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(54) **GAS GENERANT COMPOSITION**

GASERZEUGENDE ZUSAMMENSETZUNG

COMPOSITION DE GENERATION DE GAZ

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Description

Technical Field

- 5 **[0001]** The present invention relates to a gas generating composition suitable for an airbag restraining system of an automobile or the like, a molded article thereof, and an airbag inflator using them.

Background ART

- 10 **[0002]** Heretofore, compositions containing sodium azide have been often used as airbag gas generating agents for occupant-protecting devices in automobiles. However, the toxic effects of sodium azide on the human body [LD50 (oral-rat) = 27 mg/kg] and hazardous nature thereof at the time of handling have been perceived as problems. As an alternative to such compositions, therefore, gas generating compositions containing various kinds of nitrogen-containing organic compounds have been developed as so-called non-azide gas generating compositions.
- 15 **[0003]** U.S. Pat. No. 4,909,549 discloses a composition that includes a hydrogen-containing tetrazole, a triazole compound and an oxygen-containing oxidizing agent. U.S. Pat. No. 4,370,181 discloses a gas generating composition that includes a metal salt of bitetrazole containing no hydrogen and an oxidizing agent containing no oxygen. U.S. Pat. No. 4,369,079 discloses a gas generating composition that includes a metal salt of bitetrazole containing no hydrogen and alkali metal nitrate; alkali metal nitrite; alkaline earth metal nitrate; alkaline earth metal nitrite or a mixture thereof. U.S.
- 20 Pat No. 5,542,999 discloses a gas generating agents that includes fuel such as GZT, triaminonitroguanidine (TAGN), nitroguanidine (NG) or NTO; basic copper nitrate; a catalyst for decreasing toxic gas and a coolant. JP-A 10-72273 discloses a gas generating agent that includes a metal salt of bitetrazole; an ammonium salt of bitetrazole; aminotetrazole and ammonium nitrate.
- 25 **[0004]** However, although azide-based gas generating agents generate only nitrogen in general after combustion, non-azide-based gas generating compositions have a disadvantage such that small amounts of toxic carbon monoxide and nitrogen oxides are generated because each of the composition contains carbon, nitrogen and oxygen in general. In addition, compared with the azide-based gas generating agents, the non-azide-based gas generating agents have so high combustion temperatures that they may need a large amount of coolant in actual use. For reducing produced amounts of toxic carbon monoxide and nitrogen oxides after combustion, addition of a metal oxide or a DeNOx agent
- 30 (a nitrogen-oxide reducing agent) to the gas generating agent is known. For example, in the case of the gas generating composition as disclosed in DE Pat No. 4,401,213, a heavy-metal oxide such as V_2O_5/MOO_3 is added as a catalyst for reducing the produced amounts of toxic carbon monoxide and nitrogen oxides. However, the heavy-metal oxide is considered to be toxic, and addition of a metal oxide leads to a decrease of efficiency of gas generation from the gas generating agent.
- 35 **[0005]** WO 98/04507 discloses reduction of the produced amount of a nitrogen oxide in combustion gas by using a combination of a DeNOx agent such as ammonium sulfate, ammonium carbonate or urea and a gas generating agent. However, use of ammonium sulfate will generate toxic sulfur oxide and then ammonium carbonate and urea have problems in their thermal stability. Furthermore, if the DeNOx agents are added, the oxidizing agent in the gas generating agent will be consumed and a produced amount of toxic carbon monoxide is increased.
- 40 **[0006]** EP 1254880 A1 relates to a gas-generating composition comprising a triazine derivative, a basic metal nitrate, a binder and, optionally, an additive.
- [0007]** EP 1241138 A1 discloses a gas-generating composition comprising at least one guanidine derivative selected from the group consisting of tetrazole derivatives, guanidine, guanidine carbonate, nitroguanidine, dicyandiamide, nitroaminoguanidine and nitroaminoguanidine nitrate, and further a basic metal nitrate.
- 45 **[0008]** US 5, 656, 793 discloses a gas-generating composition comprising a hydrazodicarbonamide serving as a reducing agent for generating a gas when oxidized, an oxoacid salt serving as an oxidizing agent for oxidizing the reducing agent, and a combustion controller with a catalytic function which contains at least one element selected from the group consisting of boron, aluminum and zirconium.
- [0009]** EP 0801045 A1 discloses an airbag gas-generating composition comprising as an active components biscarbamoylhydrazine as a gas-generating base, an oxohalogen acid salt as an oxidizing agent, a nitrate as an oxidizing agent, and a burning catalyst.
- 50 **[0010]** EP 1415962 relates to a gas-generating composition comprising a fuel and a metal containing oxidizing agent. The fuel component comprises triazine derivatives, triazole derivatives, tetrazole derivatives, guanidine derivatives as well as hydrazine derivatives.
- 55 **[0011]** US 6, 039, 820 discloses a gas generating composition comprising a complex of a metal cation, at least one neutral ligand containing hydrogen and nitrogen, and sufficient oxidizing anion to balance the charge of the metal cation such that when the complex combusts, a mixture of gases containing nitrogen gas and water vapor is produced; and at least one cool burning organic nitrogen-containing compound.

[0012] US 3, 862, 866 relates to a deflagration composition for generating a gas comprising principally carbon dioxide and water vapor comprising a substantially homogeneous mixture of:

an oxygen bearing oxidizing powder having an average particle size less than about 25 microns; selected from the group consisting of potassium chlorate, potassium perchlorate sodium chlorate, and sodium perchlorate;
 an organic reducing powder selected from the group consisting of sucrose, starch, cellulose, dextrose, dextrin, fructose, lactose, ascorbic acid, benzoic acid, maltose monohydrate, mannitol, mannoheptose, mannoheptose monohydrate, oxalic acid, propanediolic acid and glyoxylic acid, the organic reducing powder having an average particle size less than about 15 microns and solid below about 165F, the proportion of oxidizing and reducing powders being sufficiently near stoichiometry to produce a gas upon deflagration comprising principally carbon dioxide and water vapor and an inorganic salt that is volatile at the temperature of deflagration and free of substantial carbon monoxide, nitrogen compounds, sulfur compounds and fluorine compounds; and
 an endothermic decomposition coolant powder having an average particle size less than about 25 microns and having a thermal decomposition product selected from the class consisting of carbon dioxide and water and substantially free of ions or radicals that react with the inorganic salt during deflagration, the coolant powder being selected from the group consisting of magnesium carbonate, zinc carbonate, hydrated magnesium carbonate, borax and hydrated salts of metals having oxides stable in the presence of water, and wherein the proportion by weight comprises about one part reducing powder, three parts oxidizing powder, and from one to four parts coolant powder.

