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(54) AIR BAG GAS-GENERATING COMPOSITION WITH ONLY A SMALL AMOUNT OF RESIDUE

(57) A gas generating composition for use in an air bag generating a large volume of gases and forming less amount of solid and liquid particles (residues) upon burning and capable of downsizing a gas generator.

A gas generating composition comprising an oxidizer comprising a mixture comprising a phase stabilized ammonium nitrate (PSAN), and nitroguanidine as essential ingredients wherein the content of nitroguanidine in the composition is 35% by weight or less.

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Description

TECHNICAL FIELD:

[0001] The present invention concerns a gas generating composition for use in an air bag. More specifically, it relates to a gas generating composition with less residues for use in an air bag which forms an operation gas in an air bag system mounted in traffic facilities such as automobiles and used for protecting passengers.

BACKGROUND OF THE INVENTION:

[0002] At present, gas generating base agents used generally for air bag systems include inorganic azide compounds, particularly, sodium azide. Compositions comprising such inorganic azide compounds have no particular problems in view of burning characteristics and are generally put to practical use at present. However, sodium azide essentially has various undesired properties. For example, it is an extremely toxic substance and, further, sodium azide readily reacts with a heavy metal such as copper or lead to form a highly sensitive compound tending to cause abrupt ignition or explosion. Accordingly, a special handling is required for production, storage and disposal of such compositions.

[0003] In order to compensate such drawbacks, so-called non-azide gas generating agents have been proposed as replacements for sodium azide. For example, JP-A 3-208878 discloses a composition comprising, as essential ingredients, tetrazole, triazole or a metal salt thereof and an oxygen-containing oxidizer such as an alkali metal nitrate. In the composition, although the toxicity is remarkably reduced compared with the azide type composition, the gas generating efficiency is not so high since a great amount of solid and liquid particles are still contained in exhaust products.

[0004] Further, a gas generating agent comprising a phase stabilized ammonium nitrate (PSAN) and nitrogen-containing compound such as triaminoguanidine nitrate is disclosed in the specification of WO95/04710. Further, a gas generating agent comprising a mixture of ammonium nitrate phase-stabilized with 7 to 20% by weight of a potassium salt and nitroguanidine is disclosed in US-A 5,545,272 and WO96/27574. Such compositions enable to increase the gas generating efficiency upon burning to a high level. However, heat of combustion is rather great and theoretical combustion temperature exceeds 2500K, and CO and NO_X gases at high concentrations are generated.

[0005] Nitrogen-containing compounds have a drawback that the heat of combustion is greater and the combustion temperature is higher compared with those of azide compounds in general combustion, when using an oxidizer in a stoichiometrical amount, that is, in an amount sufficient to form oxygen required for burning of carbon, hydrogen and other elements in the compound. There is a possibility that excessively high combustion temperature generates CO and NO_X gases by an amount much more than an allowable value to a human body. Further, if a great amount of a metal compound (for example, metal oxide) is used in the gas generating composition, solid and liquid particles formed discharged from a gas generator may hit directly against a bag to possibly break the bag. Additional parts are required for confining such particles in the gas generator, which makes it difficult to down size the gas generator itself. That is, it can be said that an excellent gas generating agent has characteristics of low combustion temperature at combustion, generating a large volume of gases and generating small amount of solid and liquid particles. Accordingly, known gas generating compositions described above are not yet satisfactory for application use to air bag systems.

DISCLOSURE OF THE INVENTION:

[0006] The present inventors have made earnest studies for solving the foregoing problems and have accomplished the present invention.

[0007] That is, the present invention provides a gas generating composition which generates less residues and a great amount of gases by combustion for inflating an air bag suitable to various purposes including the use as a shock absorbing safety bag for traffic facilities such as automobiles, wherein the composition comprises an oxidizer comprising a mixture comprising a phase stabilized ammonium nitrate (PSAN) and nitroguanidine as essential ingredients and the content of nitroguanidine in the composition is 35% by weight or less.

[0008] In the gas generating composition according to the present invention, the amount of residues generated is decreased compared with gas generating compositions disclosed so far and the use of the gas generating composition according to the present invention can remarkably decrease the number and the amount of additional parts for removing residues, to make way to the downsize of a gas generator itself.

