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(54) **PROPELLANT FOR GAS GENERATORS**

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(57) **ABSTRACT**

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**Related U.S. Application Data**

(63) Continuation of application No. 09/524,563, filed on Mar. 13, 2000, now abandoned, which is a continuation of application No. 08/354,745, filed on Dec. 8, 1994, now abandoned, which is a continuation of application No. 07/901,698, filed on Jun. 22, 1992, now abandoned.

A propellant for gas generators, especially for lifesaving systems, contains one or several tetrazole derivative(s) or respectively one or several compounds from the groups of (A) cyanic acid derivatives and their salts, (B) triazine and triazine derivatives, (C) urea, its salts, derivatives, and compounds evolved therefrom and their salts, wherein the aforementioned compounds can also be present as mixtures; and an oxidizing agent from the group of peroxides of zinc, calcium, strontium or magnesium or such peroxides with nitrates of ammonium, sodium, potassium, magnesium, calcium and iron, wherein it is possible to add further gas generating components, coolants, reducing agents, catalysts and/or porosity-producing media.

## PROPELLANT FOR GAS GENERATORS

## BACKGROUND OF THE INVENTION

[0001] Gas generators have become of increasing interest for lifesaving purposes, for example in vehicles. Worldwide, the most popular mixture for gas generation contains sodium azide. However, sodium azide is toxic, requiring special measures during the manufacture of the raw material, during the preparation of the gas charge composition, and during its processing, quality control, and waste removal. This holds true, in particular, in connection with the scrapping of vehicles.

[0002] There has been a large number of attempts to utilize substances other than sodium azide. Thus, DE-A-2,142,578 describes a press-molded propellant charge for the rapid inflation of a hollow body by the reaction of tetrazylazene with oxygen carriers. DE-A-1,806,550 proposes a propellant charge which generates pressure gas, yielding cool gases, based on ammonium nitrate, activated carbon, and a compound that is subject to endothermal decomposition or sublimation. However, this system produces a large proportion of steam, representing a drawback since water leads to a strong increase in temperature due to its high heat of condensation.

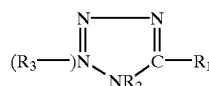
[0003] DE-A-1,222,418 discloses mixtures generating pressurized gas, based on inorganic perchlorate oxidizers, polymeric fuel binders, and a coolant. Preparations having high proportions of chlorate or perchlorate, however, lead to chlorine components in the reaction gases. Thus, EP-A-372, 733 likewise yields an unsatisfactory mixture inasmuch as the propellant charge for the proposed airbag contains about 40% ammonium perchlorate. Even nitrocellulose and nitroglycerin compositions can be found in the literature. Such suggestions cannot be considered for use in lifesaving systems. Nitrocellulose and nitroglycerin mixtures, or also other energetic compounds rich in carbon must be eliminated on account of carbon monoxide formation.

[0004] The propellant charges in DE-A-1,250,318, containing aminotetrazole, potassium dichromate, calcium resinate, and metallic silicon, do not meet up-to-date safety requirements, either. The same holds true for DE-C-2,004, 620 wherein the compressed gas-producing charges contain azotetrazole and/or ditetrazole and chlorates or perchlorates. The propellant charges of U.S. Pat. No. 3,734,789 which contain 5-aminotetrazole nitrate and polyisoprene binders, although burning up rapidly, also generate carbon monoxide owing to the carbon-rich binder proportion, in health-endangering concentrations.

## SUMMARY OF THE INVENTION

[0005] Accordingly, the invention is based on the object of making available gas compositions, the manufacture and processing and/or handling of which are harmless and the reaction products of which are nontoxic.

[0006] This object has been attained by a propellant or gas generating composition for gas generators containing, as the nitrogenous compound, (a) tetrazole or one or more tetrazole derivative(s) of the following formula I



[I]

[0007] wherein  $R_2$  and  $R_2$  or  $R_3$  can be identical or different (but either  $R_2$  or  $R_3$  is present) and can be: hydrogen, hydroxy, amino, carboxy, an alkyl residue of 1-7 carbon atoms, an alkenyl residue of 2-7 carbon atoms, an alkylamino residue of 1-10 carbon atoms, an aryl residue optionally substituted by one or several substituents which can be identical or different, selected from the amino group, the nitro group, the alkyl residues of 1-4 carbon atoms, or an arylamino residue wherein the aryl residue can be optionally substituted, or their sodium, potassium, and guanidinium salts, or containing, as the nitrogenous compounds,

[0008] (b) respectively one or several compounds from the groups of

[0009] (A) cyanic acid derivatives and their salts,

[0010] (B) triazine and triazine derivatives,

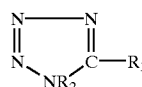
[0011] (C) urea, its salts, derivatives, and compounds evolved therefrom and their salts,

[0012] wherein the compounds recited under (a) and (b) can also be present as mixtures,

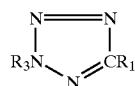
[0013] and containing an oxidizing agent from the group of the peroxides, or from the group of the peroxides together with oxidizing agents from the group of the nitrates.

## DETAILED DESCRIPTION OF THE INVENTION

[0014] By the formula I, applicants are referring to tetrazole or derivatives of tetrazole of either the 1-H or 2-H tautomeric forms as shown in the following formulae IA and IB, respectively:



IA



IB

[0015] The nitrogen-containing compounds to be used according to this invention are those forming, in a mixture with oxidizing agents, during their thermal-chemical reaction, primarily  $\text{CO}_2$ ,  $\text{N}_2$  and  $\text{H}_2\text{O}$ , but not releasing any gases, such as  $\text{CO}$  or  $\text{NO}_x$  in health-endangering concentrations. An especially significant feature resides in that the addition of binders is not absolutely necessary.

