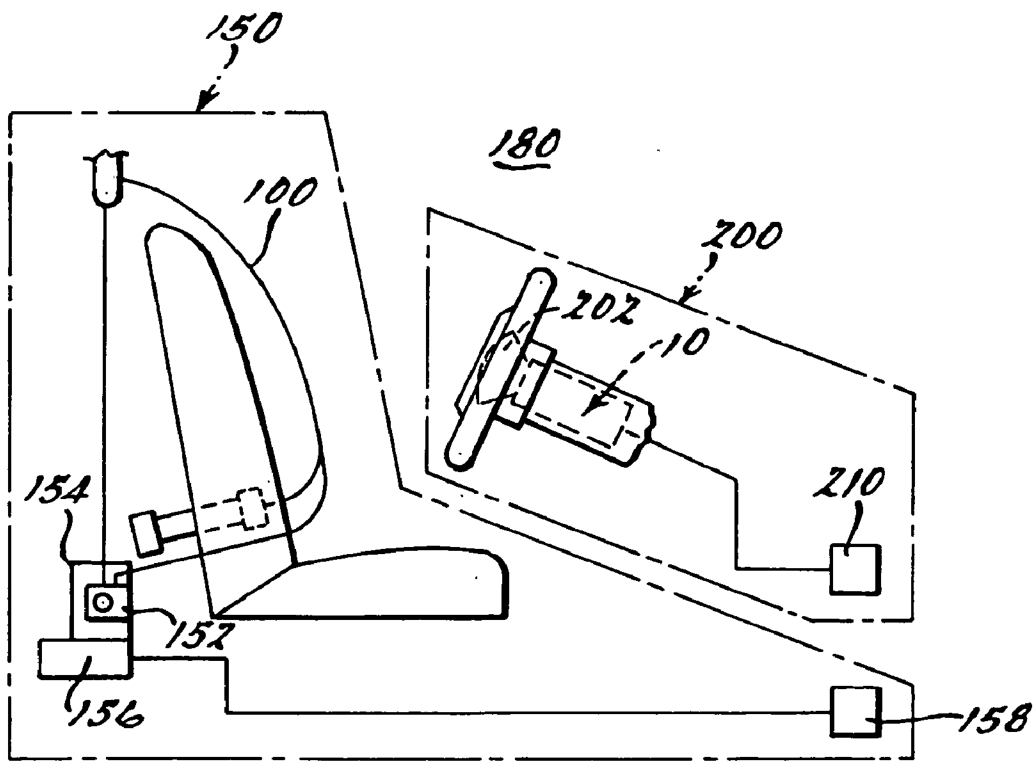



FIG. 2.

# GAS GENERATING SYSTEM

## CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] The present application claims the benefit of U.S. Provisional Application Ser. No. 60/666,964 having a filing date of Mar. 31, 2005.

## 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 $NO_x$ for example, depending on the composition of the associated additives such as plasticizers and binders.

[0008] Even so, the addition of additives such as binders is often necessary to retain the shape of the propellant or gas generant tablets, and inhibit fragmentation of the same over time. Certain water soluble binders, such as carboxyl cellulosic binders, exhibit hygroscopic properties given their water solubility. Accordingly, these types of binders result in compositions that often have poor thermal stability, and in particular with compositions containing preferred oxidizers such as phase stabilized ammonium nitrate.

[0009] Accordingly, ongoing efforts in the design of automotive gas generating systems, for example, include initiatives that desirably produce more gas and less solids without the drawbacks mentioned above.

## SUMMARY OF THE INVENTION

[0010] The above-referenced concerns are resolved by gas generating systems including a gas generant composition containing an alkyl cellulosic binder such as cellulose acetate, cellulose acetate propionate, and cellulose acetate butyrate. Stated another way, compositions of the present invention contain a primary cellulosic binder containing alkyl substitutions, an oxidizer, and an ignition catalyst or burn inhibitor selected from the group including molybdenum trioxide and other molybdenum compounds, dibutylthalates, dicyclohexourea, triacetin, and mixtures thereof. Known fuels, oxidizers, and other additives may be incorporated into these compositions as known in the art and as determined by design criteria. In accordance with the present invention, gas generating systems such as airbag inflators and vehicle occupant protection systems incorporate these gas generating compositions.

