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(54) AZIDE-FREE, GAS-GENERATING COMPOSITION

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(57) ABSTRACT

The present invention relates to an azide-free gas-generating composition, in particular for use in safety devices for motor vehicles, comprising a fuel in a proportion of 20 to 60% by weight and consisting of one or more components, and an oxidizer mixture in a proportion of 40 to 80% by weight and consisting of at least three components, each in relation to the total composition. In accordance with the invention, the fuel consists of a guanidine compound in a proportion of at least 95% by weight and a further fuel component in a proportion of 0 to less than 5% by weight, each in relation to the fuel, and the oxidizer mixture consists of one or more transition metal oxides in a proportion of 20 to 80% by weight, basic copper nitrate in a proportion of 0 to 50% by weight, metal chlorate, metal perchlorate, ammonium perchlorate or mixtures thereof in a proportion of 1 to 15% by weight and alkali metal nitrate, alkaline earth metal nitrate or mixtures thereof in a proportion of 1 to 15% by weight, each in relation to the oxidizer mixture.

AZIDE-FREE, GAS-GENERATING COMPOSITION

[0001] The present invention relates to an azide-free, gas-generating composition, in particular for use in safety devices for motor vehicles.

BACKGROUND OF THE INVENTION

[0002] Gas-generating compositions which are used in safety devices for motor vehicles generally consist of a fuel based on sodium azide and an oxidation agent. Owing to the toxicity of sodium azide, however, a search for alternatives to the gas-generating mixtures containing azide was already begun early on.

[0003] The U.S. Pat. No. 5,608,183 describes a gas-generating mixture which contains between approximately 30 and 85% by weight of a fuel and between approximately 15 and approximately 70% by weight of an oxidation agent. At least 60% by weight of the fuel consists of the nitrate salt of an acidic polyamine or of a C_2-C_3-alkyl diamine, such as for example the nitrate salts of urea, guanidine, aminoguanidine, diaminoguanidine, semicarbazide, ethylene diamine, 1,3-propane diamine or 1,2-propane diamine, or mixtures thereof. The oxidation agent comprises at least 60% by weight basic copper nitrate and/or cobalt triamine tri-nitrate. The processing of the mixtures takes place in a wet process.

[0004] The gas-generating mixture known from the U.S. Pat. No. 5,608,183 has an insufficient readiness to ignite and also a combustion rate which is too low. Owing to the high proportion of basic copper nitrate, in addition an increased proportion of toxic gases is to be found in the released gas mixture. The processing of the mixture in a wet process requires additional drying stages and is therefore cost-intensive.

[0005] The German Utility Model No. 298 06 504 provides a gas-generating composition which comprises a fuel mixture consisting of at least two components, in a proportion of 20 to 60% by weight and an oxidizer mixture consisting of at least three components in a proportion of 40 to 80% by weight, each in relation to the total composition. The fuel mixture of the known composition is composed of 5 to 95% by weight of a guanidine compound, 5 to 95% by weight of a heterocyclic organic acid, for example cyanuric acid, and 0 to 20% by weight of further fuels. The oxidizer mixture of the known composition consists of one or more transition metal oxides in a proportion of 20 to 70% by weight and 10 to 50% by weight basic copper nitrate and 2 to 30% by weight metal chlorate, metal perchlorate, ammonium perchlorate, alkali metal nitrate, alkaline earth metal nitrate or mixtures thereof.

[0006] The use of an additional fuel, such as cyanuric acid for example, in a proportion of more than 5%, however, results in a distinctly reduced combustion rate of the composition. The composition is therefore unsuitable for use in gas generators for the driver's side, in which owing to the shorter distance between the vehicle occupant and the vehicle components, high combustion rates are preferred. As the additionally used fuels have a lower oxygen balance than guanidine nitrate, in addition a higher proportion of oxidizer must be used to balance out the mixture and to achieve an optimally reduced emission of harmful gas. The higher oxidizer proportion, however, leads to an increased proportion of solid matter in the gas mixture and hence to an increased particle output.