PREFERRED EMBODIMENT OF THE INVENTION:

[0009] The gas generating composition according to the present invention suppresses the formation of solid residues as much as possible thereby enabling to remarkably decrease the number and the amount of additional parts compared with conventional gas generators, by utilizing the features that ammonium nitrate is entirely converted into non corrosive gases without forming solid residues upon combustion and generating no corrosive gases such as chlorine and hydrogen chloride.

[0010] In the present invention, the combustion temperature can be lowered by about 150 to 300K and the heat of combustion can also be reduced to some extent compared with the existent compositions, by defining the content of nitroguanidine to 35% by weight or less, preferably, 5 to 33% by weight in the composition. Lowering of the combustion temperature is advantageous for decreasing toxic CO and NO_x gases. Further, low combustion temperature and less heat of combustion are also advantageous for reducing additional parts in a gas generator.

[0011] Table 1 shows the result of theoretical calculation for the combustion temperature and the heat of combustion with respect to the composition of the present invention in which nitroguanidine is blended by 35% by weight or less and an conventional composition.

[0012] In Table 1, PSANKP10 indicates a phase stabilized ammonium nitrate comprising 90% by weight of ammonium nitrate and 10% by weight of potassium perchlorate and NQ indicates nitroguanidine.

Table 1

No.	Composition (wt%)	NQ (wt%)	Oxygen balance (g/g,×10^{-2})	Combustion temperature (K)	Heat of combustion (Kcal/g)	amount of gas generation (mol/100g)	NO_x (mol%)	CO (mol%)	Remarks
1	PSANKP10:NQ = 57.6:42.4	42.4	-0.03	2498	1.106	4.006	0.21	0.58	Comparative composition
2	PSANKP10:NQ = 65.0:35.0	35.0	3.92	2311	1.023	4.002	0.41	0.06	Present invention
3	PSANKP10:NQ = 70.0/30.0	30.0	6.59	2158	0.954	4.010	0.38	0.01	
4	PSANKP10:NQ = 75.0/25.0	25.0	9.26	2000	0.884	4.019	0.30	0.00	
5	PSANKP10:NQ = 80.0/20.0	20.0	11.93	1838	0.815	4.026	0.21	0.00	
6	PSANKP10:NQ:CuO = 69.5/30.0/0.5	30.0	6.48	2151	0.948	3.988	0.37	0.01	

[0013] Pure ammonium nitrate causes phase transition with about 3% volumic change when passing a temperature of 32°C. Great volumic change of a molding product may possibly cause occurrence of abnormal combustion or burning which is not desirable for a gas generating agent. Accordingly, a phase stabilized ammonium nitrate is used in the present invention.

[0014] For the phase stabilized ammonium nitrate used in the present invention, a mixture of 98 to 70% by weight of ammonium nitrate and 2 to 30% by weight of a phase stabilizer is preferred. It has been known generally to stabilize the phase of ammonium nitrate, for example, by introducing potassium cations into crystal lattices of ammonium nitrate. In the present invention, it is preferred to use at least one compound selected from the group consisting of organic or inorganic potassium salts being soluble in hot water. Phase transition of ammonium nitrate can be prevented by blending a phase stabilizer in an amount of 2% by weight or more in the phase stabilized ammonium nitrate. However, since an excessive blending amount of the phase stabilizer is disadvantageous for the purpose of decreasing solid residues, the blending amount of the phase stabilizer in the phase stabilized ammonium nitrate is preferably about from 2 to 30% by weight.

[0015] The organic or inorganic potassium salts being soluble in hot water used as the phase stabilizer in the present invention can include at least one compound selected from the group consisting of potassium nitrate, potassium perchlorate, potassium sulfate, potassium chloride, potassium chlorate, potassium chromate, potassium bichromate, potassium permanganate and potassium oxalate.

[0016] The gas generating composition according to the present invention comprises an oxidizer comprising a mixture comprising the phase stabilized ammonium nitrate, and the oxidizer according to the present invention is preferably blended with an oxygen-containing oxidizer, a metal oxide or a mixture thereof in addition to the phase stabilized ammonium nitrate.

[0017] The oxygen-containing oxidizer used in the present invention can include, for example, at least one compound selected from the group consisting of alkali metal salts, alkaline earth metal salts and ammonium salts of nitric acid, perchloric acid and chloric acid and, specifically, they include potassium perchlorate, ammonium perchlorate, potassium chlorate, potassium nitrate, sodium nitrate and strontium nitrate.

[0018] The metal oxide used in the present invention can include oxides or composite oxides of metals selected from the group consisting of copper, cobalt, iron, manganese, nickel, chromium, zinc, molybdenum and bismuth.