[0013] WO 98/17607 discloses an azide-free solid mixture for pyrotechnically generating gas, in particular propellant gas for motor vehicle passenger protection systems, containing a fuel, an oxidizer and a coolant selected from the group of inorganic carbonates.

Disclosure of the Invention

[0014] A purpose of the present invention is to provide a gas generating composition having small produced amounts of toxic monoxide carbon and nitrogen oxides in combustion gas of a gas generating agent and having a low combustion temperature; a molded article thereof and an airbag inflator using the same.

[0015] The inventors of the present invention have completed the present invention by finding out that the produced amounts of toxic carbon monoxide, ammonium and nitrogen oxides in combustion gas can be reduced by selecting a specific combination for a gas generating composition to decrease the combustion temperature.

[0016] As means for solving the problem, the present invention provides a gas generating composition comprising the following components (a), (b), and (c) and optionally the component (d) and/or the component (e):

- (a) 10 to 60% by mass of an organic compound as fuel, wherein the organic compound is at least one selected from guanidine compounds;
- (b) 10 to 85% by mass of at least one oxidizing agent selected from the group consisting of (b-1) basic metal nitrates, nitrates and ammonium nitrate and (b-2) perchlorates and chlorates ;
- (c) 0.1 to 20% by mass of aluminum hydroxide with an average particle size of from 2 to 30 μm ;
- (d) 20% by mass or less of a binder; and
- (e) 20% by mass of an additive selected from metal oxides and metal carbides.

[0017] Furthermore, as another means for solving the problem, the present invention provides a molded article of the gas generating composition, which is obtained by molding the gas generating composition described above, and an airbag inflator using the gas generating composition described above or the molded article of a gas generating composition described above.

[0018] The gas generating composition and the molded article thereof have low combustion temperatures and small produced amounts of carbon monoxide and nitrogen oxides at the time of combustion.

Embodiment of the Invention

[0019] As the organic compound to use for the component (a) of fuel in the present invention, it includes at least one compound selected from guanidine.

[0020] The guanidine compounds preferably are guanidine nitrates, amino guanidine nitrate, nitro guanidine, triamino guanidine nitrate and the like.

[0021] The oxygen-containing oxidizing agent to use as the component (b) in the present invention preferably includes at least one selected from: (b-1) basic metal nitrates, nitrate salts and ammonium nitrates and (b-2) perchlorates and chlorates.

[0022] As the basic metallic nitrates of the component (b-1), at least one selected from basic copper nitrates, basic cobalt nitrates, basic zinc nitrates, basic manganese nitrates, basic iron nitrates, basic molybdenum nitrates, basic bismuth nitrates and basic cerium nitrates can be included.

[0023] For increasing the burning velocity, the basic metal nitrate has preferably an average particle size of 30 μm or less, more preferably of 10 μm or less. Furthermore, the average particle sizes were measured by a particle size distribution method with scattered laser beams. A measured sample is prepared by dispersing a basic metal nitrate in water and exposing it to ultrasonic waves for 3 minutes. A 50%-accumulated value (D50) of the number of particles is determined and an average value of two measurements is taken as an average particle size.

[0024] As the nitrates of the component (b-1), alkali metal nitrates such as potassium nitrate or sodium nitrate and alkaline earth metal nitrates such as strontium nitrate can be included.

[0025] The perchlorates and chlorates of the component (b-2) are that having a combustion promotion action as well as an oxidative action. The oxidative action means a function to proceed combustion efficiently with oxygen generated during burning and then another function to decrease the produced amount of toxic gas such as ammonia or carbon monoxide. The combustion promotion action, on the other hand, means a function to improve ignition of a gas generating composition and to increase a burning velocity.

[0026] As the perchlorates and chlorates, at least one selected from ammonium perchlorate, potassium perchlorate, sodium perchlorate, potassium chlorate and sodium chlorate can be included.

[0027] The aluminum hydroxide to use as the component (c) in the present invention is one used for condensing floating matters in river water for water-purifying procedures of public water supply, for a household non-phosphorus detergent and also as an additive to resin or rubber, having characteristics of a low toxicity and a high decomposition-initiating temperature.

[0028] Furthermore, it absorbs a large amount of heat when thermally decomposed to generate aluminum oxide and water. Therefore, the combustion temperature of the gas generating composition is lowered by incorporating aluminum hydroxide so that the composition will act to reduce the produced amounts of toxic nitrogen oxide and carbon monoxide after the combustion. Such reduction of the toxic gas is quite remarkable when the component (b-2) is used as the oxidizing agent.

[0029] The overall dispersibility of the mixed components (a) to (c) can be improved by adjusting the average particle size of aluminum hydroxide. Therefore the mixing operation is made easier and then ignition of the obtained gas generating composition is improved.

[0030] The average particle size of aluminum hydroxide is 2 to 30 μm . The method for measuring the average particle size of the aluminum hydroxide is the same as one used for measuring the average particle size of the basic metal nitrate.

[0031] The binder to use as the component (d) in the present invention may be a component to use optionally in combination with the components (a) to (c) or with the components (a) to (c) and the component (e). It is capable of increasing moldability of the gas generating composition and also increasing strength of the molded article of a gas generating composition. When the molding strength of the molded article of a gas generating composition is not high, there is a possibility that the molded article will be broken at actual combustion and burn too rapidly, not being able to control.

