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NON-TOXIC GAS GENERATION

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ABSTRACT OF THE DISCLOSURE

There are disclosed compositions of solid materials capable of producing non-toxic gases by a rapid chemical reaction upon initiation of the reaction. The solid materials comprise a solid inorganic reducing agent and a solid inorganic oxidizing agent mixed together in finely divided or granular form and compacted without the presence of either a binder or solvent. Typical solid inorganic reducing agents are the salts of hydrazine, hydroxylamine and hydrazoic acid. Typical solid oxidizing compounds are the salts of nitric acid, nitrous acid, chloric acid and perchloric acid. The gases typically produced are some or all of nitrogen, water and oxygen, and without the presence of toxic gases such as those containing carbon. The gases are developed spontaneously within milliseconds but without explosive force.

This invention relates to gas generation and particularly to generation of non-toxic gases.

An object is to generate gases which are non-injurious to humans or animals.

There are circumstances under which it can be desirable to generate non-toxic gases such as those normally present in the air, for example, in space craft, submarines, underground mines, and other enclosed places. An important use of such generated gas is in the filling of air bags such as those used and proposed for use in vehicles for passenger safety purposes.

Gas generation and gas generators have long been well-known. It has, for example, been well-known to use propellant compositions for gas generation such as for creating jets for driving aircraft and missiles or for driving other mechanisms. The compositions ordinarily used for such purposes have comprised an oxidizer and a binder within which the oxidizer is dispersed, and in such compositions there has been combustion of the binder material ordinarily containing carbonaceous matter, and this has generated toxic or dangerous end products such as carbon monoxide and carbon dioxide, as well as water which is non-toxic. Other gas generator propellants heretofore in use have been based on nitrocellulose both as a single base propellant and also in combination with nitroglycerin as a double base propellant, which carries the oxidizer in an intra-molecular form. The gas generation from the nitrocellulose base substances also occurs in a combustion process. Since the nitrocellulose base propellants likewise contain carbon, there are developed the same kinds of carbonaceous end products, toxic or dangerous insofar as constituting an environment for human life is concerned.

These previously known gas-producing materials obviously cannot be used safely in an atmosphere intended for sustaining human life. In the case of air bags, these have been used and proposed for protecting occupants of vehicles from injury in the case of accident. Thus, in the event of a vehicle collision, a suitable mechanism sets a gas generator into operation to rapidly inflate the air bag which thereupon assumes a position between an occupant of the vehicle and parts of the vehicle with which he would be brought in contact except for the presence of the inflated air bag. Such bags are required

to be inflated within a small fraction of a second and also they are generally designed to release the gas from the bag at a controlled rate. It would obviously be dangerous to release into the interior of a vehicle or other enclosed space, a toxic gas or a gas which would not permit the continued presence of oxygen. The rapid reaction process should be a controlled process and proceed without explosive force.

In accordance with the present invention, there are provided compositions of solid materials without either binder or solvent, capable of producing gases in a rapid chemical reaction free from undesirable toxic carbonaceous gases.

The compositions according to the present invention produce nitrogen, water and oxygen as typical non-toxic gases, such as are also found in the air, and they supply the gas spontaneously within milliseconds after initiation of the reaction, and without explosive force. Such gases therefore fulfill the requirement of toxic-free gases such as can be safely used in air bags and other confined places where human or animal life is to be sustained.

It is not always essential that every one of these non-toxic gases be found in the product of a generator for the non-toxic gases. For example, under some circumstances, the generated gas need not have oxygen, and this can be a safe condition under those circumstances where the generated gas is to be injected into an atmosphere which already contains sufficient oxygen.

We carry out our present invention by use of a binderless mixture of solid inorganic oxidizer material and solid inorganic reducing agent, capable of entering into an exothermal chemical reaction, producing toxic-free and safe gases. Typical solid inorganic reducing agents useable for this purpose are the salts of hydrazine, hydroxylamine, and hydrazoic acid. Typical solid oxidizing compounds useable for the purpose are the salts of nitric acid, nitrous acid, chloric acid and perchloric acid. One or more of the inorganic reducing agents is mixed with one or more of the inorganic oxidizing agents, and for this purpose, the materials can be ground and blended to a proper particle size which permits compaction of the mixture with a minimum of voids.