[0011] Typical micro gas generators use nitrocellulose or smokeless powder compositions for gas generation in a device. These compositions often result in relatively higher amounts of carbon monoxide. Furthermore, ballistic tailoring is not readily accomplished with the use of nitrocellulose. These are non-nitrocellulose compositions containing an oxidizer, a fuel, and a binder. Performance characteristics (i.e. ballistic output) related to burning rate can be varied based on the particle size distribution of the oxidizer component. In general, as the particle size distribution of the oxidizer is reduced, the burning rate of the propellant composition increases thereby enhancing the ballistic properties. As the particle size increases, the burning rate decreases and thus the ballistic output is reduced. Accordingly, the ballistic properties may be tailored in this manner. Average particle size ranges from 10 to 150 microns. Combinations of particle size distributions within said range can also be considered for the purpose of modifying performance. Ballistic tailoring can also be achieved by varying the shape, size and surface treatment, or any combination thereof of the propellant grains. Various propellant processes and techniques affecting propellant grain density, porosity, and surface finish (i.e. high or low exposed burning surface area) can also be employed to tailor ballistic output, for instance to achieve a regressive burn profile. A discreet propellant geometry such as a small cylinder, processed in a particular way such as extrusion, exhibits a porous center and also exhibits a regressive type burn profile. Limiting damage to equipment incorporating gas generants, seatbelt pretensioners for example, is thereby facilitated.

[0012] In sum, the present invention includes gas generant compositions that optimize the production of gas combustion products and minimize solid combustion products while retaining other design requirements such as reduced hygroscopicity and thermal stability. These and other advantages will be apparent upon a review of the detailed description.

## BRIEF DESCRIPTION OF THE DRAWINGS

[0013] **FIG. 1** is an exemplary airbag inflator containing a gas generant composition formed in accordance with the present invention.

[0014] **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)

[0015] The present invention generally includes gas generant compositions that contain a fuel, an oxidizer, molybdenum trioxide, and a primary binder. The primary binder is selected from the group of cellulosic binders such as cellulose acetate, cellulose acetate propionate, and cellulose acetate butyrate. Stated another way, compositions of the present invention preferably contain a primary cellulosic binder containing alkyl substitutions. Alkyl substitutions include acetyl, propionyl, butyryl groups with hydroxyl groups. The primary binder is generally provided at about 5-30% by weight of the composition.

[0016] In accordance with the present invention, burn inhibitors and burn suppressants may also be included and are selected from the group containing dibutylthalates, dicyclohexourea, triacetin, and other known burn inhibitors, and mixtures thereof. The burn inhibitor or ignition catalyst may be provided in a weight percent from about 0.1-20% by weight. By inhibiting the burn, potential damage to associated gas generating systems, seatbelt assemblies and pretensioners for example, are mitigated. In accordance with one aspect of the present invention, therefore, with the addition of the burn inhibitor it has been found that the overall ignition temperature is substantially reduced thereby preserving the integrity of associated equipment such as seatbelt pretensioners.

## EXAMPLE 1

[0017] A composition was homogeneously mixed in a known manner, the composition containing nitroguanidine, potassium perchlorate, and cellulose acetate butyrate. Upon applying heat from a hot plate, the composition did not autoignite at 320 C, and a black char resulted.

## EXAMPLE 2

[0018] It has been shown that the addition of ammonium molybdate at about 1% by weight to the composition of Example 1 containing cellulose acetate butyrate, nitroguanidine, and potassium perchlorate resulted in an ignition temperature of 260 C, as measured by hot plate.

## EXAMPLE 3 and EXAMPLE 4

[0019] It has been shown that the addition of molybdenum trioxide at about 1% or 2% by weight to the composition of Example 1 containing cellulose acetate butyrate, nitroguanidine, and potassium perchlorate resulted in an ignition temperature of 262 C., as measured by hot plate.

[0020] It can be seen from the examples presented that the use of a burn inhibitor or ignition catalyst, in accordance with the present invention, results in ignitable compositions that effectively mitigate the harm to associated equipment.

[0021] In yet another aspect of the invention, carbon monoxide scavengers may also be provided thereby maintaining the required effluent rates notwithstanding the use of a cellulosic binder. Metal oxides such as manganese oxide and cupric oxide, sulfates such as ammonium sulfate, and other scavengers are contemplated at about 0.1-20% by weight of the composition when optionally employed. By employing CO scavengers, the overall cost of the gas generant composition may be reduced by increasing the relative amount of binder/fuel and reducing the amount of other fuels typically employed in gas generant compositions.