[0032] As the binder, at least one selected from carboxymethylcellulose, sodium carboxymethylcellulose, potassium carboxymethylcellulose, ammonium carboxymethylcellulose, cellulose acetate, cellulose acetate butyrate, methylcellulose, ethylcellulose, hydroxyethylcellulose, ethylhydroxyethylcellulose, hydroxypropylcellulose, carboxymethylethylcellulose, microcrystalline cellulose, polyacrylamide, an aminated product of polyacrylamide, polyacrylhydrazide, a copolymer of acrylamide and a metal acrylate, a copolymer of polyacrylamide and a polyacrylic ester, polyvinyl alcohol, acrylic rubber, guar gum, starch and silicone can be included.

[0033] The additive, selected from metal oxides and metal carbides, to use as the component (e) in the present invention, is a component to use optionally in combination with the components (a) to (c) or with the components (a) to (c) and the component (d) and is added for assisting the action of aluminum hydroxide, that is, for decreasing the combustion temperature of the gas generating agent, adjusting the burning velocity thereof and reducing the produced amount of toxic nitrogen oxide and carbon monoxide after combustion.

[0034] As the additives, at least one selected from metal oxides such as copper oxide, iron oxide, zinc oxide, cobalt oxide, manganese oxide, molybdenum oxide, nickel oxide, bismuth oxide, silica or alumina; metal carbonates or basic metal carbonates such as cobalt carbonate, calcium carbonate, basic zinc carbonate or basic copper carbonate; composite compounds of metal oxides or metal hydroxides such as acid clay, porcelain clay (Kaolin), talc, bentonite, diatomaceous earth or hydrotalcite; metal acid salts such as sodium silicate, mica molybdate, cobalt molybdate or ammonium molybdate; molybdenum disulfide; calcium stearate; silicon nitride or silicon carbide can be included.

[0035] The contents of the respective components included in the gas generating composition of the present invention and also exemplified compositions thereof are described below.

(1) A composition containing the components (a) to (c)

[0036] The content of the organic compound provided as the component (a) is 10 to 60% by mass, preferably 5 to 60% by mass, more preferably 10 to 55% by mass;

[0037] The content of the oxidizing agent provided as the component (b-1) is 10 to 85% by mass, preferably 20 to 70% by mass, more preferably 30 to 60% by mass;

[0038] The content of the oxidizing agent provided as the component (b-2) is preferably 0.5 to 20% by mass, more preferably 1 to 10% by mass, still more preferably 1 to 5% by mass;

[0039] The content of the aluminum hydroxide provided as the component (c) is 0.1 to 20% by mass, preferably 3 to 15% by mass, more preferably 4 to 10% by mass.

(composition example 1)

[0040]

- (a) guanidine nitrate 30-60 mass%
- (b) basic copper nitrate 30-60 mass%
- (c) aluminum hydroxide 3-10 mass%

(composition example 2)

[0041]

- (a) nitroguanidine 25-60 mass%
- (b) basic copper nitrate 30-60 mass%
- (c) aluminum hydroxide 3-15 mass%

(composition example 3)

[0042]

- (a) guanidine nitrate
- (b-1) basic copper nitrate
- (b-2) at least one perchlorate selected from sodium perchlorate, potassium perchlorate and ammonium perchlorate
- (C) aluminium hydroxide

(composition example 4)

[0043]

- (a) guanidine nitrate
- (b-1) basic copper nitrate
- (b-2) sodium chlorate or potassium chlorate
- (c) aluminium hydroxide

[0044] (3) A composition containing either one or both of the components (d) and (e) in addition to the compositions (a) to (c).

[0045] The content of the component (d) is preferably 20% by mass or less, more preferably 0.5 to 10% by mass, still more preferably 1 to 7% by mass;

[0046] The content of the component (e) is preferably 20% by mass or less, more preferably 1 to 15% by mass, still more preferably 3 to 10% by mass.

(composition example 5)

[0047]

- (a) nitroguanidine
- (b) strontium nitrate

- (c) aluminium hydroxide
- (d) sodium carboxymethylcellulose or guar gum

(composition example 6)

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[0048]

- (a) nitroguanidine
- (b) basic copper nitrate
- (c) aluminium hydroxide
- (d) guar gum

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(composition example 7)

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[0049]

- (a) guanidine nitrate
- (b) basic copper nitrate
- (c) aluminium hydroxide
- (d) sodium carboxymethylcellulose or guar gum

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(composition example 8)

[0050]

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- (a) a mixed fuel of 2 or 3 components selected from guanidine nitrate, nitroguanidine and melamine
- (b) basic copper nitrate
- (c) aluminium hydroxide
- (d) sodium carboxymethylcellulose or guar gum

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(composition example 9)

[0051]

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- (a) guanidine nitrate
- (b-1) basic copper nitrate
- (b-2) at least one perchlorate selected from sodium perchlorate, potassium perchlorate and ammonium perchlorate
- (c) aluminium hydroxide.
- (d) sodium carboxymethylcellulose or guar gum

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(composition example 10)

[0052]

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- (a) guanidine nitrate
- (b-1) basic copper nitrate
- (b-2) sodium chlorate or potassium perchlorate

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- (a) aluminium hydroxide
- (d) sodium carboxymethylcellulose or guar gum

[0053] The gas generating composition of the present invention can be molded in a desired shape, for example a molded article in the shape of a single-perforated cylinder, a porous cylinder or a pellet.

[0054] The molded article can be manufactured by adding and mixing water or an organic solvent with a gas generating composition and subjecting the resultant mixture to an extrusion molding (a single-perforated or porous cylindrical-shaped molded article) or by subjecting the mixture to a compression molding with a tablet machine or the like (a pellet-shaped molded article). The single-perforated or porous cylindrical-shaped molded article may be either one having a through-hole in the long direction or one having no through-hole but a recess.

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[0055] The gas generating composition of the present invention and the molded article obtained therefrom can be applied to, for example, an airbag inflator for a driver seat, an airbag inflator for a passenger seat, a side-airbag inflator, an inflatable curtain inflator, a knee-bolster inflator, an inflatable seatbelt inflator, a tubular system inflator and a pretensioner gas generator in each of various kinds of vehicles.