[0007] A need therefore continues to exist for improved azide-free, gas-generating compositions for use in safety devices for motor vehicles, with which a high combustion rate can be achieved with, at the same time, a low particle output.

SUMMARY OF THE INVENTION

[0008] The present invention provides such a composition, which comprises a fuel in a proportion of 20 to 60% by weight and consisting of one or more components, and an oxidizer mixture in a proportion of 40 to 80% by weight and consisting of at least three components, each in relation to the total composition. The composition is characterized in that the fuel consists of a guanidine compound in a proportion of at least 95% by weight and of a further fuel component in a proportion of 0 to less than 5% by weight, each in relation to the fuel. In addition, the oxidizer mixture consists of one or more transition metal oxides in a proportion of 20 to 80% by weight, basic copper nitrate in a proportion of 0 to 50% by weight, metal chlorate, metal perchlorate, ammonium perchlorate or mixtures thereof in a proportion of 1 to 15% by weight and alkali nitrate, alkaline earth nitrate or mixtures thereof in a proportion of 1 to 15% by weight, each in relation to the oxidizer mixture.

[0009] Preferably guanidine carbonate, guanidine nitrate, guanidine perchlorate, aminoguanidine nitrate, diaminoguanidine nitrate, triaminoguanidine nitrate, nitroguanidine or mixtures thereof are used as the guanidine compound.

[0010] The further fuel component is preferably an organic compound which has an oxygen balance of more than −90%. Particularly preferred as further fuel component are cyanuric acid, urea, oxamide, urazol, alloxane, alloxantine and parabanic acid or mixtures thereof.

[0011] The "oxygen balance" is to be understood to mean the quantity of oxygen in percentage by weight which becomes free with complete conversion of a compound or of a mixture to CO_2, H_2O, Al_2O_3, B_2O_3 etc. (O_2 excess balance). If the available oxygen is not sufficient for this, then the missing quantity necessary for the complete conversion is indicated with a minus sign (O_2 deficit balance).

[0012] The transition metal oxide present as a component of the oxidizer mixture can be selected from the group consisting of Cr_2O_3, MnO_2, Fe_2O_3, Fe_3O_4, CuO, Cu_2O or mixtures thereof.

[0013] The oxidizer mixture preferably contains a mixture of Fe_2O_3 and CuO, besides the further components of the oxidizer mixture.

[0014] Preferably, the Fe_2O_3 is present in an amount of at least 4% by weight, and more preferably in an amount of at least 9% by weight, in relation to the total composition. By using Fe_2O_3 and Cuo simultaneously, the amount of toxic gases in the combustion products can be further reduced.

[0015] The composition can contain in addition conventional processing aids in a proportion of up to 5% by weight in relation to the total composition, the processing aids preferably being selected from the group consisting of trickling aids, pressurizing aids and/or lubricants.

[0016] A preferred composition according to the invention consists of 30 to 60% by weight guanidine nitrate, 0 to

3.15% by weight cyanuric acid, 15 to 30% by weight CuO, 15 to 30% by weight basic copper nitrate, 1 to 5% by weight ammonium perchlorate and 1 to 5% by weight alkali- and/or alkaline earth metal nitrate, each in relation to the total composition. Preferably, part of the CuO can be replaced by Fe_2O_3.

[0017] The compositions according to the invention are distinguished compared with the mixtures known hitherto by an improved combustion behavior and in particular by an extremely low particle output in combination with a high combustion rate. They are therefore particularly suitable for use in driver's airbag systems. The improved combustion behavior of the compositions according to the invention is promoted by the use of at least one organic compound of the group of guanidine compounds as fuel. The use of guanidine nitrate is particularly preferred owing to its favorable oxygen balance of −26.2%.

[0018] Compared with other organic compounds or mixtures thereof with guanidine nitrate, therefore less oxidizer is required to balance out the mixture. Through this step, therefore, a lower particle output is already achieved.