[0016]  $R_1$  preferably is hydrogen, amino, hydroxy, carboxy, a methyl, ethyl, propyl or isopropyl, butyl, isobutyl or tert-butyl, n-pentyl, n-hexyl or n-heptyl residue, a methylamino, ethylamino, dimethylamino, n-heptylamino, n-oc-

tylamino or n-decylamino residue, a phenylamino residue, or a phenyl or aminophenyl residue.

[0017]  $R_2$  or  $R_3$  is preferably hydrogen, a methyl or ethyl residue, or a phenyl or aminophenyl residue.

[0018] The following tetrazole derivatives are especially preferred:

[0019] 5-Aminotetrazole, sodium, potassium or calcium 5-aminotetrazolate, 1-(4-aminophenyl)tetrazole, 1-methyl-5-dimethylaminotetrazole, 1-methyl-5-methyl-aminotetrazole, 1-methyltetrazole, 1-phenyl-5-aminotetrazole, 1-phenyl-5-hydroxytetrazole, 1-phenyltetrazole, 2-ethyl-5-aminotetrazole, 2-methyl-5-aminotetrazole, 2-methyl-5-carboxytetrazole, 2-methyl-5-methylaminotetrazole, 2-methyltetrazole, 2-phenyltetrazole, 5-(p-tolyl)tetrazole, 5-diallylaminotetrazole, 5-dimethylaminotetrazole, 5-ethylaminotetrazole, 5-hydroxytetrazole, 5-methyltetrazole, 5-methylaminotetrazole, 5-n-decylaminotetrazole, 5-n-heptylaminotetrazole, 5-n-octylaminotetrazole, 5-phenyltetrazole, 5-phenylaminotetrazole, or bis(aminoguanidine)azotetrazole.

[0020] Cyanic acid derivatives used with preference are sodium cyanate, cyanuric acid, 1-cyanoguanidine and/or disodium cyanamide; triazine derivatives used with preference are 1,3,5-triazine, cyanuric acid esters and/or cyanuric acid amide (melamine); and urea derivatives used with preference are biuret, guanidine, nitroguanidine, guanidine nitrate, aminoguanidine, aminoguanidine nitrate, triaminoguanidine nitrate, aminoguanidine hydrogen carbonate, azodicarboxylic acid diamide, dicyandiamidine nitrate, dicyandiamidine sulfate, tetrazene and/or semicarbazide nitrate.

[0021] Besides being acceptable from health viewpoints, the mixtures according to this invention exhibit a high thermal and weather stability, which is a prerequisite for perfect action even after long-term storage.

[0022] Suitable oxidizing agents are nitrates of ammonium, sodium, potassium, magnesium, calcium or iron, preferably sodium nitrate, or peroxides of zinc, calcium, strontium or magnesium.

[0023] The peroxides are used with an oxygen value as obtainable from stable compounds. For zinc peroxide, this value is about 11 to 14% by weight. The corresponding molar ratio of nitrogen-containing compound to peroxide is in a range from 1:2 to 5.5. Calcium peroxide can exhibit an active oxygen value of, for example, 18.26% by weight, and grain sizes of 15.5  $\mu\text{m}$  and is advantageously utilized in a molar ratio of nitrogen-containing compound/peroxide of 1:3. In general, the aforementioned peroxides can be used in a molar ratio of nitrogen-containing compound to peroxide in a range of 1:1 to 20.

[0024] Calcium peroxide and/or zinc peroxide is used with preference. It is also possible to employ mixtures of the peroxides with one another or mixtures with other oxidizing agents. Other oxidizing agents are, for example, the above-mentioned nitrates of ammonium, sodium, potassium, magnesium, calcium or iron, preferably sodium nitrate.

[0025] When using magnesium peroxide and, in particular, calcium or strontium peroxide, the alkaline-acting

hydrolysis products may evoke reactions with the other components of the mixture. In this case, coating of the peroxides with inorganic or organic materials in accordance with conventional methods is suitable. Such a coating offers, moreover, the advantage of improved handling ability since the thus-treated propellant will no longer be dusty.

[0026] The mixtures to be utilized according to this invention of the tetrazole and/or its derivatives with the compounds from groups (A), (B) and/or (C) permit a finely graded staggering of the propellants with regard to their reaction rate and the thus-formed vapors and gases. This is a staggering needed for providing a maximum variety of uses for the propellant charges of this invention. Depending on the given structure of the generator housing of an airbag, for example, or of a belt tightening device, the propellant charges of this invention must be blended in a controlled fashion. Only in this way is it possible to attain an effect that is at an optimum in each case. The degree of efficiency of the propellant charges according to this invention is, after all, affected not only by the composition, but furthermore by the ignition, and also by the tamping resulting from the construction, and by the flow-off behavior of the thus-evolving vapors and gases. Evaluation of the degree of efficiency can be accomplished, for example, by determination of the gas pressure rise gradient of the respective mixture in the given external environment in each case dependent on the structure, and the type of ignition selected. The thus-formed gas concentrations, especially those of the toxic gases, must not exceed specific maximum values. These values result from the MAK (maximale Arbeitsplatzkonzentration=maximum working site concentration) values (or TLV (threshold-limit value) values in the United States). Technical requirements are derived from these values in conjunction with the exposure times permitted and must be met by the respective propellant charges. When determining these requirements, the differing passenger cells, for example, also enter into the consideration. In order to fulfill these demands, the respective propellant charge must be mixed in controlled fashion.

