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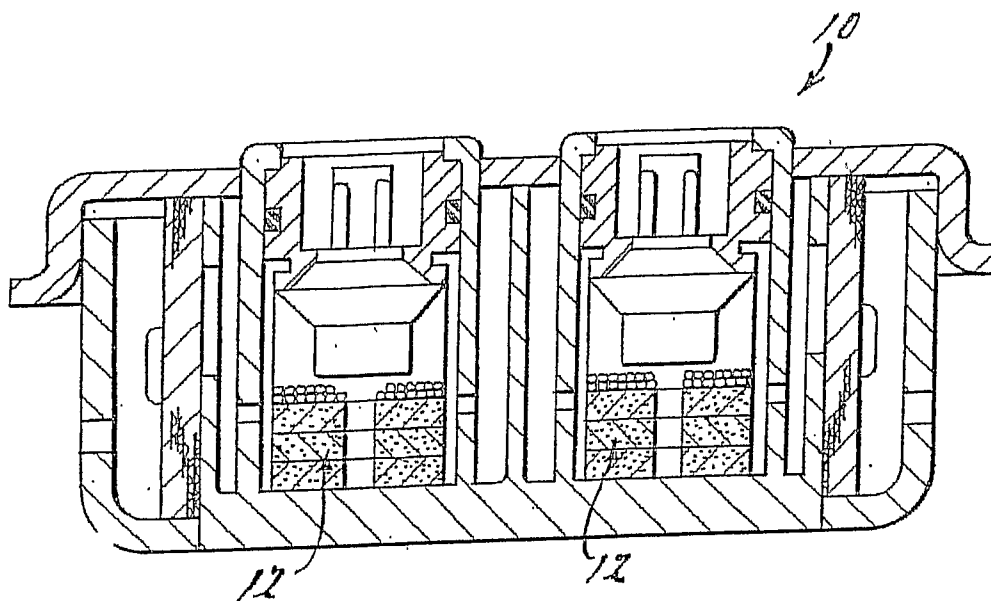
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(54) Title: **AUTOIGNITION/BOOSTER COMPOSITION**



(57) Abstract: A gas generator 10 includes a composition that contains a metal chlorate such as potassium chlorate as an oxidizer, a carboxylic acid such as DL-tartaric acid as a primary fuel, a secondary oxidizer such as strontium nitrate, and if desired, a secondary fuel such as 5-aminotetrazole. Gas generating systems 180 such as vehicle occupant protection systems 180, containing the gas generator 10, are also provided.

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## **AUTOIGNITION/BOOSTER COMPOSITION**

### **CROSS-REFERENCE TO RELATED APPLICATIONS**

This application claims the benefit of U.S. Provisional Application Serial No.

5 60/703,998 filed on July 29, 2005.

### **TECHNICAL FIELD**

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

### **BACKGROUND OF THE INVENTION**

The present invention relates to autoignition compositions that upon ignition provide the flame front and pressure front necessary to safely ignite gas generant compositions in combustible communication therewith. As known in the art, gas generators are typically provided with an autoignition composition that in the event of a fire ignites responsive to a desired threshold temperature. As a result, the gas generant is ignited prior to melting for example, thereby safely igniting the main gas generant composition to inhibit or prevent the likelihood of an explosive event once the gas generant begins to combust.

An ongoing challenge is to simplify the manufacture of a gas generator by reducing the constituents required in the production thereof. For example, in many gas generators used in vehicle occupant protection systems, several discrete compositions are provided to serve correspondingly discrete functions. These compositions often include a primary gas generating composition that when combusted is employed to provide sufficient quantities of gaseous products to operate the associated restraint device, such as an airbag or seatbelt pretensioner. A booster composition is utilized to elevate the pressure and heat within the gas generator prior to combustion of the primary gas generant, thereby creating favorable conditions within the inflator for acceptable combustion of the primary gas generant. Of course, still yet another composition is the auto-ignition composition employed to provide safe combustion of the other compositions in the event of a fire. The auto-ignition composition is designed to ignite at temperatures below the melting point of the primary gas generant for example, thereby ensuring the controlled combustion of the primary gas generant, as opposed to an explosive reaction perhaps.

