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(54) **Gas generating composition**

(57) To provide a gas generating composition with a good ignition property and combustibility and generating suppressed amounts of toxic gases such as NO_x and ammonia at the time of combustion, the gas generating composition comprises (A) a nitrogen-containing compound as fuel, (B) a basic metal nitrate and (C) a

chloric acid compound as oxidizing agents, the chloric acid compound (C) is (C-1) a perchloric acid salt and/or (C-2) a chloric acid salt and the content of the component (C) is less than 5% by mass in the total oxidizing agents.

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Description

Technical Field of the Invention

[0001] The invention relates to a gas generating composition to be used for a gas generator for an air bag.

Prior arts

[0002] A gas generating composition comprises fuel, an oxidizing agent and a variety of additives to be added based on the necessity, and the composition is required to satisfy that the gas generated by combustion is clean, in other words, the gas contains no nitrogen oxide (NOx), CO, or the like.

[0003] It has been known that basic copper nitrate (BCN) known as an oxidizing agent decreases the combustion temperature. because of low combustion heat generation and suppresses the production amount of NOx and thus has an effect to clean the discharged gas, and it also has an effect to improve the ignition and the combustion properties and therefore, it has been used widely as an oxidizing agent.

[0004] However, if the content of BCN as an oxidizing agent is too high, it results in a problem that the generation amounts of NOx and ammonia are adversely increased.

[0005] A chloric acid compound also well-known as an oxidizing agent causes NOx removal reaction and becomes a supply source of oxygen required to decompose NOx into nitrogen and water, and therefore it has been used widely.

[0006] However, if the content of the chloric acid compound as an oxidizing agent is too much, the supply of oxygen so exceeds as to rather increase the generation amounts of NOx and mist.

[0007] In EP-B No. 1, 006, 096 and US-A1 No. 2003/0145921, BCN is used as an oxidizing agent to decrease the combustion temperature and accordingly the discharged gas is cleaned and a satisfactory burning rate is obtained. However, in EP-B No. 1,006,096 and US-A1 No. 2003/0145921, the use ratio of the perchloric acid salt to BCN is high and the supply of oxygen becomes excess, so that, the generation amounts of NOx and mist are unsatisfactorily increased.

[0008] In US-B No. 5, 608, 183, as described in EP-B No. 1, 006, 096, neither sufficient ignition property nor burning rate can be obtained. Further, normally in this system, so much BCN is contained that the cleanness level of the discharged gas is low.

Summary of the Invention

[0009] A purpose of the invention is to provide a gas generating composition with a good ignition property and combustibility and generating suppressed amounts of toxic gases such as NOx and ammonia at the time of combustion.

[0010] As a means for solving the above-mentioned problems, the invention provides a gas generating composition comprising (A) a nitrogen-containing compound as fuel and (B) a basic metal nitrate and (C) a chloric acid compound as oxidizing agents, the chloric acid compound (C) being selected from (C-1) a perchloric acid salt and (C-2) a chloric acid salt, the content of the component (C) being less than 5% by mass in the total oxidizing agents.

Detailed explanation of the invention

[0011] The composition of the invention has a good ignition property and combustibility (a high burning rate) and can decrease the generation amounts of NOx and ammonia gas at the time of combustion, so that the amounts of NOx and ammonia to be contained in the combustion gas can be suppressed.

[0012] Therefore, if the composition of the invention is applied to a gas generator for an air bag, a necessary amount of a gas for expansion can be generated within a time to reliably protect a passenger and at the same time, the toxic gas amount can remarkably be suppressed in the gas for expanding the air bag and thus, the safety can be enhanced.

[0013] The fuel to be used in the invention contains a nitrogen-containing compound as the component (A), and as the nitrogen-containing compound, at least one selected from tetrazole compounds, guanidine compounds, triazine compounds and nitroamine compounds. In addition, other than the nitrogen-containing compound, known fuel may be contained and in such a case, the ratio of the nitrogen-containing compound in the fuel is preferably 20% or more by mass.

As the tetrazoles, 5-aminotetrazole and bitetrazole ammonium are preferable. As the guanidines, guanidine nitric acid salt (nitric acid guanidine), aminoguanidine nitric acid salt, nitroguanidine, and triaminoguanidine nitric acid salt are preferable. As triazines, melamine, cyanuric acid, ammeline, ammelide, and ammeland are preferable. As nitroamines, cyclo-1,3,5-trimethine-2,4,6-trinitramine is preferable. Among them, guanidine nitric acid salt is particularly preferable.

[0014] The content of the component (A) is preferably 15 to 50% by mass, more preferably 20 to 55% by mass, and even more preferably 25 to 50% by mass.