[0019] The blending amount of the phase stabilized ammonium nitrate in the composition of the present invention is preferably from 60 to 85% by weight. Further, the blending amount of the oxygen-containing oxidizer, metal oxide or a mixture thereof in the composition according to the present invention is preferably from 0 to 25% by weight.

[0020] In the composition of the present invention, a combustion rate accelerating catalyst is preferably blended for accelerating the combustion rate. The combustion rate accelerating catalyst used in the present invention can include at least one compound selected from the group consisting of powdery copper, copper compounds, iron compounds, nickel compounds and chromium compounds. The copper compound used in the present invention can include, for example, copper oxide and copper chromite, the iron compound can include, for example, iron oxide, ferrocene and a derivative thereof, the nickel compound can include, for example, nickel oxide and tire chromium compound can include, for example, chromium oxide, ammonium bichromate and potassium bichromate. The blending amount of the combustion rate accelerating catalyst in the composition according to the present invention is preferably 10% by weight or less.

[0021] In the present invention, the combustion rate of the composition can be selected properly within a wide range by blending the oxygen-containing oxidizer, the metal oxide or the combustion rate accelerating catalyst as described above. Further, the shape, the grain size and the like of the oxidizer or the catalyst can be selected properly.

[0022] The gas generating composition according to the present invention can comprise an organic or inorganic binder by 20% by weight or less for forming and maintaining a molding product. A powdery mixture can be molded into a molding product by the addition of such organic or inorganic binder. There is no particular restriction for the kind of the binder and usual organic or inorganic binders can be used within a range not deteriorating the performance of the gas generating agent. Specific examples of the organic or inorganic binder can include organic binders such as sodium salt of carboxymethyl cellulose, cellulose acetate, starch, polyvinyl alcohol and sodium polyacrylate, and inorganic binders such as sodium silicate, bentonite, glass fiber and silicon rubber. The amount of the binder used is preferably 20% by weight or less since use of an excessive amount deteriorates the performance of the gas generating agent. Further, it has been well-known that combustion behavior of the gas generating agent essentially undergoes the effect of a geometrical structure of a molding product in combustion, and the gas generating composition of the present invention may be molded into an optimal geometrical structure depending on the composition selected, with no particular restriction.

EXAMPLES:

[0023] The present invention is to be explained specifically with reference to examples and comparative examples, but the present invention is not restricted only to such examples.

[0024] In the example "%" is on the weight basis unless otherwise specified.

Synthesis Example 1

(Preparation of Phase Stabilized Ammonium Nitrate)

[0025] A solution prepared by dissolving a mixture of 90% of ammonium nitrate (AN) and 10% of potassium perchlorate ($KClO_4$) under stirring into a sufficient amount of distilled water was put in a heat drier at about 85°C (preferably under reduced pressure) to evaporate water. After evaporation of most of water, formed solids were distributed thinly on a stainless steel tray and dried thoroughly at about 85°C. Drying products were collected and ground in a mortar so as to pass a 300 µm sieve. It was confirmed if the phase stabilized ammonium (PSAN) was formed or not and whether it was homogeneous or not by detecting thermally varying peaks and the content of ammonium nitrate of products by TG-DTA. As a result of TG-DTA analysis for the phase stabilized ammonium nitrate thus obtained (hereinafter simply referred to as PSANKP10, AN/$KClO_4$ (weight ratio) = 90/10), a peak at about 53°C characteristic to DTA of usual ammonium nitrate containing products disappeared and a new peak appeared at a position for 113°C. As a result of TG analysis, the ammonium nitrate content was 90%.

Example 1

[0026] A powder of a composition formed by blending 70% of PSANKP10 (AN/$KClO_4$ = 90/10) obtained in Synthesis Example 1 and 30% of nitroguanidine was thoroughly mixed in a dry process, and a powdery product was compression molded into a strand of about 12.7 mm height and about 10 mm diameter by a oil pressure cylinder at a pressure of 100 kg/cm^2. The strand was coated with a non-combustible epoxy type resin. When the combustion rate was measured under a nitrogen pressure of 70 kg/cm^2, the strand showed a combustion rate of 7.6 mm/s. The composition showed a theoretical combustion temperature of 2158K and a theoretical residue (amount of metal compound formed per 100 g of composition) of 3.8 g.