The use of potassium chlorate within an autoignition composition has been

considered given the autoignition properties of this oxidizer. Furthermore, carboxylic acid in combination with potassium chlorate typically provides a desired autoignition temperature of 200 degrees Celsius or less. Nevertheless, these types of compositions typically do not provide anything but auto-ignition function when employed in gas generators used in vehicle occupant protection systems, for example.

### **SUMMARY OF THE INVENTION**

The above-referenced concerns and others may be resolved by gas generating systems including an autoignition composition containing a first oxidizer selected from metal chlorates, such as potassium chlorate, a carboxylic acid or dicarboxylic acid as a primary fuel, a secondary oxidizer selected from metal and nonmetal nitrates, nitrites, oxides, basic metal nitrates, and other known oxidizers, and a secondary fuel selected from azoles including tetrazoles, triazoles, and furazans, and salts thereof. Other constituents including extrusion aids, such as fumed silica and/or graphite, may be included in relatively small amounts. **(IS THIS ACCURATE? SHOULD WE CLAIM ANY BROADER? NOTE THAT IF OTHER CONSTITUENTS ARE CONTEMPLATED, WE SHOULD HAVE LABORATORY DATA TO INDICATE THAT OTHER FUELS OR OXIDIZERS WOULD BE USEFUL IN THE PRESENT INVENTION WITHIN AN AUTOIGNITION/BOOSTER COMPOSITION AS DESCRIBED HEREIN.)**

In further accordance with the present invention, a gas generator and a vehicle occupant protection system incorporating the autoignition system are also included.

### **BRIEF DESCRIPTION OF THE DRAWINGS**

FIG. 1 is a cross-sectional side view showing the general structure of an inflator in accordance with the present invention;

FIG. 2 is a schematic representation of an exemplary vehicle occupant restraint system containing a gas generant composition in accordance with the present invention.

### **DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT(S)**

The present compositions contain a first oxidizer selected from alkali, alkaline earth, and transitional metal chlorates, and mixtures thereof, such as potassium chlorate, at about 10-60 weight%; a primary fuel selected from carboxylic acids and dicarboxylic acids, such as DL-tartaric acid, at about 15-45 weight%; a secondary oxidizer selected from metal and nonmetal nitrates, nitrites, oxides, and other known oxidizers at about 30-50%; and a secondary fuel selected from tetrazoles, triazoles, furazans, and salts thereof at about 0-30 weight %, said weight percent calculated with regard to the weight of the total composition. Extrusion aids or processing additives

such as graphite or fumed silica may be added in relatively smaller amounts, such as 0.1-2% by weight of the total composition for example.

The present compositions contain a metal chlorate such as potassium chlorate; a primary fuel selected from carboxylic acids and dicarboxylic including DL-tartaric acid, L-tartaric acid, D-tartaric acid, succinic acid, glutamic acid, adipic acid, mucic acid, fumaric acid, oxalic acid, galactaric acid, citric acid, glycolic acid, L-malic acid, and compounds having at least one -COOH- group, and mixtures thereof; a second fuel selected from an azole including tetrazoles, triazoles, furazans, salts thereof, and mixtures thereof; a secondary oxidizer selected from metal and nonmetal nitrates or other known oxidizers not containing a perchlorate. The carboxylic acid or dicarboxylic acid will preferably have a primary hydrogen or PKA less than or equal to 3. Nevertheless, it has been found that with certain fuels/salts, the pKa of the base acid may range up to 5.0 or less.

In one embodiment, the total fuel constituent including the carboxylic fuel and the second fuel is provided at about 20-45% by weight of the total composition; the oxidizer constituent is provided at about 20-50% by weight of the total composition; and the potassium chlorate or metal chlorate is provided at about 10-60% by weight of the total composition wherein the weight percent of the chlorate is separately calculated from that of the oxidizer. The composition may be formed by wet or dry mixing the constituents in a granulated form in a known manner, and then pelletizing or otherwise forming the composition for further use. The constituents may be provided by Fisher Chemical, Aldrich Chemical, GFS, and other known suppliers.