[0027] The values indicated in the tables were determined by igniting, in a cup in a loose bulk, 4 g of the respective propellant charge by means of a hot wire in a pressurized bomb tube having a volume of 25 ml. After ignition, a pressure-time curve was recorded. The thus-obtained values were evaluated as follows:

[0028] (1) Maximum pressure (bar): with the weighed-in amounts being the same, differences can be ascribed directly to the thus-produced gas volumes. These are determined by gas yield and thermal content of the reaction.

[0029] (2) Rise in gas pressure for the range of 40-60% of maximum pressure: In this region, the curve is no longer falsified by the ignition and/or the cooling-off characteristic of the vapors by the inner surface of the bomb tube. The indicated times in milliseconds (ms) represent the pressure rise and signify differing reaction rates. Such values are also obtained in the respective cases of application, for example in the diverse, structurally modified, gas generator housings. They permit a precise tuning of the propellant charges of this invention with a view toward the efficiency requirements. By the indication of the pressure rise times in a range of 40-60% of the

maximum pressure, the reaction rate of the propellant charges of the invention is adequately characterized. The time periods for the reaction until the occurrence of maximum pressure serve as additional information.

**[0030]** The gas temperature can be kept low in a controlled fashion by addition of diammonium oxalate, oxalic acid diamide, dicyandiamide, or carbonates and, respectively, bicarbonates. If thermal stability is not a factor, and smoke formation upon addition of inorganic carbonates or bicarbonates is to be avoided, it is possible to use aminoguanidine bicarbonate as the organic bicarbonate. Other additives can be constituted by oxalic acid or urea, generally added in an amount of up to 5% by weight, based on the mixture.

**[0031]** Suitable reducing agents are metal powders of iron, magnesium, zirconium or titanium which, in contrast to the nonmetallic compound boron, have no strong effect on the deflagration velocity, but in case of the latter do have an influence on the heat production of the reaction and on the reaction products. The proportion of the reducing agents can amount to up to 5% by weight.

**[0032]** Suitable catalysts for a mixture of such heterogeneous composition are compounds having an effect on the decomposition of peroxides, such as, for example, metals or their oxides, e.g. manganese dioxide. Additions of vanadium pentoxide or cerium dioxide lead to an increase in the reaction velocity. When adding up to 5% by weight of molybdenum(VI) oxide, the velocity is only slightly changed, and this also applies in the presence of cerium(III) nitrate hexahydrate. These additives are effective in amounts of up to a few percent by weight. Further catalysts are metal complexes, of which ferrocene can here be cited as an example; the addition of this compound with up to about 3% by weight markedly raises the reaction velocity.

**[0033]** The gas compositions described in accordance with this invention are manufactured by mixing the components according to conventional methods, optionally with the preparation of a harmless premix to which additional components are added. This mixture can already be utilized in powdered form. Unmixing on account of varying densities of the components can be counteracted by granulation of the mixture.

**[0034]** In the majority of applications by far, the mixture will be formed by press-molding or similar measures. To simplify this procedure, press-molding aids can be added to the mixture. Suitable as such are graphite, molybdenum disulfide, "Teflon", talc, zinc stearate or boron nitride. These agents have an effect even in minimum quantities and affect the properties and deflagration behavior either not at all or only to a minor extent.

**[0035]** It may be advantageous in some cases to influence the deflagration characteristic of the press-molded item by producing porosity. Such a method resides in admixing additives, such as salts, to the mixture prior to the actual shaping step; these additives can be removed again after molding by extraction with water or solvents. Another method resides in adding materials of low thermal resistance which decompose when the molded item is heated. The surface of the mixture can also be enlarged by adding to the mixture, prior to press-molding, hollow microspheres of glass or synthetic resins. The density of the press-molded

article that can be attained thereby can deviate by approximately up to 20% from that of the untreated press-molded article; in this connection, this value is to be merely a roughly governing value and does not represent a limitation. This treatment leads to an extreme acceleration of the deflagration process.

**[0036]** A further treatment of the molded articles can consist in surface coating. In this case, besides achieving an effect on the deflagration characteristic, protection against environmental influences is obtained, in particular. Such a measure can also be suitable for increasing the strength of the molded item. In extreme cases, the use of suitable fibers for stabilization purposes would have to be additionally provided for. A side effect of the coating procedure is a decreased abrasion of the items during transport stresses.

**[0037]** The thus-treated molded articles can be introduced in loose bulk or in oriented fashion into appropriate pressure-proof containers. They are ignited according to conventional methods with the aid of initiator charges or thermal charges wherein the thus-formed gases, optionally after flowing through a suitable filter, lead to inflation of the lifesaving system within fractions of a second.

**[0038]** The propellants of this invention are especially suited for so-called airbags, impact bags which are utilized in automotive vehicles or airplanes for occupants' protection. In case of vehicle impact, the airbag must fill up within a minimum time period with gas quantities of about 50 to 300 liters, depending on system and automobile size. The propellants of this invention are likewise suitable for use in belt-tightening devices.

**[0039]** Lifesaving systems containing the propellants of this invention likewise form the subject matter of the present invention.

#### EXAMPLE 1

**[0040]** 167 g of 5-aminotetrazole (5-ATZ) (produced from aminoguanidine sulfate, sodium nitrite and nitric acid) is recrystallized from about 600 ml of water under continuous agitation, dried at 110° C. after filtration, ground up, and separated from coarse proportions with a 250 gm screen (5-ATZ specification: mp/decomp.: >203° C., average grain size 80  $\mu$ m and H<sub>2</sub>O proportion <0.05%). From ZnSO<sub>4</sub>·7H<sub>2</sub>O and hydrogen peroxide in aqueous ammonia, ZnO<sub>2</sub> is produced, washed with dilute acetic acid as well as water, and dried at 60° C. (specification of ZnO<sub>2</sub>: 13.47% by weight of active oxygen, average grain size 20.3  $\mu$ m).