[0019] It is known that the addition of further fuel components, such as cyanuric acid for example, to the guanidine compounds exerts a favorable influence on the carbon monoxide and NO_x components in the released hot gas. Surprisingly, however, it was found that the proportion of further fuel components has to be kept below 5% by weight, in relation to the total quantity of fuel, in order to keep the combustion rate sufficiently high and, at the same time, to minimize the particle output. Higher proportions of further fuel components result in an undue reduction of the combustion rate and increase to the emitted particle quantity. Depending on the requirements set for the gas-generating composition, the addition of the further fuel components can also be dispensed with entirely.

[0020] The proportion of basic copper nitrate in the oxidizer mixture should in any case amount to a maximum of 50% by weight in relation to the oxidizer mixture. In addition to a high burning speed and extremely low carbon monoxide- and NO_x emissions, a good readiness of the mixture to ignite and also an excellent retaining capability with regard to the solid combustion residues are achieved. A higher proportion of basic copper nitrate is not desired, because hereby in particular the NO_x proportions in the gas would rise unduly.

[0021] A gas-generating mixture which is particularly preferred according to the invention consists of 40 to 55% by weight guanidine nitrate, 0 to 2.9% by weight cyanuric acid, respectively 15 to 30% by weight copper oxide and basic copper nitrate and also respectively 1 to 5% by weight ammonium perchlorate and alkali- or alkaline earth metal nitrate. Owing to the low proportion of cyanuric acid, this composition ensures a sufficient combustion rate for driver's airbag systems. The simultaneous presence of ammonium perchlorate and alkali- or alkaline earth metal nitrate in a molar ratio of approximately 1:1 (alkali) or respectively 2:1 (alkaline earth) has proved to be particularly favorable for a further reduction of the particle output, because through this combination, compared with mixtures of the other oxidizers, to achieve identical oxidation equivalents, the smallest quantities of solid combustion residues are produced. At the same time, the occurrence of HCl as toxic combustion product is prevented. The addition of small quantities of ammonium perchlorate and metal nitrate has, in addition, a favorable influence on the combustion rate.

DESCRIPTION OF PREFERRED EMBODIMENTS

[0022] The invention is described below with the aid of particularly preferred working embodiments which, however, are to be understood as being non-restrictive.

EXAMPLE 1

[0023] 473 g micronized guanidine nitrate, 20 g ground cyanuric acid, 231 g each copper oxide and basic copper nitrate and 26 g ammonium perchlorate and 19 g sodium nitrate were weighed in together into a ball mill, ground for three hours and mixed with each other. The obtained mixture was directly pressed into tablets without further processing steps. Tests showed a very good readiness to ignite with a combustion rate of 17 mm/s. The solid component in the released gas mixture amounted to 1.7%.

EXAMPLE 2

[0024] 493 g micronized guanidine nitrate, 231 g each copper oxide and basic copper nitrate and 26 g ammonium perchlorate and 19 g sodium nitrate were weighed in together into a ball mill. In addition 5 g calcium stearate were added to the preparation and worked up as in Example 1. On firing of the obtained tablets, a good ignition readiness resulted and a combustion rate of 17 mm/s, with a solid component in the generated gas of 1.8%. The NO_x content of the generated gas, measured in a 60 l test canister, amounted to 550 ppm.

COMPARATIVE EXAMPLE 1

[0025] 29.5 g micronized guanidine nitrate, 12.8 g cyanuric acid, respectively 25.65 g copper oxide and basic copper nitrate and 6.4 g potassium perchlorate were mixed in a ball mill, as described in Example 1, and pressed into tablets. In tests, the mixture showed only moderate readiness to ignite; the combustion rate amounted to 10 mm/s. The solid component in the gas mixture amounted to 3.1%. The NO_x content determined in a 60 l test canister was 550 ppm.

COMPARATIVE EXAMPLE 2

[0026] A mixture of 47.1 parts guanidine nitrate and 52.9 parts basic copper nitrate was produced according to the specification described in Example 1 of the U.S. Pat. No. 5,608,183. The mixture showed a poor ignition readiness and only a combustion rate. The NO_x component of the generated gas measured in the test canister amounted to 1300 ppm.