The present invention is exemplified by the following Examples:

#### COMPARATIVE EXAMPLE 1

A known autoignition composition was prepared by homogeneously mixing dried and granulated D-glucose at about 26.875 wt% and potassium chlorate at about 73.125 wt%, the percents stated by weight of the total composition. The composition autoignited at about 144 C as measured by DSC analysis. The propellant formed from the constituents resulted in an approximate 55.5% gas yield. The impact sensitivity of this formulation had an HD50 of 2.0 inches as conducted in conformance with the Bruceton Test.

#### EXAMPLE 2

An exemplary formulation was provided that functions as a booster, an autoignition, and a gas generant composition. The formulation contains 5-aminotetrazole at about 19.0 wt%, DL-tartaric acid at about 20.0 wt%, strontium nitrate at about 35.0 wt%, and potassium chlorate at about 26.0 wt%. The constituents were previously and separately

ground to a relatively small size in a known manner. They were then dry-mixed to form a substantially homogeneous composition. The composition autoignited at about 140 C as measured by DSC analysis. The propellant formed from the constituents resulted in an approximate 67% gas yield. The impact sensitivity of this formulation had an HD50 of 11.5 inches as conducted in conformance with the Bruceton Test. The composition was aged for about 480 hours at 107C and still autoignited at about 145.1C as determined by DSC analysis.

### EXAMPLE 3

An exemplary formulation was provided that functions as a booster, an autoignition, and a gas generant composition. The formulation contains 5-aminotetrazole at about 19.0 wt%, DL-tartaric acid at about 19.0 wt%, strontium nitrate at about 50.0 wt%, and potassium chlorate at about 12.0 wt%. The constituents were granulated and dry-mixed to form a substantially homogeneous composition. The composition autoignited at about 141 C as measured by DSC analysis. The propellant formed from the constituents resulted in an approximate 68.2% gas yield. The impact sensitivity of this formulation had an HD50 of 8.8 inches as conducted in conformance with the Bruceton Test. As shown in FIG. 3, the composition reflected a relatively strong burn rate across several pressure regimes, and in particular indicated burn rates of over 0.8 inches per second (ips). Again referring to FIG. 3, it can be seen that the composition exhibited a burn rate of about 0.2 ips at about 200 psig, about 0.35 ips at about 550 psig, about 0.5 ips at about 1000 psig, about 0.55 ips at about 1500 psig, about 0.85 ips at about 2000 psig, about 0.9 ips at about 2500 psig, about 0.85 ips at about 3000 psig; and about 1.2 ips at about 3900 psig. It can therefore be seen that a composition in accordance with the present invention exhibits a satisfactory burn rate (typically 0.4 ips or more at about 2500-3000 psig) thereby ensuring satisfactory functionality as a primary gas generant. The composition was aged for about 480 hours at 107C and still autoignited at about 174.7C as determined by DSC analysis.

## EXAMPLE 4

An exemplary formulation was provided that functions as a booster, an autoignition, and a gas generant composition. The formulation contains DL-tartaric acid at about 28.0 wt%, strontium nitrate at about 32.0 wt%, and potassium chlorate at about 30.0 wt%. The constituents were previously and separately ground to a relatively small size in a known manner. They were then dry-mixed to form a substantially homogeneous composition. The composition autoignited at about 153 C as measured by DSC analysis. The propellant formed from the constituents resulted in an approximate 66.1% gas yield. The impact sensitivity of this formulation had an HD50 of 8.1 inches as conducted in conformance with the Bruceton Test.