**[0041]** 5-ATZ and ZnO<sub>2</sub>, as the components for nontoxic gas charges, are homogenized together in a weight ratio of 1 to 7 (corresponding to a molar ratio of about 1:5) in plastic containers in a tumbler mixer for 1-2 hours. Of this sample, 3.0 g is made to react in bulk in a 25 ml size stainless steel bomb tube by means of an electrically heatable Fe wire, and the pressure-time curve is recorded by means of a piezo-electric measuring device. After about 30 ms, a maximum gas pressure of about 200 bar is produced, due primarily to the formation of CO<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub> and H<sub>2</sub>O. The reaction has a strongly exothermal character of about 471 cal/g (about 1970 J/g). ZnO remains as the reaction residue. The CO proportion corresponds to requirements. The deflagration point is at 219° C., the friction sensitivity is at 240 N, the impact sensitivity is at 20 J.

EXAMPLES 2-24

[0042] The use of 5-ATZ and ZnO<sub>2</sub> as components in nontoxic gas charges corresponds to Example 1 with the use of further additives. Examples 2-24 below describe the reaction of other mixtures produced by conventional procedures. The results are compiled in Tables 1-4.

[0043] In the Tables, the first comment in the column labeled "Reaction Velocity" refers to Example No. 2, the second to Example No. 3 and so on.

g of NH<sub>4</sub>NO<sub>3</sub> (mp 167-169° C., grain size 250-315 μm), molar ratio 1:3:2.5, is blended in accordance with Example 1 and pressed into tablets (diameter=6 mm, height=2.77 mm, density=2.18 g/CM<sup>3</sup>, radial pressure force=155.5±28.4 N) with a pressure of 4 tons. The deflagration behavior of the press-molded items, as tested in correspondence with Example 1, is slower than that of the bulk material and requires 0.1 g of B/KNO<sub>3</sub> or Ti/ZnO<sub>2</sub> as initiating mixture. The reaction velocity rises with a drop in the pressing force

TABLE 1

| Example No.                    | Organic Additives (Noles) |     |     |     |     |     |     |     |                      | Reaction Velocity<br>(as Measured in<br>Example 1) |
|--------------------------------|---------------------------|-----|-----|-----|-----|-----|-----|-----|----------------------|----------------------------------------------------|
|                                | 2                         | 3   | 4   | 5   | 6   | 7   | 8   | 9   | 10                   |                                                    |
| 5-Aminotetrazole               | 1                         | 1   | 1   | 1   | 1   | 1   | 1   | 1   | 1                    |                                                    |
| Zinc peroxide                  | 3                         | 3   | 3   | 3   | 3   | 3   | 3   | 3   | 3                    |                                                    |
| Ammonium nitrate               | 2.5                       | 2.5 | 2.5 | 2.5 | 2.5 | 2.5 | 2.5 | 2.5 | 2.5                  | Rose as compared with 1                            |
| Aminoguanidine nitrate         |                           | 1   |     |     |     |     |     |     |                      | Rose as compared with 2                            |
| Urea                           |                           |     | 1   |     |     |     |     |     |                      | Dropped as compared with 2                         |
| Oxalic acid dihydrate          |                           |     |     | 1   |     |     |     |     |                      | Dropped as compared with 2                         |
| Oxalic acid diamide            |                           |     |     |     | 1   |     |     |     |                      | Dropped as compared with 2                         |
| Diammonium oxalate monohydrate |                           |     |     |     |     | 1   |     |     |                      | Dropped as compared with 2                         |
| Semicarbazide nitrate          |                           |     |     |     |     |     | 1   |     |                      | Rose as compared with 2                            |
| Aminoguanidine bicarbonate     |                           |     |     |     |     |     |     | 1   |                      | Dropped as compared with 2                         |
| Ferrocene                      |                           |     |     |     |     |     |     |     | 1 × 10 <sup>-3</sup> | Rose as compared with 2                            |

[0044]

TABLE 2

| Example No.              | Inorganic Additives (Moles) |                      |                      |    |    |     | Reaction Velocity<br>(as Measured in<br>Example 1) |
|--------------------------|-----------------------------|----------------------|----------------------|----|----|-----|----------------------------------------------------|
|                          | 11                          | 12                   | 13                   | 14 | 15 | 16  |                                                    |
| 5-Aminotetrazole         | 1                           | 1                    | 1                    | 1  | 1  | 1   |                                                    |
| Zinc peroxide            | 3                           | 3                    | 3                    | 3  | 3  | 1.5 |                                                    |
| Ammonium nitrate         | 1.5                         | 2.5                  | 2.5                  |    |    | 2.5 |                                                    |
| Iron nitrate nonahydrate | 1.6 · 10 <sup>-2</sup>      |                      |                      |    |    |     | Dropped as compared with 2                         |
| Zinc carbonate           |                             | 2 · 10 <sup>-3</sup> |                      |    |    |     | Dropped as compared with 2                         |
| Molybdenum(VI) oxide     |                             |                      | 3 · 10 <sup>-3</sup> |    |    |     | Comparable to 2                                    |
| Sodium nitrate           |                             |                      |                      | 1  |    |     | Dropped as compared with 2                         |
| Strontium nitrate        |                             |                      |                      |    | 1  |     | Dropped as compared with 2                         |
| Calcium peroxide         |                             |                      |                      |    |    | 1.5 | Comparable to 2                                    |

EXAMPLE 25

[0045] The gas charge mixtures described in Examples 1-24 can also be utilized in press-molded form. A mixture of 10 g of 5-ATZ (H<sub>2</sub>O proportion <0.1%, mp [decomposition] >203° C., grain size 200-250 gm), 43.9 g of ZnO<sub>2</sub> (12.85% by weight of active oxygen, grain size about 14 μm) and 23.5

and drops with the size of the pressed material. The residue from the reactions remains extensively preserved in the form of the pressed items.