EXAMPLE 3

[0027] 1147 g micronized guanidine nitrate, 612 g basic copper nitrate, 316 g copper oxide (CuO), 242 g iron oxide (Fe_2O_3), 103 g ammonium perchlorate, 75 g sodium nitrate and 5 g calcium stearate were weighed in together into a ball mill and processed as described in Example 1. The test also showed a good readiness to ignit and a combustion rate of about 15 mm/s.

[0028] The analysis of toxic components in the combustion gases showed that the combination of iron oxide and copper oxide as the metal oxide component in the propellant mixture had a highly favourable influence on the emission of carbon monoxide (CO) and ammonia (NH_3). The following emission of gases has been determined by igniting gas generators having the typical performance of gas generators for the driver's side (about 2.3 bar in a 146 l canister):

	Co concentration [ppm]	NH_3-concentration [ppm]
Gas generator loaded with 150 g propellant in accordance with Comparative Example 1	541	266
Gas generator loaded with 136 g propellant according to Example 3	374	33

[0029] The test data show that simultaneously using Fe_2O_3 and CuO as one of the components of the oxidizer mixture result in a further reduction of the emission of toxic gases.

1. An azide-free gas-generating composition, in particular for use in safety devices for motor vehicles, comprising a fuel in a proportion of 20 to 60% by weight and consisting of one or more components, and an oxidizer mixture in a proportion of 40 to 80% by weight and consisting of at least three components, each in relation to the total composition, wherein the fuel consists of a guanidine compound in a proportion of at least 95% by weight and a further fuel component in a proportion of 0 to less than 5% by weight, each in relation to the fuel, and wherein the oxidizer mixture consists of one or more transition metal oxides in a proportion of 20 to 80% by weight, basic copper nitrate in a proportion of 0 to 50% by weight, metal chlorate, metal perchlorate, ammonium perchlorate or mixtures thereof in a proportion of 1 to 15% by weight and alkali metal nitrate, alkaline earth metal nitrate or mixtures thereof in a proportion of 1 to 15% by weight, each in relation to the oxidizer mixture.

2. The composition according to claim 1, wherein the guanidine compound is selected from the group consisting of guanidine carbonate, guanidine nitrate, guanidine perchlorate, aminoguanidine nitrate, diaminoguanidine nitrate, triaminoguanidine nitrate, nitroguanidine or mixtures thereof.

3. The composition according to claim 1, wherein the further fuel component is an organic compound which has an oxygen balance of more than −90%.

4. The composition according to claim 1, wherein the further fuel component is selected from the group consisting of cyanuric acid, urea, oxamide, urazol, alloxane, alloxantine and parabanic acid or mixtures thereof.

5. The composition according to claim 1, wherein the transition metal oxide is selected from the group consisting of Cr_2O_3, MnO_2, Fe_2O_3, Fe_3O_4, CuO, Cu_2O or mixtures thereof.

6. The composition according to claim 1, further comprising processing aids in a proportion of up to 5% by weight, in relation to the total composition, the processing aids being selected from the group consisting of trickling aids, pressurizing aids and/or lubricants.

7. The composition according to claim 1, essentially consisting of 30 to 60% by weight guanidine nitrate, 0 to 3.15% by weight cyanuric acid, 15 to 30% by weight CuO, 15 to 30% by weight basic copper nitrate, 0.1 to 5% by weight ammonium perchlorate and 1 to 5% by weight alkali- and/or alkaline earth metal nitrate, each in relation to the total composition.

8. The composition according to claim 1, wherein the oxidizer mixture simultaneously contains Fe_2O_3 and CuO.

9. The composition of claim 8, wherein the Fe_2O_3 is present in an amount of at least 4% by weight, in relation to the total composition.

10. The composition of claim 7, wherein CuO is partly replaced by Fe_2O_3.

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