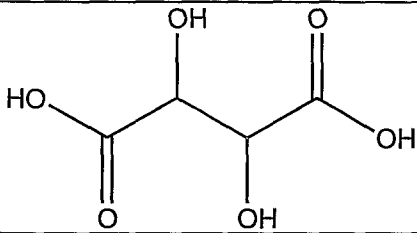
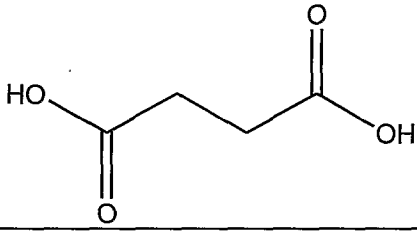
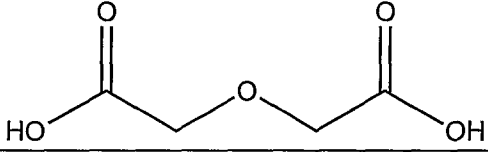
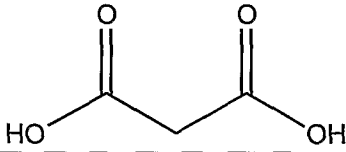
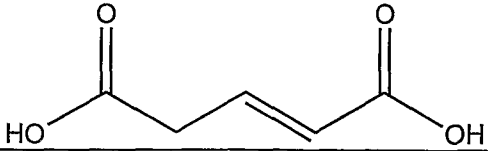
As indicates in Examples 1-4, compositions formed in accordance with the present invention (Examples 2-4) preferably autoignite at or below about 180C and provide a booster function as well. The compositions of the present invention may also produce substantial quantities of gas, and exhibit sufficient burn rates thereby producing sufficient amounts of gas when activated. Compositions employing a secondary oxidizer, such as strontium nitrate, provide relative increased quantities of gas and an improved sensitivity. A Bruceton sensitivity result wherein  $H_{50} = 3.9$  or more relaxes the packaging requirements as per U.S.D.O.T regulations. Accordingly, compositions having a sensitivity result of 3.9 or greater provide substantial packaging advantages. It will further be appreciated that the use of a secondary fuel, such as 5-aminotetrazole, in conjunction with the carboxylic or dicarboxylic acid, the secondary oxidizer, and the potassium chlorate produces greater amounts of gas, acceptable autoignition temperatures, and booster functionality. As such, compositions formed in this manner may be provided to singularly replace the three discrete booster, autoignition, and primary gas generant compositions normally found in a gas generator.

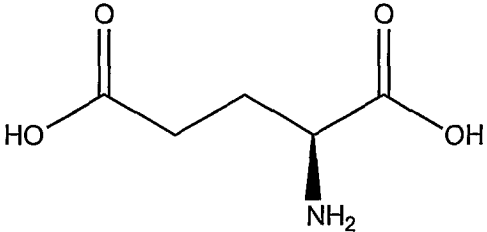
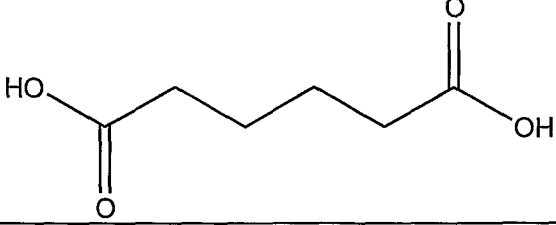
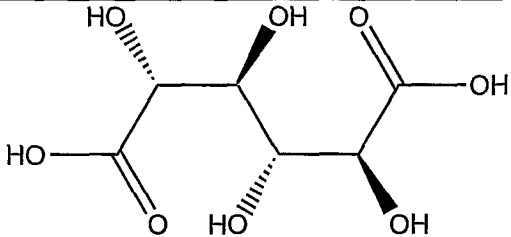
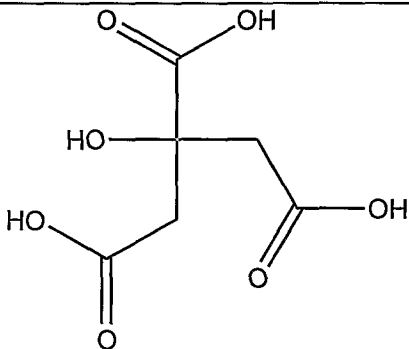
## EXAMPLES 5-16