[0056] The inflator using the gas generating composition of the present invention or the molded article obtained therefrom may be either of a pyro type in which gas is supplied only from the gas generating agent or a hybrid type in which the gas is supplied from both compression gas such as argon and the gas generating agent.

[0057] Furthermore, the gas generating composition of the present invention or the molded article obtained therefrom may be used as an igniting agent referred to as an enhancer agent (or a booster) for transferring energy from a percussion cap or a squib to the gas generating agent.

Examples

[0058] Hereinafter, the present invention will be described in more detail with reference to examples. However, the present invention is not limited to these examples.

Examples 1 to 18 and Comparative Examples 1 to 7

[0059] Gas generating compositions having compositions shown in Table 1 were prepared. A combustion temperature and a gas-generating efficiency (unit: mol / 100 g represents the number of moles of the generated gas per 100 g of the composition gas) were obtained on these compositions, based on theoretical calculation. The results are shown in Table 1.

Table 1

	composition (ratio: mass %)	burning velocity (k)	gas yield (mol/100g)
Com. Ex. 1	NQ/Sr(NO ₃) ₂ (56.9/43.1)	2647	2.96
Ex.1	NQ/Sr(NO ₃) ₂ /Al(OH) ₃ (54.1/40.9/5)	2502	2.90
Ex.2	NQ/Sr(NO ₃) ₂ /Al(OH) ₃ (51.3/38.7/10)	2341	2.84
Ex.3	NQ/Sr(NO ₃) ₂ /Al(OH) ₃ (48.6/36.4/15)	2279	2.80
Com. Ex. 2	NQ/BCN (51.3/48.7)	2270	2.87
Ex.4	NQ/BCN/Al(OH) ₃ (48.8/46.2/5)	2131	2.83
Ex.5	NQ/BCN/Al(OH) ₃ (46.4/43.6/10)	1991	2.78
Ex.6	NQ/BCN/Al(OH) ₃ (43.9/41.1/15)	1852	2.74
Com. Ex. 3	GN/BCN (53.4/46.6)	1911	3.01
Ex.7	GN/BCN/Al(OH) ₃ (52.8/42.2/5)	1619	3.04
Ex.8	GN/BCN/Al(OH) ₃ (50.2/39.8/10)	1527	2.99
Ex.9	GN/BCN/Al(OH) ₃ (47.5/37.5/15)	1419	2.94
Com. Ex. 4	melamine/BCN (20.8/79.2)	1503	2.14
Com. Ex.5	NQ/Sr(NO ₃) ₂ /CMCNa (38.4/52.2/9.4)	2494	2.65
Ex.10	NQ/Sr(NO ₃) ₂ /Al(OH) ₃ /CMCNa(35.7/49.9/5/9.4)	2328	2.60
Ex.11	NQ/Sr(NO ₃) ₂ /Al(OH) ₃ /CMCNa(32.9/47.7/10/9.4)	2252	2.55
Ex.12	NQ/Sr(NO ₃) ₂ /Al(OH) ₃ /CMCNa(30.2/45.4/15/9.4)	2104	2.49
Com. Ex. 6	NQ/BCN/guar gum (39.4/55.6/5)	2097	2.68
Ex. 13	NQ/BCN/Al(OH) ₃ /guar gum (37.0/53.0/5/5)	1950	2.64
Ex. 14	NQ/BCN/Al(OH) ₃ /guar gum(34.5/50.5/10/5)	1806	2.6
Ex. 15	NQ/BCN/Al(OH) ₃ /guar gum (32.0/48.0/15/5)	1663	2.55
Com. Ex. 7	GN/BCN/guar gum (42.7/52.3/5)	1678	2.86
Ex. 16	GN/BCN/Al(OH) ₃ /guar gum (40.0/50.0/5/5)	1564	2.80

(continued)

	composition (ratio: mass %)	burning velocity (k)	gas yield (mol/100g)
Ex. 17	GN/BCN/Al(OH) ₃ /guar gum (37.3/47.7/10/5)	1451	2.75
Ex. 18	GN/BCN/Al(OH) ₃ /guar gum (34.7/45.3/15/5)	1358	2.70

[0060] In Table 1, GN is guanidine nitrate, NQ is nitroguanidine, BCN is basic copper nitrate and CMCNa is sodium carboxymethylcellulose. The other tables are also shown in the same manner. The average particle size of basic copper nitrate of Table 1 is 4.7 μm (applied to the other tables) and the average particle size of aluminum hydroxide is 11 μm (applied to the other tables).

[0061] The combustion temperatures of the compositions of Examples 1 to 18, including added aluminum hydroxide, are lower than those of the corresponding Comparative Examples 1 to 7 containing no aluminum hydroxide.

Examples 19 to 24

[0062] Gas generating compositions having compositions shown in Table 2 were prepared. These compositions were tested by an explosive performance examination method of JIS K4810-1979 in term of friction sensitivity and drop hammer sensitivity. Results are shown in Table 2.

Table 2

	composition (ratio: mass %)	friction sensitivity (N)	drop hammer sensitivity (cm)
Ex. 19	NQ/Sr(NO ₃) ₂ /Al(OH) ₃ (51.3/38.7/10)	>353	60 ~ 70
Ex. 20	NQ/Sr(NO ₃) ₂ /Al(OH) ₃ /CMCNa (32.9/47.7/10/9.4)	>353	60~70
Ex. 21	/BCN/Al(OH) ₃ /CMCNa (16.7/70.3/10/3)	>353	>100
Ex. 22	GN/BCN/Al(OH) ₃ /guar gum (40.0/50.0/5/5)	>353	40~50
Ex. 23	GN/BCN/Al(OH) ₃ /CMCNa(41.3/48.7/5/5)	>353	40~50
Ex. 24	NQ/BCN/Al(OH) ₃ /guar gum (34.5/50.5/10/5)	>353	50~60

[0063] In Examples 19 to 24, the friction sensitivities are higher than 353 N and the drop hammer sensitivities are 40 cm or more. Therefore, the friction drop hammer sensitivities are so insufficient that a good safety can be attained at the time of handling.