[0022] Gas generant compositions of the present invention may also contain the following constituents in the weight percents indicated. A secondary fuel is selected from the group containing azoles such as 5-aminotetrazole; nonmetal salts of azoles such as potassium 5-aminotetrazole; nonmetal salts of azoles such as mono- or diammonium salt of 5,5'-bis-1H-tetrazole; nitrate salts of azoles such as 5-aminotetrazole nitrate; nitramine derivatives of azoles such as 5-nitraminotetrazole; metal salts of nitramine derivatives of azoles such as dipotassium 5-nitraminotetrazole; metal salts of nitramine derivatives of azoles such as dipotassium 5-nitraminotetrazole; nonmetal salts of nitramine derivatives such as mono- or diammonium 5-nitraminotetrazole and; guanidines such as dicyandiamide, nitroguanidine, and guanidine nitrate; salts of guanidines such as guanidine nitrate; nitro derivatives of gaunidines such as nitroguanidine; azoamides such as azodicarbonamide; nitrate salts of azoamides such as azodicarbonamidine dinitrate; and mixtures thereof. The secondary fuel is typically employed at 0.1-50%, and more preferably at about 5-40% by weight of the total gas generant composition. It will be appreciated that in certain compositions, the amount of binder employed will also provide fuel effective amounts of the binder whereby the binder functions as a binder/fuel. Accordingly, in that instance, the secondary fuel may not be included in the composition. An optional third fuel selected from the same group of fuels is typically provided at about 0-50%, and more preferably at about 0-30% by weight.

[0023] A nonmetal or metal primary oxidizer may be selected from nitrate salts such as ammonium nitrate, phase stabilized ammonium nitrate stabilized in a known manner and more preferably with about 10% by weight of potassium nitrate, potassium nitrate, and strontium nitrate; nitrite salts such as potassium nitrite; chlorate salts such as potassium chlorate; perchlorate salts such as ammonium perchlorate and potassium perchlorate; oxides such as iron oxide and copper oxide; basic nitrate salts such as basic copper nitrate and basic iron nitrate; and mixtures thereof. The primary oxidizer may be provided at about 0.1-70% by weight, and more preferably at about 30-70% by weight. Secondary oxidizers may also be employed and are selected from the oxidizers described above. The secondary oxidizers are typically provided at about 0-50%, and more preferably 0-30%, by weight of the gas generant composition.

[0024] An optional secondary binder may be selected from cellulose derivatives such as cellulose acetate, cellulose acetate butyrate, carboxymethylcellulose, salts of carboxymethylcellulose; silicone; polyalkene carbonates such as polypropylene carbonate and polyethylene carbonate; and mixtures thereof. When employed, secondary binders may be provided at about 0-10%, and more preferably, 0-5% by weight.

[0025] An optional slag former may be selected from silicon compounds such as elemental silicon and silicon dioxide; silicones such as polydimethylsiloxane; silicates such as potassium silicates; natural minerals such as clays, talcs, and micas; fumed metal oxides such as fumed silica and fumed alumina. When employed, slag formers may be provided at about 0-10%, and more preferably, 0-5% by weight.

[0026] Other exemplary fuels, oxidizers, and other gas generant constituents are described in U.S. Pat. Nos. 5,035,757, 5,756,929, 5,872,329, 6,074,502, 6,287,400, 6,210,505, and 6,306,232, each herein incorporated by reference in its entirety. The gas generant constituents of the present invention may be provided by known suppliers such as Aldrich Chemical Company, Fisher Chemical, and Eastman Chemical Company.

[0027] Gas generant compositions of the present invention may be formed as known in the art. Examples of typical manufacturing processes include: (1) blending and/or grinding oxidizer, fuel, binders, and other components without solvent and compacting the powdered material on a press; (2) solvating the cellulosic binder in an organic, aqueous, or aqueous/organic solution depending on the binder chemistry and functionality, adding the desired constituents such as fuel, oxidizer, and other additives, and molding into a propellant grain. The solvent is then dried off; (3) Solvating the cellulosic binder, adding oxidizers, fuels, and other components and extruding the propellant under pressure through a die to form various shapes. The shapes may then be cut to length and the solvent evaporated or heated off. It will be appreciated that the oxidizer is chosen to tailor the overall oxygen balance in a known manner to reduce CO and other undesirable effluents.