The reactants are preferably pulverized to the smallest particle size possible, dried to be free of moisture and then mixed in an inert humidity-free atmosphere. This integrated mixture then is pressed into a mold. Suitable presses are a Carver press or a pill press that compress the loose powder mixture to almost theoretical density. The resulting compression formed product may have the shape of a tablet, a cylinder, a cube, a cone, a hollow cylinder, or a sphere, depending on the selected mold. The compression usually forms a hard shaped charge that reaches 96–99% of theoretical density.

Initiation of the chemical reaction of such a mixture can be done in a conventional manner as for example with a hot electric wire, or a typical prime initiator such as commonly used in explosive devices, or by a hammer ball as in a pistol or any shock similar to that commonly required for the ignition of explosive charges. Once the reaction is thus initiated, the exotherm assures the continuation and completeness of the chemical reaction.

As an example the reaction following equation (1) of Table I was conducted under pressurized helium environment in a Crawford Bomb. The gas analysis after completion of the chemical reaction produced 67 mol percent of nitrogen, 30 mol percent of oxygen, and traces of water. Under the conditions of this experiment the water to be produced in the reaction appeared in condensed form and only the amount of water vapor required for the saturation of these gases was found in gas analysis. The residual composition was identified to be sodium chloride. The formation of the reaction gases followed essentially the

equation (1) of Table I. Only a minor amount of nitrous oxide was identified as a product of a minor side reaction probably formed during the ignition phase. Nitrous oxide is a non-toxic gas used for medicinal purposes. The reaction proceeded in a measurable form. Table III and Table IV hereinafter prove the composition of matter does not act as an exposure but as a mixture that produces the gases in a chemical reaction without explosive force.

This selection of reducing agents and oxidizing agents produces in their chemical reaction only such gases as contain no carbon, nor any toxic gases such as NO_2 or NO. The materials are mixed in proportions which form compositions which are preferably stoichiometric, although a degree of off-stoichiometric mixing can be tolerated without incurring toxic gases. A material present in an off-stoichiometric amount should not be off-stoichiometric to an extent which changes the reaction mechanism and no longer insures safe gases.

Typical reducing agents suitable for use are sodium azide (NaN_3), hydroxylamine hydrochloride

$$(NH_2OH.HCl),$$

sodium nitride (Na_3N), silicon nitride (Si_3N_4), sodium amide ($NaNH_2$), magnesium nitride (Mg_3N_2), sodium hyponitrite ($Na_2N_2O_2$), hydrazine sulphate

$$(N_2H_4.H_2SO_4),$$

hydrazine hydrochloride ($N_2H\cdot 2HCl$), titanium hydride (TiH_4), zirconium hydride (ZrH_2), magnesium hydride (Mg_3N_2), and calcium nitride (Ca_3N_2).

Typical oxidizers useful are ammonium perchlorate (NH_4ClO_4), sodium perchlorate ($NaClO_4$), potassium perchlorate ($KClO_4$), sodium chlorate ($NaClO_3$), potassium chlorate ($KClO_3$), sodium nitrate ($NaNO_3$), potassium nitrate (KNO_3), lithium nitrate ($LiNO_3$), ammonium nitrate (NH_4NO_3), barium nitrate ($Ba(NO_3)_2$), strontium nitrate ($Sr(NO_3)_2$), calcium nitrate

$$(Ca(NO_3)_2),$$

magnesium nitrate ($Mg(NO_3)_2$), zinc nitrate

$$(Zn(NO_3)_2).$$

Sodium peroxide, barium peroxide, and potassium peroxide are capable of use either as a reducing agent or as an oxidizing agent depending on the particular selection of ingredients, and the same is true of sodium and potassium nitrite. Sodium azide, mentioned above as a reducing agent, can under certain exceptional circumstances be used as an oxidizing agent.

Typical reactions utilizing the foregoing identified materials are as shown in Table I below, and in these reaction equations, the respective reducing and oxidizing agents are indicated by the letters *r* and *o*, respectively placed over the corresponding compound or compound groups.