Examples 25 to 33

[0064] Gas generating compositions having compositions shown in Table 3 were prepared. These compositions were molded in the shape of strand and were subjected to the measurements of burning velocity at a pressure of 4,900, 6, 860 or 8,820 kPa in nitrogen atmosphere. Burning velocity at 6,860 kPa and pressure index between 4,900 and 8,820 kPa are shown in Table 3. The pressure index was calculated from the following equation: $rb = \alpha P^n$ (wherein rb: burning velocity, α : coefficient, P: pressure, and n: pressure index).

Table 3

	composition (ratio: mass %)	burning velocity (mm/sec)	pressure index
Ex. 25	NQ/Sr(NO ₃) ₂ /Al(OH) ₃ /CMCNa (35.3/50.3/5.0/9.4)	11.20	0.52
Ex. 26	NQ/Sr(NO ₃) ₂ /Al(OH) ₃ /CMCNa (34.2/49.4/7.0/9.4)	10.35	0.62
Ex. 27	NQ/Sr(NO ₃) ₂ /Al(OH) ₃ /CMCNa (33.1 /48.5/9.0/9.4)	9.47	0.58
Ex. 28	NQ/BCN/Al(OH) ₃ /guar gum(37.0/53.0/5.0/5.0)	13.75	0.19
Ex. 29	NQ/BCN/Al(OH) ₃ /guar gum (34.5/50.5/10.0/5.0)	12.87	0.24
Ex. 30	NQ/BCN/Al(OH) ₃ /guar gum (32.2/55.8/5.0/7.0)	13.74	0.30
Ex. 31	NQ/BCN/Al(OH) ₃ /guar gum (29.8/53.2/10.0/5.0)	11.28	0.33

EP 1 538 137 B1

(continued)

	composition (ratio: mass %)	burning velocity (mm/sec)	pressure index
Ex. 32	GN/BCN/Al(OH) ₃ /CMCNa (41.3/48.7/5.0/5.0)	7.32	0.22
Ex. 33	GN/BCN/Al(OH) ₃ /guar gum(40.0/50.0/5.0/5.0)	7.33	0.27

[0065] As described above, each of the numeric values represented in Examples 25 to 33 shows that practical conditions for the inflator gas generating compositions are satisfied.

Examples 34 to 37

[0066] Gas generating compositions having compositions shown in Table 4 were prepared. These compositions were molded in the shape of 2 g of strand. Each of the strands was displaced in a closed gas bombé of one liter. Nitrogen gas was purged therein. The pressure was elevated up to 6,860 Pa with nitrogen and the strand was ignited by passage of an electric current through a nichrome wire to burn the strand completely. After approximately 20 seconds from the electrification, the combustion gas was sampled into a gas-sampling bag and was immediately analyzed in terms of concentrations of NO, NO₂, CO and CO₂.

Table 4

	composition (ratio: mass %)	yield of NO(ppm)	yield of NO ₂ (ppm)	yield of CO(ppm)	yield of CO ₂ (ppm)
Ex. 34	NQ/Sr(NO ₃) ₂ /Al(OH) ₃ /CMCNa (36.4/51.2/3/9.4)	23	0	420	2800
Ex. 35	NQ/Sr(NO ₃) ₂ /Al(OH) ₃ /CMCNa(33.1/48.5/9/9.4)	32	0	350	2600
Ex. 36	NQ/Sr(NO ₃) ₂ /Al(OH) ₃ /CMCNa (31.7/51.9/7/9.4)	45	0	70	2600
Ex. 37	NQ/Sr(NO ₃) ₂ /Al(OH) ₃ /CMCNa (33.7/49.9/7/9.4)	35	0	280	2800
ppm is based on weight					

Examples 38 to 49 and Comparative Examples 8 to 10

[0067] Gas generating compositions having compositions shown in Table 5 were prepared. A combustion temperature based on theoretical calculation and a gas yield (the unit of mol / 100 g represents the number of moles of the generated gas per 100 g of the composition) were obtained about the compositions. Results are shown in Table 5.

Table 5

	composition (ratio: mass %)	burning velocity (k)	gas yield (mol/100g)
Com. Ex. 8	NQ/Sr(NO ₃) ₂ (56.9/43.1)	2647	2.96
Com. Ex. 9	GN/BCN (53.4/46.6)	1911	3.01
Ex. 38	GN/BCN/Al(OH) ₃ /NH ₄ ClO ₄ (50.0/35.0/10/5)	1770	3.07
Ex. 39	GN/BCN/Al(OH) ₃ /KClO ₄ (51.09/33.91/10/5)	1756	3.02
Ex. 40	GN/BCN/Al(OH) ₃ /NaClO ₄ (51.63/33.37/10/5)	1749	3.14
Ex. 41	GN/BCN/Al(OH) ₃ /NaClO ₃ (50.99/34.01/10/5)	1756	3.01
Ex. 42	GN/BCN/Al(OH) ₃ /KClO ₃ (50.46/34.54/10/5)	1735	2.99
Ex. 43	GN/BCN/Al(OH) ₃ /NH ₄ ClO ₄ /CMCNa (38.4/41.6/10/5/5)	1694	2.85
Ex. 44	GN/BCN/Al(OH) ₃ /KClO ₄ /CMCNa (39.48/40.52/10/5/5)	1680	2.78

EP 1 538 137 B1

(continued)

	composition (ratio: mass %)	burning velocity (k)	gas yield (mol/100g)
Ex. 45	GN/BCN/Al(OH) ₃ /NaClO ₄ /CMCNa (39.03/43.47/10/2.5/5)	1645	2.77
Ex. 46	GN/BCN/Al(OH) ₃ /NaClO ₄ /CMCNa (40.03/39.97/10/5/5)	1714	2.80
Ex. 47	GN/BCN/Al(OH) ₃ /NaClO ₄ /CMCNa (41.02/36.48/10/7.5/5)	1778	2.83
Ex. 48	GN/BCN/Al(OH) ₃ /NaClO ₃ /CMCNa (38.86/41.14/10/5/5)	1695	2.77
Ex. 49	GN/BCN/Al(OH) ₃ /KClO ₃ /CMCNa (39.39/40.16/10/5/5)	1665	2.75
Com. Ex. 10	Melamine/BCN (20.8/79.2)	1503	2.14

[0068] The combustion temperatures of the compositions, with added aluminum hydroxide, of Examples 38 to 49 are lower than those of Comparative Examples 8 to 10 containing no aluminum hydroxide.