Example 2

[0027] A composition formed by blending 69.5% of PSANKP10 obtained in Synthesis Example 1, 30% of nitroguanidine and 0.5% of copper oxide was thoroughly mixed in a dry process, and a strand was prepared in the same manner as in Example 1. The combustion rate of the strand measured under a nitrogen pressure of 70 kg/cm^2 was 11.5 mm/s. The composition showed a theoretical combustion temperature of 2151K and the theoretical amount of residues was 4.1 g.

Example 3

[0028] A composition formed by blending 64% of PSANKP10, 30% of nitroguanidine, 5.0% of sodium salt of carboxymethyl cellulose and 1.0% of copper oxide was thoroughly mixed in a dry process, and a strand was prepared in the same manner as in Example 1. The combustion rate of the strand measured under a nitrogen pressure of 70 kg/cm^2 was 11.3 mm/s. The composition showed a theoretical combustion temperature of 2435K and the theoretical amount of residue was 4.8 g.

Claims

1. A gas generating composition comprising an oxidizer comprising a mixture comprising a phase stabilized ammonium nitrate (PSAN), and nitroguanidine as essential ingredients, wherein the content of nitroguanidine of the composition is 35% by weight or less.

2. A gas generating composition as defined in claim 1, wherein the phase stabilized ammonium nitrate (PSAN) comprises a mixture of 98 to 70% by weight of ammonium nitrate and 2 to 30% by weight of a phase stabilizer.

3. A gas generating composition as defined in claim 2, wherein the phase stabilizer is at least one compound selected from the group consisting of organic or inorganic potassium salts being soluble in hot water.

4. A gas generating composition as defined in claim 3, wherein the organic or inorganic potassium salt being soluble in hot water is at least one compound selected from the group consisting of potassium nitrate, potassium perchlorate, potassium sulfate, potassium chloride, potassium chlorate, potassium chromate, potassium dichromate, potassium permanganate and potassium oxalate.

5. A gas generating composition as defined in claim 1, wherein the oxidizer comprises a phase stabilized ammonium nitrate (PSAN), and an oxygen-containing oxidizer, a metal oxide or a mixture thereof.

6. A gas generating composition as defined in claim 5, wherein the oxygen-containing oxidizer is at least one compound selected from the group consisting of alkali metal salts, alkaline earth metal salts and ammonium salts of nitric acid, perchloric acid and chloric acid.

7. A gas generating composition as defined in claim 5 or 6, wherein the metal oxide comprises an oxide or a composite oxide of a metal selected from the group consisting of copper, cobalt, iron, manganese, nickel, chromium, zinc, molybdenum and bismuth.

8. A gas generating composition as defined in claim 1, further comprising a combustion rate accelerating catalyst by 10% by weight or less.

9. A gas generating composition as defined in claim 8, wherein the combustion rate accelerating catalyst is at least one compound selected from the group consisting of powdery copper, copper compound, iron compound, nickel compound and chromium compound.

10. A gas generating composition as defined in claim 1 further comprising an organic or inorganic binder by 20% by weight or less.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP98/01125

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl^6 C06D5/00, C06B31/36

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
Int.Cl^6 C06D5/00, C06B31/36

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
CA (STN), REGISTRY (STN), WPIDS (STN)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US, 5545272, A (Olin Corporation) August 13, 1996 (13. 08. 96), Claim 1 (Family: none)	1-10
X	JP, 6-92770, A (S.N.C. Livbag), April 5, 1994 (05. 04. 94), Claim 1 ; Par. Nos. [0026], [0027] & EP, 576326, A1	1-10
X	JP, 7-215790, A (Societe Nationale des Poudres et Explosifs), August 15, 1995 (15. 08. 95), Claim 1 ; Par. Nos. [0018] to [0020] & EP, 659712, A1 & US, 5525171, A	1-10
P	US, 5641938, A (Primex Technologies), June 24, 1997 (24. 06. 97), Claim 12 (Family: none)	1-10

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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Date of the actual completion of the international search May 7, 1998 (07. 05. 98)	Date of mailing of the international search report May 19, 1998 (19. 05. 98)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

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INTERNATIONAL SEARCH REPORT

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P	WO, 98/04507, A1 (AUTOMOTIVE SYSTEMS LABORATORY, INC.), February 5, 1998 (05. 02. 98), Claim 6 (Family: none)	1-10

Form PCT/ISA/210 (continuation of second sheet) (July 1992)