EXAMPLES 26-32

[0046] As described in Example 1, further mixtures were prepared from gas-generating components and oxygen-

yielding compounds, such as zinc peroxide, with an active oxygen proportion of 13.07% by weight and an average grain size of 11.8  $\mu\text{m}$  or, in case of sodium nitrate, with an average grain size of <45  $\mu\text{m}$ .

[0047] Table 4 below contains additional data on the mixtures.

TABLE 4

| Component                             | Melting Point<br>(° C.) | Molar Ratios or Mixture |      |       |      |      |      |      |
|---------------------------------------|-------------------------|-------------------------|------|-------|------|------|------|------|
|                                       |                         | 26                      | 27   | 28    | 29   | 30   | 31   | 32   |
| 5-Aminotetrazole                      | 206–208                 | 1                       |      |       |      |      |      |      |
| Potassium 5-aminotetrazolate          | 269                     |                         | 1    |       |      |      |      |      |
| Bis (aminoguanidine)-<br>azotetrazole | 224–226                 |                         |      | 1     |      |      |      |      |
| Nitroguanidine                        | 252                     |                         |      |       | 1    |      |      |      |
| Guanidine nitrate                     | 210–214                 |                         |      |       |      | 1    |      |      |
| Semicarbazide nitrate                 | 115–119                 |                         |      |       |      |      | 1    |      |
| 1-Cyanoguanidine                      | 208–210                 |                         |      |       |      |      |      | 1    |
| Zinc peroxide                         | 200 (decomp.)           | 2.48                    | 2.48 | 10.64 | 1.42 | 1.42 | 0.71 | 4.25 |
| Sodium nitrate                        | —                       | 0.83                    | 0.83 | 3.55  | 0.47 | 0.47 | 0.24 | 1.42 |

[0048] The components were homogenized in containers of plastic for a ½ hour with a tumbler-mixer, a ½ hour with a vibrator, and again for a ½ hour with a tumbler-mixer.

[0049] Of the thus-homogenized mixture, 4 g was introduced as described in Example 1 into a stainless steel pressure bomb tube and, under seal, made to react upon ignition with an incandescent wire. The following items were measured:

[0050] the arising pressure (bar) up to the maximum value,

[0051] the time (milliseconds, ms) up to maximum pressure value,

[0052] the pressure increase gradient (dp/dt) between a pressure reaching 40-60% of the maximum pressure value. The rise time served as the yardstick.

[0053] Table 5 below shows the values for the maximum pressure (bar) and the time in ms up to maximum pressure, ranging within regions as described in Example 1 for a gas charge of 5-aminotetrazole and zinc peroxide. In addition, the time between 40 and 60% of maximum pressure was determined.

TABLE 5

| Example No. | Max. Pressure (bar) | Time (ms)        |                            |
|-------------|---------------------|------------------|----------------------------|
|             |                     | to Max. Pressure | to 40–60% of Max. Pressure |
| 26          | 359                 | 30               | 1.2                        |
| 27          | 217                 | 123              | 13.1                       |
| 28          | 352                 | 29               | 1.5                        |
| 29          | 473                 | 39               | 1.3                        |
| 30          | 549                 | 14               | 0.5                        |
| 31          | 917                 | 7                | 0.2                        |
| 32          | 148                 | 220              | 20.1                       |

[0054] By adaption of the parameters and admixture of further components, it is possible to set the specifications required for the respective gas charge.

[0055] Another sample of the previously recited mixtures was studied with regard to physical and safety properties. The results are set forth in Table 6.

TABLE 6

| Ex No. | Deflagration Point<br>(° C.)* | Friction Impact Sensitivities |     | Heat of Explosion<br>(J/g) |
|--------|-------------------------------|-------------------------------|-----|----------------------------|
|        |                               | (N)                           | (J) |                            |
| 26     | 180                           | >360                          | 7.5 | 2451                       |
| 27     | 207                           | >360                          | 10  | 2293                       |
| 28     | 197                           | >360                          | 4   | 2411                       |
| 29     | 215                           | >360                          | 20  | 2964                       |
| 30     | 364                           | >360                          | 15  | 2777                       |
| 31     | 210                           | >360                          | 2   | 3128                       |
| 32     | 194                           | >360                          | 30  | 2101                       |

\*Determination took place according to the method of “Bundesanstalt fuer Materialpruefung” (BAM) [Federal Institute for Testing Materials] in Berlin.

[0056] The components are suitable for the production of gas charges on account of their miscibility, processability, press-molding ability for shaping, as well as compatibility with one another and with other additives, as well as due to their characteristic safety data.

EXAMPLES 33-44

[0057] As described in Examples 26-32, the mixtures of Examples 33-44 were produced from zinc peroxide (active oxygen proportion 12.0% by weight, average grain size 4.8  $\mu\text{m}$ ), aminotetrazole (average grain size  $\leq 125 \mu\text{m}$ ), sodium nitrate (grain size  $\leq 45 \mu\text{m}$ ), and the listed components with a grain size of <125  $\mu\text{m}$ .