[0015] The oxidizing agent to be used in the invention includes the basic metal nitrate (B) , the chloric acid compound (C) , and additionally other oxidizing agents to be used based on the necessity.

[0016] An example of the basic metal nitrate of the component (B) can be at least one of the compounds selected from basic copper nitrate, basic cobalt nitrate, basic zinc nitrate, basic manganese nitrate, basic iron nitrate, basic molybdenum nitrate, basic bismuth nitrate, and basic cerium nitrate.

[0017] To increase the burning rate, the basic metal nitrate is preferable to have the average particle diameter of 30 μm or smaller, more preferably 10 μm or smaller. The average particle diameter is measured according to a particle size distribution method using laser scattered beam. The measurement sample is prepared by dispersing the basic metal nitrate in water and radiating ultrasonic wave for 3 minutes, and 50% cumulative values (D_{50}) of the particles are calculated and the average of the values measured twice is employed as the average particle diameter.

[0018] The chloric acid compound of the component (C) is a component having an oxidizing function and a combustion promoting function. The oxidizing function means to generate oxygen during the combustion and accordingly to efficiently promote combustion as well as to suppress the production amount of the toxic gases such as NOx, ammonia, carbon monoxide and the like. On the other hand, the combustion promoting function means to improve the ignition property of the gas generating composition or to improve the burning rate (enhancing the combustibility).

[0019] The chloric acid compound of the component (C) may include the perchloric acid salt (C-1) and/or the chloric acid salt (C-2).

[0020] The perchloric acid salt of the component (C-1) may include ammonium perchlorate, potassium perchlorate, and sodium perchlorate. The chloric acid salt of the component (C-2) may include chloric acid, potassium chlorate, and sodium chlorate, and among them, sodium perchlorate is particularly preferable.

[0021] The chloric acid compound of the component (C) is preferable to have the average particle diameter of 1 to 500 μm , more preferably 2 to 50 μm . The measurement method of the average particle diameter is the same as that of the average particle diameter of the component (B).

[0022] The total content of the oxidizing agents of the component (B) and component (C) is preferably 30 to 70% by mass, more preferably 35 to 60% by mass, and even more preferably 40 to 55% by mass in the gas generating composition.

[0023] The content of the component (C) in the total oxidizing agent is less than 5% by mass, preferably 1 to 5% by mass, and even more preferably 2 to 5% by mass. If the content of the component (C) is less than 5% by mass, the combustion temperature can be lowered.

[0024] The mass ratio (B)/(C) of the basic copper nitrate (B) and the chloric acid compound (C) in the oxidizing agents is preferably in the range of 3 to 70, more preferably 3 to 25, furthermore preferably 5 to 25, still more preferably 7 to 20, and most preferably 5 to 20.

[0025] If the mass ratio (B)/(C) is in the above ranges, the ignition property of the composition is improved and the combustibility (the burning rate) is also improved and at the same time, the production amounts of NOx and ammonia are suppressed at the time of the combustion and therefore, the combustion gas is clean.

[0026] When known oxidizing agents other than the components (B) and (C) are contained, the content of the basic copper nitrate (B) in the total oxidizing agents is 50% by mass or more, preferably 60% by mass or more, and still preferably 70% by mass or more. If the content of component (B) is in the above range, the ignition property of the composition is improved and the combustibility (the burning rate) is also improved.

[0027] The composition of the invention may further contain the component (D) of a metal hydroxide, a hydrated metal oxide, or a combination thereof as a coolant. The coolant has a function for lowering the combustion temperature. The component (D) greatly absorbs heat when it is thermally decomposed and produced an oxide and water. Therefore, addition of the component (D) is effective to decrease the combustion temperature of the composition and suppress the production amounts of toxic NOx and carbon monoxide.

[0028] An example of the metal hydroxide of the component (D) can be magnesium hydroxide, aluminum hydroxide, calcium hydroxide, zirconium hydroxide, cobalt hydroxide and copper hydroxide, and an example of the hydrated metal oxide can be hydrated aluminum oxide.

[0029] By adjusting an average particle diameter, the component (D) can improve the entire dispersibility when the components (A) to (C) are mixed, so that the mixing work is made easy and the ignition property of the obtained composition can be improved.

[0030] The average particle diameter of the component (D) is preferably 0.1 to 70 μm , more preferably 0.5 to 50 μm , and even more preferably 2 to 30 μm . The measurement method of the average particle diameter is the same measurement method of the average particle diameter of the component (B).

[0031] The content of the component (D) in the gas generating composition is preferably 1 to 15% by mass, more preferably 3 to 12% by mass, and even more preferably 5 to 10% by mass.