Examples 50 to 56

[0069] Gas generating compositions having compositions shown in Table 6 were prepared. These compositions were tested by an explosive performance examination method of JIS K4810-1979 in terms of friction sensitivity and drop hammer sensitivity. Results are shown in Table 6.

Table 6

	composition (ratio: mass %)	friction sensitivity (N)	drop hammer sensitivity (cm)
Ex. 50	GN/BCN/Al(OH) ₃ /NH ₄ ClO ₄ (50.0/35.0/10/5)	>353	>60
Ex. 51	GN/BCN/Al(OH) ₃ /NH ₄ ClO ₄ /CMCNa (38.40/41.60/10/5/5)	>353	>60
Ex. 52	GN/BCN/Al(OH) ₃ /KClO ₄ /CMCNa (39.48/40.52/10/5/5)	>353	>60
Ex. 53	GN/BCN/Al(OH) ₃ /NaClO ₄ /CMCNa (40.03/39.97/10/5/5)	>353	>60
Ex. 54	GN/BCN/Al(OH) ₃ /NaClO ₄ /CMCNa (41.02/36.48/10/7.5/5)	>353	>60
Ex. 55	GN/BCN/Al(OH) ₃ /NaClO ₃ /CMCNa (38.86/41.14/10/5/5)	>353	>60
Ex. 56	GN/BCN/Al(OH) ₃ /KClO ₃ /CMCNa (39.39/40.16/10/5/5)	>353	50-60

[0070] In Examples 50 to 56, the friction sensitivities are higher than 353 N and the drop hammer sensitivities are 50 cm or more. Therefore, the friction drop hammer sensitivities are so insufficient that a high safety can be attained at the time of handling.

Examples 57 to 61

[0071] Gas generating compositions having compositions shown in Table 7 were prepared. The compositions were molded in the shape of strand and subjected to measurements of burning velocity at pressure of 4,900, 6,860 or 8,820 kPa in a nitrogen atmosphere. Burning velocity at 6,860 kPa and pressure index between 4,900 and 8,820 kPa were shown in Table 7. The pressure index was calculated from the following equation: $rb = \alpha P^n$ (wherein rb : burning velocity, α : coefficient, P : pressure, and n : pressure index).

Table 7

	composition (ratio: mass %)	burning velocity (mm/sec)	pressure index
Ex. 57	GN/BCN/Al(OH) ₃ /KClO ₄ /CMCNa (39.48/40.52/10/5/5)	7.78	0.30
Ex. 58	GN/BCN/Al(OH) ₃ /NH ₄ ClO ₄ /CMCNa (38.40/41.60/10/5/5)	7.86	0.40
Ex. 59	GN/BCN/Al(OH) ₃ /NaClO ₄ /CMCNa (40.03/39.97/10/5/5)	8.12	0.28
Ex. 60	GN/BCN/Al(OH) ₃ /KClO ₃ /CMCNa (38.86/41.14/10/5/5)	7.56	0.27
Ex. 61	GN/BCN/Al(OH) ₃ /NaClO ₃ /CMCNa (39.39/40.16/10/5/5)	9.16	0.30

[0072] As described above, each of the numeric values represented in Examples 57 to 61 shows that practical conditions for the inflator gas generating compositions are satisfied. In addition, the burning velocity was increased by containing the component (d), compared with the burning velocity (7.32 mm/sec.) of Example 41 (GN/BCN/Al(OH)₃/CMCNa) in Table 3 containing no component (d).

[0073] The increase in burning velocity allows more selected methods of manufacturing the gas generating agent. For instance, the molded article of a gas generating composition is required to be thin so that the gas generating agent is completely combusted within a predetermined time when the burning velocity is small. Molding into pellets by a compression molding or the like, on the other hand, is involved in difficulty in tableting too thin pellets. A large burning velocity will solve such a problem in molding.

Examples 62 to 66

[0074] Gas generating compositions having compositions shown in Table 8 were prepared. The compositions were molded into 2 g of strand. Each of the strands was displaced in a closed gas bomb of one liter. Nitrogen gas was purged therein. The pressure was elevated up to 6,860 Pa with nitrogen and the strand was ignited by passage of an electric current through a nichrome wire to burn the strand completely. After approximately 20 seconds from the electrification, the combustion gas was sampled into a gas-sampling bag and was immediately analyzed in terms of concentrations of NO, NO₂, NH₃, CO, and CO₂. Results are shown in Table 8.

Table 8

	composition (ratio:mass %)	yield of NO(ppm)	yield of NO ₂ (ppm)	yield of NH ₃ (ppm)	yield of CO(ppm)	yield of CO ₂ (ppm)
Ex. 62	GN/BCN/Al(OH) ₃ /KClO ₄ /CMCNa (39.48/40.52/10/5/5)	7.5	0	7.5	220	3400
Ex. 63	GN/BCN/Al(OH) ₃ /NH ₄ ClO ₄ /CMCNa (38.40/41.60/10/5/5)	15	0	0	270	3500
Ex. 64	GN/BCN/Al(OH) ₃ /NaClO ₄ /CMCNa (40.03/39.97/10/5/5)	12	0	7	220	3500
Ex. 65	GN/BCN/Al(OH) ₃ /KClO ₃ /CMCNa (38.86/41.14/10/5/5)	19	0	17	290	3250
Ex. 66	GN/BCN/Al(OH) ₃ /NaClO ₃ /CMCNa (39.39/40.16/10/5/5)	13	0	7	215	3100
ppm is based on mass						

Claims

1. A gas generating composition comprising the following components (a), (b) and (c) and optionally the component (d) and/or the component (e):

(a) 10 to 60% by mass of an organic compound as fuel, wherein the organic compound is at least one selected from guanidine compounds,

- (b) 10 to 85% by mass of at least one oxidizing agent selected from the group consisting of (b-1) basic metal nitrates, nitrates and ammonium nitrate and (b-2) perchlorates and chlorates,
 (c) 0.1 to 20% by mass of aluminum hydroxide with an average particle size of from 2 to 30 μm ,
 (d) 20% by mass or less of a binder
 (e) 20% by mass or less of an additive selected from metal oxides and metal carbides.