[0058] The friction sensitivity, measured according to the method of BAM, was in all cases >360 N. The additionally listed components are disclosed in the literature.

[0059] Tables 7 and 8 below contain additional data on the mixtures.

| TABLE 7      |                              |          |                   |
|--------------|------------------------------|----------|-------------------|
| Formulations |                              | % by Wt. | Molar Proportions |
| Ex.No. 33    | 5-ATZ                        | 29.8     | 1.4               |
|              | Zinc peroxide                | 23.4     | 0.75              |
|              | Sodium nitrate               | 46.8     | 2.2               |
| Ex.No. 34    | 5-ATZ                        | 19.5     | 1.0               |
|              | Dicyandiamidine nitrate      | 15.2     | 0.4               |
|              | Zinc peroxide                | 21.5     | 0.75              |
| Ex.No. 35    | Sodium nitrate               | 43.8     | 2.24              |
|              | 5-ATZ                        | 18.1     | 1.0               |
|              | Dicyandiamidine sulfate      | 12.8     | 0.2               |
| Ex.No. 36    | zinc peroxide                | 19.8     | 0.75              |
|              | Sodium nitrate               | 49.3     | 2.73              |
|              | 5-ATZ                        | 19.5     | 1.0               |
| Ex.No. 37    | 1-Cyanoguanidine             | 7.7      | 0.4               |
|              | Zinc peroxide                | 21.4     | 0.75              |
|              | Sodium nitrate               | 51.4     | 2.64              |
| Ex.No. 38    | 5-ATZ                        | 16.9     | 1.0               |
|              | Melamine                     | 10.0     | 0.4               |
|              | Zinc peroxide                | 18.6     | 0.75              |
| Ex.No. 39    | Sodium nitrate               | 54.5     | 3.22              |
|              | 5-ATZ                        | 20.2     | 1.0               |
|              | Azodicarboxylic acid diamide | 11.0     | 0.4               |
| Ex.No. 40    | Zinc peroxide                | 22.2     | 0.75              |
|              | Sodium nitrate               | 46.6     | 2.31              |

| TABLE 7-continued |                        |          |                   |
|-------------------|------------------------|----------|-------------------|
| Formulations      |                        | % by Wt. | Molar Proportions |
| Ex.No. 39         | 5-ATZ                  | 19.6     | 1.0               |
|                   | Cyanuric acid          | 11.9     | 0.4               |
|                   | Zinc peroxide          | 21.4     | 0.75              |
| Ex.No. 40         | Sodium nitrate         | 47.1     | 2.41              |
|                   | 5-ATZ                  | 22.5     | 1.0               |
|                   | Urea                   | 6.4      | 0.4               |
| Ex.No. 41         | Zinc peroxide          | 24.7     | 0.75              |
|                   | Sodium nitrate         | 46.4     | 2.06              |
|                   | 5-ATZ                  | 20.2     | 1.0               |
| Ex.No. 42         | Biuret                 | 9.8      | 0.4               |
|                   | Zinc peroxide          | 22.2     | 0.75              |
|                   | Sodium nitrate         | 47.8     | 2.37              |
| Ex.No. 43         | 5-ATZ                  | 21.0     | 1.0               |
|                   | Aminoguanidine nitrate | 13.5     | 0.4               |
|                   | Zinc peroxide          | 23.0     | 0.75              |
| Ex.No. 44         | Sodium nitrate         | 42.5     | 2.03              |
|                   | 5-ATZ                  | 20.5     | 1.0               |
|                   | Sodium dicyanamide     | 8.6      | 0.4               |
| Ex.No. 45         | Zinc peroxide          | 22.5     | 0.75              |
|                   | Sodium nitrate         | 48.4     | 2.37              |
|                   | 5-ATZ                  | 23.9     | 1.0               |
| Ex.No. 46         | Sodium cyanate         | 7.3      | 0.4               |
|                   | Zinc peroxide          | 26.2     | 0.75              |
|                   | Sodium nitrate         | 42.6     | 1.79              |

[0060]