[0032] If necessary, the composition of the invention may contain a binder. The binder is a component to be used together with the components (A) to (C) based on the necessity and is a component to improve the formability of the composition and increase the strength of a molded article of the gas generating agent. If the strength of a molded

article of the gas generating agent is insufficient, it may occur that the molded article breaks at the time of actual combustion and is burned too intensely to control the combustion.

[0033] The binder may be at least one compound selected from carboxymethyl cellulose, carboxymethyl cellulose sodium salt, carboxymethyl cellulose potassium salt, carboxymethyl cellulose ammonium salt, cellulose acetate, cellulose acetate butyrate, methyl cellulose, ethyl cellulose, hydroxyethyl cellulose, ethyl hydroxyethyl cellulose, hydroxypropyl cellulose, carboxymethyl ethyl cellulose, microcrystalline cellulose, polyacrylamide, amino compounds of polyacrylamide, polyacrylhydrazine, acrylamide-metal acrylate copolymer, polyacrylamide-poly(acrylic acid ester) copolymer, polyvinyl alcohol, acrylic rubber, guar gum, starch, and silicone.

[0034] The content of the binder is preferably not more than 10 part by mass to 100 part by mass of the total of the components (A) to (C).

[0035] The composition of the invention may further contain an additive selected from metal oxides and metal carbonates, based on the necessity. The additive may be added for the purpose to assist the function of the component (D), that is, to decrease the combustion temperature of the composition, adjust the burning rate and suppress the production amounts of the toxic nitrogen oxide and carbon monoxide after combustion.

[0036] The additive may be 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; complex compounds of metal oxides or hydroxides such as Japanese acid clay, kaolin, talc, bentonite, diatomaceous earth or hydrotalcite; metal acid salts such as sodium silicate, mica molybdenic acid salt, cobalt molybdate or ammonium molybdate; molybdenum disulfide, calcium stearate, silicon nitride, and silicon carbide.

[0037] The content of the additives is preferably not more than 10 part by mass to 100 part by mass of the total of the components (A) to (C).

[0038] The composition of the invention is preferable to have an oxygen balance in the range of -0.02 g/g to +0.02 g/g, more preferably -0.01 g/g to +0.01 g/g, and still more preferably -0.006 g/g to +0.006 g/g. The oxygen balance is the mass (expressed as +) of oxygen produced in the case of complete combustion of 1 gram of the gas generating composition or the mass (expressed as -) of oxygen needed in the case of complete combustion and can be calculated by adding up products of the oxygen balances and the contents (% by mass) of the respective components of the gas generating composition.

[0039] If the oxygen balance is in the above range, the production amounts of NO_x and ammonia can be decreased, so that the combustion gas becomes clean.

[0040] The composition of the invention can be molded into a desired shape, and it may be molded into a single-perforated cylinder, a perforated (porous) cylinder or a pellet.

[0041] These molded articles can be produced by an extrusion-molding method (for a single-perforated cylinder and a perforated (porous) cylinder) comprising the steps of adding water or an organic solvent to the composition and extruding the mixture, or by a compression-molding method (for a pellet) comprising the steps of compressing the above mixture using a pelletizer. The single-perforated cylinder and the perforated (porous) cylinder may have either of a longitudinal through-hole or a hollow without penetrating.

[0042] The composition of the invention and molded articles obtained therefrom may be used for an inflator for a driver side, an inflator for a passenger side next to a driver seat, an inflator for a side air bag, an inflator for an inflatable curtain, an inflator for a knee bolster, an inflator for an inflatable seat belt, an inflator for a tubular system and an inflator for a pretensioner of a variety of vehicles.

[0043] The inflators using the composition of the invention and the molded article obtained from the composition may be a pyrotechnic type in which the gas is supplied only from gas generating agent or a hybrid type in which both of compressed gas such as argon and gas from the gas generating agent are supplied.

[0044] The composition of the invention and the molded article obtained from the composition may be used as an igniting agent, so-called an enhancer (or a booster), for transmitting the energy of a detonator or a squib to the gas generating agent.

Examples

Examples 1 and 2 and Comparative Examples 1 to 3

[0045] The gas generating compositions shown in Table 1 were produced. Their oxygen balances, the combustion temperatures based on the theoretical calculation, and gas outputs (the unit, mol/100 g, means the mole number of the generated gas per 100 g of each composition) were measured. The results are shown in Table 1.