[0028] The drying process may be accelerated by applying heat to the final homogeneous mixture. Or, depending on design criteria, the drying process may be prolonged in the absence of heat, for example. Other formulation methods are contemplated including other known wet and dry mixing and compacting methods. It is contemplated that the present compositions be employed in gas generating systems. An exemplary gas generating system includes an airbag device or vehicle occupant protection system shown in **FIG. 2** to include airbag modules, airbag inflators or gas generators, and more generally, vehicle occupant restraint systems, all built or designed as well known in the art.

[0029] 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.

[0030] 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.

[0031] 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.

[0032] 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.

[0033] 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.

[0034] 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 broadly construed from the discussion given above.

We claim:

**1**. A gas generating system comprising a gas generating composition, said composition comprising:

a fuel/binder selected from the group consisting of cellulosic binders containing alkyl substitutions;

an oxidizer; and

an additive selected from dibutylthalates, dicyclohexourea, triacetin, molybdenum trioxide, molybdic acid, ammonium molybdate, sodium molybdate, phosphomolybdic acid, molybdenum disulfide, and sodium phosphomolybdate,

said additive provided at about 0.05 to 20 percent by weight of the composition.

**2**. The gas generating system of claim 1 further comprising a second additive selected from metal oxides and sulfates, said second additive provided at about 0.1 to 20% by weight of the composition.

**3**. The gas generating system of claim 2 wherein said second additive is selected from manganese oxide, cupric oxide, and ammonium sulfate.

**4**. The gas generating system of claim 1 wherein said oxidizer is selected from metallic and nonmetallic oxidizers, said oxidizer selected from nitrates, nitrites, perchlorates, chlorates, oxides, and basic metal nitrates.

**5**. The gas generating system of claim 4 wherein said oxidizer is selected from ammonium nitrate, phase stabilized ammonium nitrate stabilized, potassium nitrate, and strontium nitrate; nitrite salts such as potassium nitrite; chlorate salts such as potassium chlorate; perchlorate salts such as ammonium perchlorate and potassium perchlorate; oxides such as iron oxide and copper oxide; basic nitrate salts such as basic copper nitrate and basic iron nitrate; and mixtures thereof, said oxidizer provided at about 0.1-70% by weight.

**6**. The gas generating system of claim 1 further comprising a secondary fuel selected from azoles, nonmetal and metal salts of azoles, nitramine derivatives and salts of azoles, guanidines, guanidine derivatives, and salts of guanidines, azoamides, nitrate salts of azoamides, and mixtures thereof, said secondary fuel provided at about 0.1-50% by weight.

**7**. The gas generating system of claim 6 wherein: said azoles are selected from 5-aminotetrazole; said nonmetal salts of azoles are selected from monoammonium or diammonium salts of 5,5'-bis'1H-tetrazole, and 5-aminotetrazole nitrate; said nitramine derivatives and salts of azoles are selected from 5-nitraminotetrazole, dipotassium 5-nitraminotetrazole, monoammonium 5-nitraminotetrazole, and diammonium 5-nitraminotetrazole; said guanidines, guanidine derivatives, and salts of guanidines are selected from dicyandiamide, nitroguanidine, and guanidine nitrate; and said azoamides and nitrate salts of azoamides are selected from azodicarbonamide and azodicarbonamidine dinitrate.

**8**. The gas generating system of claim 1 wherein said cellulosic binders containing alkyl substitutions are selected from cellulosic binders containing alkyl substitutions selected from acetyl, propionyl, butyryl groups with hydroxyl groups.

**9**. The gas generating system of claim 1 wherein said cellulosic binder is selected from cellulose acetate, cellulose acetate propionate, cellulose acetate butyrate, hydroxyethylcellulose, hydrocypropyl cellulose, methyl cellulose, and ethyl hydroxyethyl cellulose.

**10**. The gas generating system of claim 1 further comprising a metal oxide at about 0.1-20% by weight of the gas generant composition.

**11**. A vehicle occupant protection system containing the gas generating system of claim 1.

**12**. A gas generant composition comprising:

a fuel/binder selected from the group consisting of cellulosic binders containing alkyl substitutions;

an oxidizer; and

an additive selected from dibutylthalates, dicyclohexourea, triacetin, molybdenum trioxide, molybdic acid, ammonium molybdate, sodium molybdate, phosphomolybdic acid, molybdenum disulfide, and sodium phosphomolybdate,

said additive provided at about 0.05 to 20 percent by weight of the composition.

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