As shown in Table 1 below, the various acids shown, when converted to salts and mixed with potassium chlorate in stoichiometric amounts exhibit acceptable autoignition temperatures for a variety of uses. Certain autoignition temperatures exceed 180 C but may still be useful in selected applications such as hybrid inflators and seatbelt pretensioners for example. It will be appreciated that these Examples reflect the autoignition character imparted by the resulting salts and the potassium chlorate. As further shown, acids exhibiting a pKa of about 3.05 or less generally provide autoignition temperatures generally less than 170-180C. However, acids exhibiting a pKa of about 5.0 or less may still be acceptable wherein autoignition temperatures of 250 or so are acceptable, for example. It will be appreciated that certain acids such as citric acid and malonic acid when stoichiometrically combined with potassium chlorate may not satisfy the autoignition

function, but still when combined with at least a second oxidizer function as a booster oxidizer and a primary gas generant. It has further been determined that the use of a desiccant as described in co-owned and co-pending U.S. Serial No. 11/479,493, herein incorporated by reference, may in certain circumstances maintain optimum environmental conditions within the gas generator thereby facilitating the tri-functionality of the composition when used as an autoignition, booster, and primary gas generating composition.

TABLE 1

| Name                         | Structure                                                                           | Lit.<br>mp  | Stoichiometric Mixture<br>w KC                                    |              |      |
|------------------------------|-------------------------------------------------------------------------------------|-------------|-------------------------------------------------------------------|--------------|------|
|                              |                                                                                     |             | DSC/TGA                                                           | Hot<br>Plate | PKa  |
| L-Tartaric<br>Acid           |    | 168-<br>170 | AI 142                                                            | <b>154</b>   | 3.02 |
| D-Tartaric<br>Acid           |                                                                                     | 168-<br>170 |                                                                   |              | 2.98 |
| DL-<br>Tartaric<br>Acid      |                                                                                     | 206         | AI 171                                                            | <b>185</b>   |      |
| Meso-<br>Tartaric<br>Acid    |                                                                                     | 140         |                                                                   |              | 3.22 |
| Succinic<br>Acid             |  | 188-<br>190 | mp 184<br>followed<br>by small<br>exo; no<br>TGA step<br>function | <b>210</b>   | 4.16 |
| Diglycolic<br>Acid           |  | 142-<br>145 | mp 130<br>followed<br>by small<br>exo; TGA<br>slow dec.           | <b>155</b>   | 3.28 |
| Malonic<br>Acid              |  | 135-<br>137 | mp 124<br>followed<br>by small<br>exo; TGA<br>slow dec.           | >250         | 2.83 |
| Trans-<br>Glutaconic<br>Acid |  | 137-<br>139 | mp 136;<br>AI 166                                                 | <b>188</b>   |      |

|                 |                                                                                    |         |                                                    |            |      |
|-----------------|------------------------------------------------------------------------------------|---------|----------------------------------------------------|------------|------|
| D-Glutamic Acid |   | 200-202 | mp 206; AI 213                                     | <b>235</b> | 2.13 |
| Adipic Acid     |   | 152-154 | mp 153; AI 222                                     | <b>237</b> | 4.43 |
| Mucic Acid      |   | 215     | AI 200                                             | <b>223</b> | 3.08 |
| Citric Acid     |  | 152-154 | mp 141 followed by small exo; no TGA step function | >250       | 3.12 |

It will be appreciated that in further accordance with the present invention, gas generators made as known in the art and also vehicle occupant protection systems manufactured as known in the art are also contemplated. As such, autoignition compositions of the present invention are employed in gas generators, seat belt assemblies, and/or vehicle occupant protection systems, all manufactured as known in the art.

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

system may contain a gas generating composition as described herein.

Extrusion aides may be selected from the group including talc, graphite, borazine [(BN)<sub>3</sub>], boron nitride, fumed silica, and fumed alumina. The extrusion aid preferably constitutes 0-10% and more preferably constitutes 0-5% of the total composition.