Table 1

	Composition (composition ratio: % by mass)	Oxygen balance (g/g)	Combustion temperature (K)	Gas generation efficiency (mol/100 g)
Comparative Example 1	NQ/Sr(NO ₃) ₂ (56.9/43.1)	0	2647	2.96
Comparative Example 2	GN/BCN (53.4/46.6)	0	1911	3.01
Comparative Example 3	GN/BCN/KClO ₄ (56.26/33.74/10)	0	2173	3.38
Example 1	GN/BCN/CMCNa/ KClO ₄ (44.1/48.4/5/2.5)	-0.009	1844	2.88
Example 2	GN/BCN/CMCNa/ NaClO ₄ (44.37/48.13/5/2.5)	-0.009	1856	2.89

[0046] In Table 1, NQ stands for nitroguanidine, GN stands for guanidine nitric acid, BCN stands for basic copper nitrate, and CMCNa stands for carboxymethyl cellulose sodium salt. They are similarly shown in the other tables.

[0047] The combustion temperatures of Examples 1 and 2 are lower than those of corresponding Comparative Examples 1 to 3.

Examples 3 and 4

[0048] The gas generating compositions shown in Table 2 were produced. The friction sensitivity test and drop hammer sensitivity test with respect to the compositions were conducted according to the explosive performance test method of JIS K4810-1979. The results are shown in Table 2.

Table 2

	Composition (composition ratio: % by mass)	Friction sensitivity (N)	Drop hammer sensitivity (cm)
Example 3	GN/BCN/CMCNa/KClO ₄ (44.1/48.4/5/2.5)	>353	>600
Example 4	GN/BCN/CMCNa/NaClO ₄ (44.37/48.13/5/2.5)	>353	>60

[0049] The compositions of Examples 3 and 4 were found having the friction sensitivity exceeding 353 N and the drop hammer sensitivity exceeding 60 cm, and they are insensitive in the friction sensitivity and the drop hammer sensitivity, and thus they have high handling safety.

Example 5

[0050] 1,888.5 g of guanidine nitric acid salt, 2,269 g of basic copper nitrate, 500 g of aluminum hydroxide, 250 g of CMCNa, 100 g of sodium perchlorate, and 700 g of water were loaded to a mixer and mixed all together. The mixture was extruded by an extruder, cut, and dried to obtain a single hole type gas generating composition having the outer diameter of 4.25 mm, the inner diameter of 1.10 mm, and the length of 4.08 mm. 40.3 g of the gas generating composition was air-tightly sealed in a chamber having the inner diameter of 57 mm and the height of 32 mm to produce an inflator for a test.

[0051] Using the inflator, a well-known 60-liter tank test (e.g. disclosed in column 22 of JP-A No. 2001-97176) and a discharged gas test of a 2800-liter tank were carried out. The 2800-liter tank test was carried out by setting the inflator in a tank made of an iron and having a capacity of 2,800 liters; igniting the inflator; measuring the concentrations of NO, NO₂, CO and NH₃ in the tank after 3 minutes, 15 minutes, and 30 minutes from the ignition; and determining the average values of the respective moments as the respective gas concentrations.

[0052] As a result, in the 60-liter tank test, the inner pressure of the inflator was 16.8 MPa and the tank pressure was 185.2 KPa and these values were satisfying the conditions for practical use. The result of the 2800-liter tank test

is shown in Table 3.

Table 3

	NO ₂	NO	CO	NH ₃
Discharged gas concentration (ppm: on the basis of mole number)	0	7	70	8.5

[0053] The concentrations of NO, NO₂, CO, and NH₃ shown in Table 3 were found extremely low, and thus it was confirmed that the safety to a passenger is high when the gas generating composition is burned to expand an air bag.

Claims

1. A gas generating composition comprising (A) a nitrogen-containing compound as fuel and (B) a basic metal nitrate and (C) a chloric acid compound as oxidizing agents, the chloric acid compound (C) being at least one selected from group consisting of (C-1) a perchloric acid salt and (C-2) a chloric acid salt, the content of the component (C) being less than 5% by mass in the total oxidizing agents.
2. The gas generating composition as claimed in claim 1, wherein the component (B) is a basic copper nitrate and the perchloric acid salt (C-1) is sodium perchlorate or potassium perchlorate and the chloric acid salt (C-2) is sodium chlorate or potassium chlorate.
3. The gas generating composition as claimed in claim 1 or 2, wherein the average particle diameter of the chloric acid compound (C) is 1 to 500 μm .
4. The gas generating composition as claimed in any one of claims 1 to 3, further comprising (D) a metal hydroxide, a hydrate of a metal oxide or a combination thereof.
5. The gas generating composition as claimed in claim 4, wherein the metal hydroxide (D) is magnesium hydroxide.
6. The gas generating composition as claimed in any one of claims 1 to 5, having an oxygen balance in the range of -0.02 g/g to +0.02 g/g.



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EUROPEAN SEARCH REPORT

Application Number
EP 04 02 4216

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Place of search The Hague		Date of completion of the search 6 December 2004	Examiner Schut, R
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EUROPEAN SEARCH REPORT

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**ANNEX TO THE EUROPEAN SEARCH REPORT
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