2. The gas generating composition as set forth in claim 1, wherein the basic metal nitrate (b) is at least one selected from the group consisting of a basic copper nitrate, a basic cobalt nitrate, a basic zinc nitrate, a basic manganese nitrate, a basic iron nitrate, a basic molybdenum nitrate, a basic bismuth nitrate and a basic cerium nitrate.
3. The gas generating composition as set forth in claim 1 or 2, wherein the perchlorate and chlorate (b-2) is at least one selected from the group consisting of ammonium perchlorate, potassium perchlorate, sodium perchlorate, potassium chlorate and sodium chlorate.
4. The gas generating composition as set forth in any one of claims 1 to 3, wherein the binder of the component (d) is at least one selected from the group consisting of carboxymethylcellulose, sodium carboxymethylcellulose, potassium carboxymethylcellulose, ammonium carboxymethylcellulose, cellulose acetate, cellulose acetate butyrate, methylcellulose, ethylcellulose, hydroxyethylcellulose, ethylhydroxyethylcellulose, hydroxypropylcellulose, carboxymethylethylcellulose, micro-crystalline cellulose, polyacrylamide, aminated products of polyacrylamide, polyacrylhydrazide, a copolymer of acrylamide and a metal salt acrylate, a copolymer of polyacrylamide and a polyacrylic ester, polyvinyl alcohol, acrylic rubber, guar gum, starch and silicone.
5. The gas generating composition as set forth in any one of claims 1 to 4, wherein the additive of the component (e) is at least one selected from the group consisting of metal oxides including copper (II) oxide, iron oxide, zinc oxide, cobalt oxide, manganese oxide, molybdenum oxide, nickel oxide, bismuth oxide, silica or alumina; metal hydroxides including cobalt hydroxide or iron hydroxides; metallic carbonate or basic metallic carbonate including cobalt carbonate, calcium carbonate, basic zinc carbonates or basic copper carbonates; composite compounds of metal oxides or hydroxides including acid clay, kaolin, talc, bentonite, diatomaceous earth, or hydrotalcite; metallic acid salts including sodium silicate, mica molybdate, cobalt molybdate or ammonium molybdate; silicone; molybdenum disulfide; calcium stearate; silicon nitride and silicon carbide.
6. A molded article of a gas generating composition having a single-perforated cylindrical shape, a porous cylindrical shape or a pellet shape, the molded article being obtained from the gas generating composition as set forth in any one of claims 1 to 5.
7. An airbag inflator using the gas generating composition as set forth in any one of claims 1 to 5 or the molded article of a gas generating composition as set forth in claim 6.

Patentansprüche

1. Gaserzeugende Zusammensetzung umfassend die folgenden Komponenten (a), (b) und (c) und gegebenenfalls die Komponente (d) und/oder die Komponente (e):
 - (a) 10 bis 60 Massen-% einer organischen Verbindung als Treibstoff, wobei die organische Verbindung wenigstens eine ausgewählt aus Guanidinverbindungen ist,
 - (b) 10 bis 85 Massen-% von wenigstens einem Oxidationsmittel, ausgewählt aus der Gruppe, bestehend aus (b-1) basischen Metallnitraten, Nitraten und Ammoniumnitrat und (b-2) Perchloraten und Chloraten,
 - (c) 0,1 bis 20 Massen-% Aluminiumhydroxid mit einer mittleren Teilchengröße von 2 bis 30 μm ,
 - (d) 20 Massen-% oder weniger von einem Bindemittel
 - (e) 20 Massen-% oder weniger von einem Additiv ausgewählt aus Metalloxiden und Metallcarbiden.
2. Gaserzeugende Zusammensetzung nach Anspruch 1, wobei das basische Metallnitrat (b) wenigstens eines, ausgewählt aus der Gruppe bestehend aus einem basischen Kupfernitrat, einem basischen Cobaltnitrat, einem basischen Zinknitrat, einem basischen Mangannitrat, einem basischen Eisennitrat, einem basischen Molybdännitrat, einem basischen Bismutnitrat und einem basischen Cernitrat, ist.
3. Gaserzeugende Zusammensetzung nach Anspruch 1 oder 2, wobei das Perchlorat und Chlorat (b-2) wenigstens

eines, ausgewählt aus der Gruppe bestehend aus Ammoniumperchlorat, Kaliumperchlorat, Natriumperchlorat, Kaliumchlorat und Natriumchlorat, ist.