5 The compositions may be dry or wet mixed using methods known in the art. The various constituents are generally provided in particulate form and mixed to form a uniform mixture with the other gas generant constituents.

10 It should be noted that all percents given herein are weight percents based on the total weight of the gas generant composition. The chemicals described herein may be supplied by companies such as Aldrich Chemical Company for example.

As shown in FIG. 1, an exemplary inflator incorporates a dual chamber design to tailor the force of deployment of an associated airbag. In general, an inflator containing a primary gas generant 12 and an autoignition/booster composition 14 formed as described herein, may be manufactured as known in the art. U.S. Patent Nos. 6,422,601, 6,805,377, 6,659,500, 15 6,749,219, and 6,752,421 exemplify typical airbag inflator designs and are each incorporated herein by reference in their entirety.

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 20 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.

25 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 30 of the belt. In addition, a safety belt pretensioner 156 containing propellant 12 and autoignition 14 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 35 in U.S. Pat. Nos. 5,743,480, 5,553,803, 5,667,161, 5,451,008, 4,558,832 and 4,597,546, each 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.

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. Patent Nos. 6,505,790 and 6,419,177, previously incorporated herein by reference, provide illustrative examples of pretensioners actuated in such a manner.

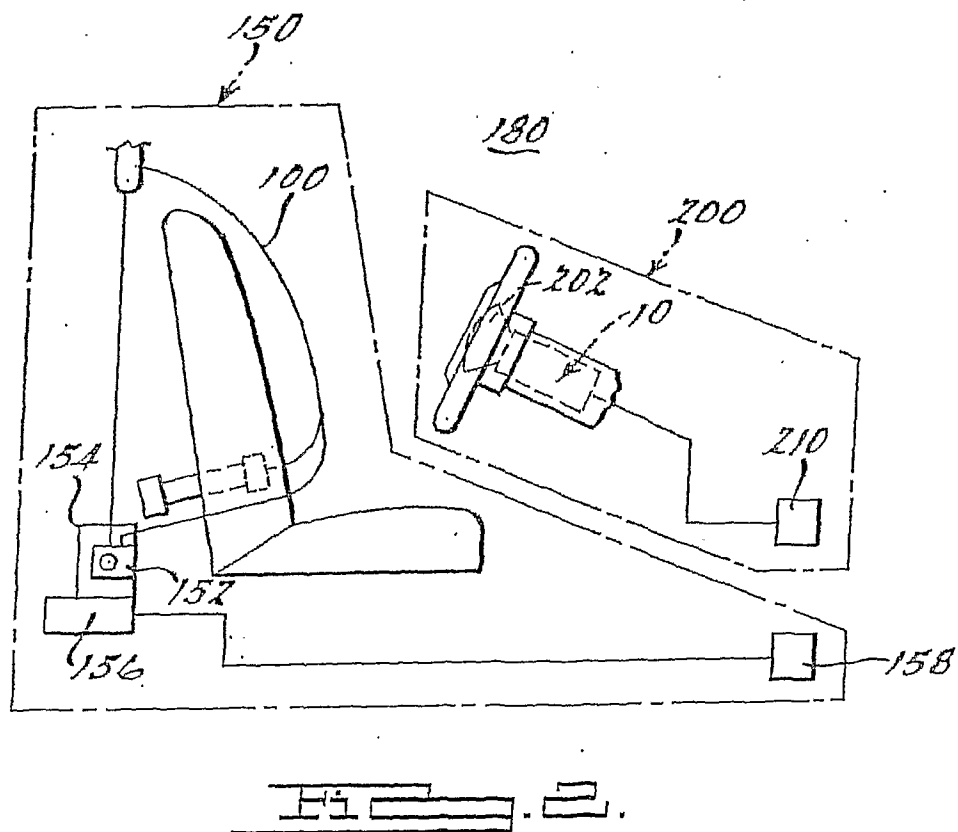
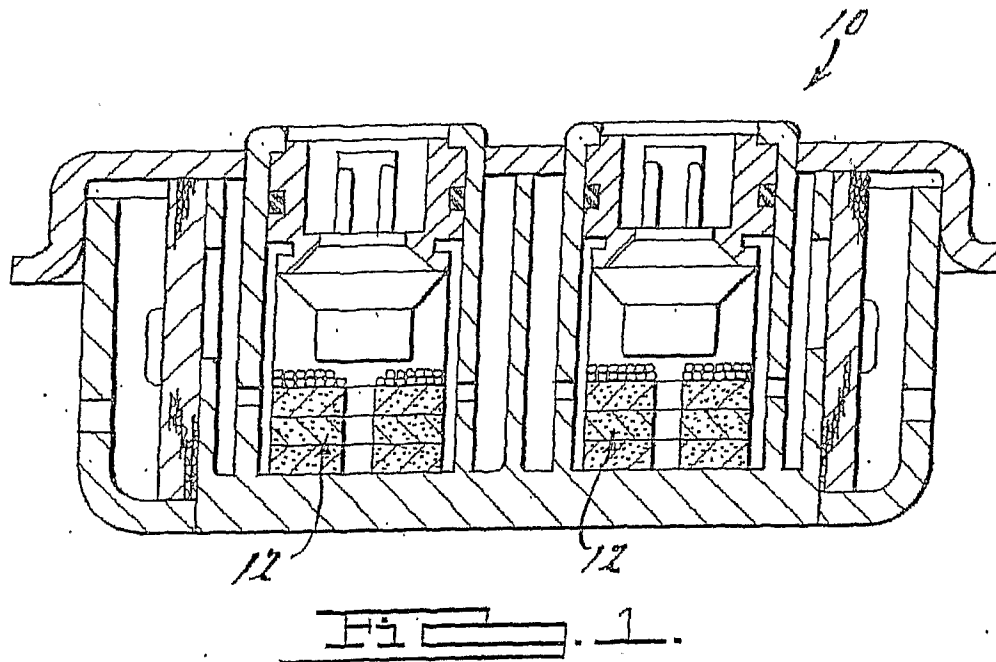
It should be appreciated that safety belt assembly 150, airbag system 200, and more broadly, vehicle occupant protection system 180 exemplify but do not limit gas generating systems contemplated in accordance with the present invention.