| TABLE 8                                    |     |                  |                       |                   |                                             |                               |                              |                              |                |                           |
|--------------------------------------------|-----|------------------|-----------------------|-------------------|---------------------------------------------|-------------------------------|------------------------------|------------------------------|----------------|---------------------------|
| Mixture Components<br>in Molar Proportions |     | Gas Pressure     |                       |                   |                                             | Heat of<br>Explosion<br>(J/g) | Impact<br>Sensitivity<br>(J) | Deflagration<br>point (° C.) | Example<br>No. |                           |
|                                            |     | Zinc<br>Peroxide | 5-Amino-<br>tetrazole | Sodium<br>Nitrate | Rise for                                    |                               |                              |                              |                |                           |
|                                            |     |                  |                       |                   | Range of<br>40–60% P <sub>max</sub><br>(ms) |                               |                              |                              |                | Maximum<br>Pressure (bar) |
|                                            |     | 0.75             | 1.4                   | 2.2               | 0.38                                        | 683                           | 3528                         | 5                            | >400           | 33                        |
| Dicyandiamidine nitrate                    | 0.4 | 0.75             | 1.0                   | 2.24              | 0.40                                        | 761                           | 3142                         | 6                            | >400           | 34                        |
| Dicyandiamidine sulfate                    | 0.2 | 0.75             | 1.0                   | 2.73              | 1.04                                        | 656                           | 2883                         | 7.5                          | 395            | 35                        |
| 1-Cyanoguanidine                           | 0.4 | 0.75             | 1.0                   | 2.64              | 0.36                                        | 661                           | 3038                         | 10                           | 367            | 36                        |
| Melamine                                   | 0.4 | 0.75             | 1.0                   | 3.22              | 1.16                                        | 652                           | 3187                         | 10                           | >400           | 37                        |
| Azodicarboxylic acid<br>diamide            | 0.4 | 0.75             | 1.0                   | 2.31              | 0.36                                        | 706                           | 3191                         | 6                            | >400           | 38                        |
| Cyanuric acid                              | 0.4 | 0.75             | 1.0                   | 2.41              | 0.80                                        | 582                           | 2732                         | 7.5                          | >400           | 39                        |
| Urea                                       | 0.4 | 0.75             | 1.0                   | 2.06              | 0.40                                        | 654                           | 3053                         | 10                           | >400           | 40                        |
| Biuret                                     | 0.4 | 0.75             | 1.0                   | 2.37              | 0.56                                        | 663                           | 2982                         | 7.5                          | 363            | 41                        |
| Aminoguanidine nitrate                     | 0.4 | 0.75             | 1.0                   | 2.03              | 0.30                                        | 693                           | 3190                         | 7.5                          | 256            | 42                        |
| Sodium dicyanamide                         | 0.4 | 0.75             | 1.0                   | 2.37              | 0.36                                        | 486                           | 3226                         | 7.5                          | 356            | 43                        |
| Sodium cyanate                             | 0.4 | 0.75             | 1.0                   | 1.79              | 0.34                                        | 458                           | 3005                         | 10                           | 349            | 44                        |

1. A propellant composition for producing reaction products not having toxic gases in health-endangering concentrations in gas generators, the components of the composition consisting essentially of:

at least one nitrogen-containing compound selected from the group consisting of

- (A) a cyanic acid derivative selected from the group consisting of sodium cyanate, cyanuric acid, 1-cyanoguanidine, disodium cyanamide and a salt of disodium cyanamide,
- (B) triazine or triazine derivative selected from the group consisting of cyanuric acid ester, cyanuric acid amide, and a salt of disodium cyanamide, and
- (C) urea, its salts and a urea derivative selected from the group consisting of biuret, guanidine, nitroguanidine, guanidine nitrate, aminoguanidine, aminoguanidine nitrate, aminoguanidine hydrogen carbonate, azodicarboxylic acid diamide, dicyandiamidine nitrate, dicyandiamidine sulfate, tetrazene, and semicarbazide nitrate; and

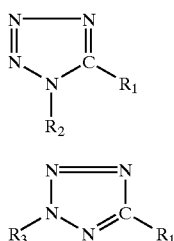
an oxidizing agent comprising an inorganic peroxide or comprising a mixture of an inorganic peroxide and a nitrate;

wherein the reaction products of the propellant composition do not contain toxic gases in health-endangering concentrations.

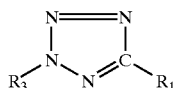
2. A propellant composition according to claim 1, wherein the reaction products of the propellant composition do not contain toxic gases in excess of at least one of MAK and TLV values.

3. A propellant composition for producing reaction products not having the toxic gases in health-endangering concentrations in gas generators, the components of the composition consisting essentially of:

- (1) at least one nitrogen-containing compound selected from the group consisting of
  - (a) tetrazole or a tetrazole derivative of the formulae IA or IB:



IA



IB

wherein  $R_1$  and  $R_2$  or  $R_3$  are identical or different and are hydrogen, hydroxy, amino, carboxy, an alkyl residue of 1-7 carbon atoms, an alkenyl residue of 2-7 carbon atoms, an alkylamino residue of 1-10 carbon atoms, an aryl residue, an arylamino residue, a substituted aryl residue or a substituted arylamino residue, the substituted aryl residue or substituted arylamino residue being substituted by one or several

substituents which are identical or different, and which are selected from the group consisting of an amino group, a nitro group and an alkyl group of 1-4 carbon atoms or a sodium, a potassium or a guanidinium salt of said tetrazole or tetrazole derivative, and

- (b) at least one compound selected from the group consisting of

- (A) a cyanic acid derivative selected from the group consisting of sodium cyanate, cyanuric acid, 1-cyanoguanidine, disodium cyanamide and a salt of disodium cyanamide,
- (B) triazine or triazine derivative selected from the group consisting of cyanuric acid ester, cyanuric acid amide, and their salts, and
- (C) urea, its salts and a urea derivative selected from the group consisting of biuret, guanidine, nitroguanidine, guanidine nitrate, aminoguanidine, aminoguanidine nitrate, aminoguanidine hydrogen carbonate, azodicarboxylic acid diamide, dicyandiamidine nitrate, dicyandiamidine sulfate, tetrazene, and semicarbazide nitrate; and

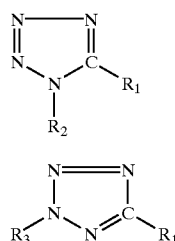
- (2) an oxidizing agent comprising a peroxide or comprising a mixture of a peroxide and a nitrate;

wherein the reaction products of the propellant composition do not contain toxic gases in health-endangering concentrations.

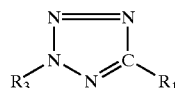
4. A propellant composition according to claim 3, wherein the reaction products of the propellant composition do not contain toxic gases in excess of at least one of MAK and TLV values.