4. Gaserzeugende Zusammensetzung nach einem der Ansprüche 1 bis 3, wobei das Bindemittel der Komponente (d) wenigstens eines, ausgewählt aus der Gruppe bestehend aus Carboxymethylcellulose, Natriumcarboxymethylcellulose, Kaliumcarboxymethylcellulose, Ammoniumcarboxymethylcellulose, Celluloseacetat, Celluloseacetatbutyrat, Methylcellulose, Ethylcellulose, Hydroxyethylcellulose, Ethylhydroxyethylcellulose, Hydroxypropylcellulose, Carboxymethylethylcellulose, mikrokristalliner Cellulose, Polyacrylamid, aminierten Produkten von Polyacrylamid, Polyacrylhydrazid, einem Copolymer von Acrylamid und einem Metallsalzacrylat, einem Copolymer von Polyacrylamid und einem Polyacrylester, Polyvinylalkohol, Acrylkautschuk, Guargummi, Stärke und Silicon, ist.
5. Gaserzeugende Zusammensetzung nach einem der Ansprüche 1 bis 4, wobei das Additiv der Komponente (e) wenigstens eines, ausgewählt aus der Gruppe bestehend aus Metaloxiden, einschließlich Kupfer(II)-oxid, Eisenoxid, Zinkoxid, Cobaltoxid, Manganoxid, Molybdänoxid, Nickeloxid, Bismutoxid, Siliciumdioxid oder Aluminiumoxid; Metallhydroxiden einschließlich Cobalhydroxid oder Eisenhydroxiden; Metallcarbonat oder basischem Metallcarbonat einschließlich Cobaltcarbonat, Calciumcarbonat, basischen Zinkcarbonaten oder basischen Kupfercarbonaten; Verbundverbindungen von Metalloxiden oder Hydroxiden einschließlich säureaktivierte Tonerde, Kaolin, Talk, Bentonit, Diatomeenerde oder Hydrotalcit; Metallsäuresalzen einschließlich Natriumsilicat, Glimmermolybdat, Cobaltmolybdat oder Ammoniummolybdat; Silicon, Molybdändisulfid; Calciumstearat; Siliciumnitrid und Siliciumcarbid, ist.
6. Formartikel aus einer gaserzeugenden Zusammensetzung mit einer einfach perforierten zylindrischen Form, einer porösen zylindrischen Form oder einer Pelletform, wobei der Formartikel aus der gaserzeugenden Zusammensetzung nach einem der Ansprüche 1 bis 5 erhalten wird.
7. Airbag-Gasgenerator, der die gaserzeugende Zusammensetzung nach einem der Ansprüche 1 bis 5 oder den Formartikel aus einer gaserzeugenden Zusammensetzung nach Anspruch 6 verwendet.

Revendications

1. Composition de génération de gaz comprenant les composants suivants (a), (b) et (c) et éventuellement le composant (e) :
 - (a) de 10 à 60 % en masse d'un composé organique comme carburant, où le composant organique est au moins l'un sélectionné parmi les composés guanidine,
 - (b) de 10 à 85 % en masse d'au moins un agent oxydant sélectionné dans le groupe constitué de (b-1) des nitrates métalliques basiques, des nitrates et du nitrate d'ammonium et (b-2) des perchlorates et des chlorates,
 - (c) de 0,1 à 20 % en masse d'hydroxyde d'aluminium avec une taille moyenne de particule allant de 2 à 30 μm ,
 - (d) 20 % en masse ou moins d'un agent liant
 - (e) 20 % en masse ou moins d'un additif sélectionné parmi les oxydes métalliques et les carbures de métaux.
2. Composition de génération de gaz telle qu'énoncée selon la revendication 1, où le nitrate métallique basique (b) est au moins l'un sélectionné dans le groupe constitué d'un nitrate de cuivre basique, d'un nitrate de cobalt basique, d'un nitrate de zinc basique, d'un nitrate de manganèse basique, d'un nitrate de fer basique, d'un nitrate de molybdène basique, d'un nitrate de bismuth basique et d'un nitrate de cérium basique.
3. Composition de génération de gaz telle qu'énoncée selon la revendication 1 ou 2, où le perchlorate et le chlorate (b-2) sont au moins l'un sélectionné dans le groupe constitué du perchlorate d'ammonium, du perchlorate de potassium, du perchlorate de sodium, du chlorate de potassium et du chlorate de sodium.
4. Composition de génération de gaz telle qu'énoncée selon l'une quelconque des revendications 1 à 3, où le liant du composant (d) est au moins l'un sélectionné parmi la carboxyméthylcellulose, la carboxyméthylcellulose sodique, la carboxyméthylcellulose de potassium, la carboxyméthylcellulose d'ammonium, l'acétate de cellulose, l'acétate butyrate de cellulose, la méthylcellulose, l'éthylcellulose, l'hydroxyéthylcellulose, l'éthylhydroxyéthylcellulose, l'hydroxypropylcellulose, la carboxyméthyléthylcellulose, la cellulose microcristalline, le polyacrylamide, les produits aminés du polyacrylamide, le polyacrylhydrazide, un copolymère d'acrylamide et un sel métallique d'acrylate, un copolymère de polyacrylamide et un ester de polyacrylique, un poly(alcool de vinyle), un caoutchouc d'acrylique, de la gomme de guar, de l'amidon et du silicone.

5. Composition de génération de gaz telle qu'énoncée selon l'une quelconque des revendications 1 à 4, où l'additif du composant (e) est au moins l'un sélectionné dans le groupe constitué des oxydes métalliques incluant l'oxyde de cuivre(II), l'oxyde de fer, l'oxyde de zinc, l'oxyde de cobalt, l'oxyde de manganèse, l'oxyde de molybdène, l'oxyde de nickel, l'oxyde de bismuth, la silice ou l'alumine ; les hydroxydes métalliques incluant l'hydroxyde de cobalt ou les hydroxydes de fer ; le carbonate métallique ou le carbonate métallique basique incluant le carbonate de cobalt, le carbonate de calcium, les carbonates de zinc basiques ou les carbonates de cuivre basiques ; les composés composites d'oxydes ou d'hydroxydes de métaux incluant l'argile acide, le kaolin, le talc, la bentonite, la terre de diatomées, ou l'hydrotalcite ; les sels d'acide métallique incluant le silicate de sodium, le molybdate de mica, le molybdate de cobalt ou le molybdate d'ammonium ; le silicone ; le disulfure de molybdène ; le stéarate de calcium ; le nitrure de silicium et le carbure de silicium.
6. Article moulé d'une composition de génération de gaz ayant une forme cylindrique à perforation unique, une forme cylindrique poreuse ou une forme de pastille, l'article moulé étant obtenu à partir de la composition de génération de gaz telle qu'exposée selon l'une quelconque des revendications 1 à 5.
7. Dispositif de gonflage d'un coussin de sécurité utilisant la composition de génération de gaz telle qu'énoncée selon l'une quelconque des revendications 1 à 5 ou article moulé d'une composition de génération de gaz tel qu'énoncé selon la revendication 6.

REFERENCES CITED IN THE DESCRIPTION

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