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.

WHAT IS CLAIMED IS:

1. A composition comprising:  
a metal chlorate as a first oxidizer;  
a primary fuel selected from carboxylic acids, dicarboxylic acids, and mixtures thereof;  
5 and  
a second oxidizer not having perchlorate character.
2. The composition of claim 1 wherein said metal chlorate is provided at about 10-20  
wt%, and said primary fuel is provided at about 15-45 wt%, and said second  
10 oxidizer is provided at about 30-50 wt%, said percentages stated by weight  
of the total composition.
3. The composition of claim 1 wherein said composition further comprises a secondary  
fuel selected from tetrazoles, triazoles, furazans, and salts thereof, said  
15 secondary fuel provided at about 0.1-30 wt%.
4. A vehicle occupant protection system comprising the composition of claim 1.
5. A gas generating system comprising the composition of claim 1.  
20
6. The composition of claim 1 wherein said primary fuel is selected from tartaric acid and its  
isomers, succinic acid, glutamic acid, adipic acid, mucic acid, oxalic acid, malonic acid, fumaric  
acid, galactaric acid, glycolic acid, citric acid, L-malic acid, and mixtures thereof.
- 25 7. The composition of claim 3 comprising DL-tartaric acid at about 19-28 wt%, potassium  
chlorate at about 12-30 wt%, 5-aminotetrazole at about 15-25 wt%, and strontium nitrate at about  
30-50 wt%, said percentages stated by weight of the total composition.
8. The composition of claim 1 wherein said secondary oxidizer is selected from metal, basic  
30 metal, and nonmetal nitrates, nitrites, oxides, and chlorates.

ABSTRACT



F16.3