5. A propellant composition for producing reaction products not having toxic gases in health-endangering concentrations in gas generators, the components of the composition consisting essentially of:

- (1) at least one nitrogen-containing compound selected from the group consisting of
  - (a) tetrazole or a tetrazole derivative of the formulae



IA



IB

wherein  $R_1$  and  $R_2$  or  $R_3$  are identical or different and are hydrogen, hydroxy, amino, carboxy, an alkyl residue of 1-7 carbon atoms, an alkenyl residue of 2-7 carbon atoms, an alkylamino residue of 1-10 carbon atoms, an aryl residue, an arylamino residue, a substituted aryl residue or a substituted arylamino residue, the substituted aryl residue or substituted arylamino residue being substituted by one or several

substituents which are identical or different, and which are selected from the group consisting of an amino group, a nitro group and an alkyl group of 1-4 carbon atoms or a sodium, a potassium or a guanidinium salt of said tetrazole or tetrazole derivative, and

(b) at least one compound selected from the group consisting of

(A) a cyanic acid derivative selected from the group consisting of sodium cyanate, cyanuric acid, 1-cyanoguanidine, disodium cyanamide and a salt of disodium cyanamide,

(B) triazine or triazine derivative selected from the group consisting of cyanuric acid ester, cyanuric acid amide and their salts, and

(C) urea, its salts and a urea derivative selected from the group consisting of biuret, guanidine, nitroguanidine, guanidine nitrate, aminoguanidine, aminoguanidine nitrate, aminoguanidine hydrogen carbonate, azodicarboxylic acid diamide, dicyandiamidine nitrate, dicyandiamidine sulfate, tetrazene, and semicarbazide nitrate;

an oxidizing agent comprising a peroxide or comprising a mixture of a peroxide and a nitrate; and

coolants, reducing agents and catalysts;

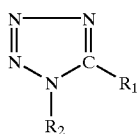
wherein the reaction products of the propellant composition do not contain toxic gases in health-endangering concentrations.

6. A propellant composition according to claim 5, wherein the reaction products of the propellant composition do not contain toxic gases in excess of at least one of MAK and TLV values.

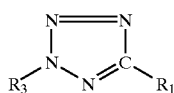
7. A propellant composition for producing reaction products not having toxic gases in health-endangering concentrations in gas generators, the components of the composition consisting essentially of:

at least one nitrogen-containing compound selected from the group consisting of

(a) tetrazole or a tetrazole derivative of the formulae IA or IB:



IA



IB

wherein R<sub>1</sub> and R<sub>2</sub> or R<sub>3</sub> are identical or different and are hydrogen, hydroxy, amino, carboxy, an alkyl residue of 1-7 carbon atoms, an alkenyl residue of 2-7 carbon atoms, an alkylamino residue of 1-10 carbon atoms, an aryl residue, an arylamino residue, a substituted aryl residue or a substituted arylamino

residue, the substituted aryl residue or substituted arylamino residue being substituted by one or several substituents which are identical or different, and which are selected from the group consisting of an amino group, a nitro group and an alkyl group of 1-4 carbon atoms or a sodium, a potassium or a guanidinium salt of said tetrazole or tetrazole derivative, and

(b) at least one compound selected from the group consisting of

(A) a cyanic acid derivative selected from the group consisting of sodium cyanate, cyanuric acid, 1-cyanoguanidine, disodium cyanamide and a salt of sodium cyanamide,

(B) triazine or triazine derivative selected from the group consisting of cyanuric acid ester, cyanuric acid amide and their salts, and

(C) urea, its salts and a urea derivative selected from the group consisting of biuret, guanidine, nitroguanidine, guanidine nitrate, aminoguanidine, aminoguanidine nitrate, aminoguanidine hydrogen carbonate, azodicarboxylic acid diamide, dicyandiamidine nitrate, dicyandiamidine sulfate, tetrazene, and semicarbazide nitrate;

an oxidizing agent comprising a peroxide or comprising a mixture of a peroxide and a nitrate; and

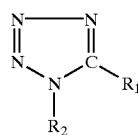
ferrocene as a catalyst;

wherein the reaction products of the propellant composition do not contain toxic gases in health-endangering concentrations.

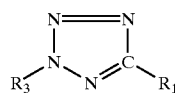
8. A propellant composition according to claim 7, wherein the reaction products of the propellant composition do not contain toxic gases in excess of at least one of MAK and TLV values.

9. A propellant composition for producing reaction products not having toxic gases in health-endangering concentrations in gas generators, the components of the composition consisting essentially of:

(1) at least one nitrogen-containing compound selected from the group consisting of tetrazole or a tetrazole derivative of the formulae IA or IB:



IA



IB

wherein  $R_1$  and  $R_2$  or  $R_3$  are identical or different and are hydrogen, hydroxy, amino, carboxy, an alkyl residue of 1-7 carbon atoms, an alkenyl residue of 2-7 carbon atoms, an alkylamino residue of 1-10 carbon atoms, an aryl residue, an arylamino residue, a substituted aryl residue or a substituted arylamino residue, the substituted aryl residue or substituted arylamino residue being substituted by one or several substituents which are identical or different, and which are selected from the group consisting of an amino group, a nitro group and an alkyl group of 1-4 carbon atoms or a sodium, a potassium or a guanidinium salt of said tetrazole or tetrazole derivative, and

(2) an oxidizing agent, wherein the oxidizing agent is an inorganic peroxide or comprising a mixture of an inorganic peroxide and a nitrate;

wherein the reaction products of the propellant composition do not contain toxic gases in health-endangering concentrations.

**10.** A propellant composition according to claim 9, wherein the reaction products of the propellant composition do not contain toxic gases in excess of at least one of MAK and TLV values.

\* \* \* \* \*