TABLE I.—REACTIONS

1. $\overset{r}{NaN_3}(c) + \overset{o}{NH_4ClO_4}(c) \longrightarrow NaCl(c) + 2N_2(g) + 2H_2O(l,g) + 02(g).$
2. $\overset{r}{NaNO_2}(c) + \overset{o}{NH_4ClO_4}(c) \longrightarrow NaCl(c) + N_2(g) + 2H_2O(l,g) + 202(g).$
3. $\overset{o}{2NaNO_3}(c) + \overset{r}{N_2H_4\cdot H_2SO_4}(c) \longrightarrow Na_2SO_4(c) + 2N_2(g) + 3H_2O(l,g) + 1/20_2(g).$
4. $\overset{o}{2NaNO_3}(c) + \overset{r}{N_2H_4\cdot H_2SO_4}(c) \longrightarrow Na_2SO_4(c) + 2N_2(g) + 3H_2O(l,g) + 3/20_2(g).$
5. $\overset{r}{NH_2OH\cdot HCl}(c) + \overset{o}{NaNO_3}(c) \longrightarrow NaCl(c) + N_2(g) + 2H_2O(l,g) + 1/20_2(g).$
6. $\overset{r}{NH_2OH\cdot HCl}(c) + \overset{o}{NaNO_3}(c) \longrightarrow NaCl(c) + N_2(g) + 2H_2O(l,g) + O_2(g).$

TABLE I—Continued

7. $\overset{r}{Na_3N}(c) + 3\overset{o}{NH_4ClO_4}(c) \longrightarrow 3NaCl(c) + 2N_2(g) + 6H_2O(l,g) + 30_2(g).$
8. $\overset{r}{Si_3N_4}(c) + 3\overset{r}{NaN_3}(c) + 3\overset{o}{NH_4ClO_4}(c) \longrightarrow 3SiO_2(c) + 3NaCl(c) + 8N_2(g) + 6H_2O(l,g).$
9. $\overset{r}{Si_3N_4}(c) + \overset{r}{Na_3N}(c) + 3\overset{o}{NH_4ClO}(c) \longrightarrow 3SiO_2(c) + 3NaCl(c) + 4N_2(g) + 6H_2O(l,g).$
10. $\overset{r}{Si_3N_4}(c) + \overset{r}{6NaNH_2} + \overset{o}{6NH_4ClO_4} \longrightarrow 3SiO_2(c) + 6NaCl(c) + 8N_2(g) + 18H_2O(l,g).$
11. $\overset{r}{NaNH_2}(c) + \overset{o}{NH_4ClO_4}(c) \longrightarrow NaCl(c) + N_2(g) + 3H_2O(l,g) + 1/20_2(g).$
12. $\overset{r}{Mg_3N_2} + \overset{o}{NaClO_3} \longrightarrow NaCl + 3MgO + N_2.$
13. $\overset{r}{Na_2O_2} + 2\overset{o}{NH_4ClO_4} \longrightarrow 2NaCl + N_2 + 4H_2O + 30_2.$
14. $\overset{r}{Na_2N_2O_2} + 2\overset{o}{NH_4ClO_4} \longrightarrow 2NaCl + 2N_2 + 30_2 + 4N_2O.$
15. $\overset{r}{KNO_2} + \overset{o}{NH_4ClO} \longrightarrow KC + N_2 + 20_2 + 2H_2O.$
16. $\overset{r}{N_2H_4\cdot H_2SO_4} + \overset{o}{Ba(NO_3)_2} \longrightarrow BaSO_4 + 2N_2 + 3H_2O + 3/20_2.$
17. $\overset{r}{N_2H_4\cdot 2HCl} + \overset{o}{2NaNO_3} \longrightarrow 2NaCl + 2N_2 + 3H_2O + 3/20_2.$
18. $\overset{r}{TiH_4} + \overset{o}{KIO_4} \longrightarrow TiO_2 + 2H_2O + KCl.$
19. $\overset{r}{ZrH_2} + \overset{o}{KClO_4} \longrightarrow ZrO_2 + H_2O + 1/20_2 + Kl.$
20. $\overset{r}{Mg_3N_2} + \overset{o}{KClO_4} \longrightarrow KCl + 4MgO + N_2 + 1/20_2.$
21. $\overset{r}{Ca_3N_2} + \overset{o}{KClO_4} \longrightarrow KCl + 3CaO + N_2 + 1/20_2.$

The parenthetical letters (c), (g) and (l) placed adjacent to the compounds or products signify their condition as "condensed," "gas," and "liquid," respectively. It will be recognized that in these equations Ba may be replaced with Sr, Ca, Mg, or Zn; and Na may be replaced with K, Li, Rb or Cs.

Following are examples of reaction procedures which have been performed and their results.

EXAMPLE 1

A mixture of 65 parts ground sodium azide (particle size 10–100 micron)+117.5 parts ground ammonium perchlorate (particle size 5–250 micron) was pressed in a Carver press until almost theoretical density was reached. The resulting compression formed product may have the shape of a tablet, cylinder, cube or cone, depending on the selected mold. The density of the mixture was 1.78–1.785 g./cm.^{3}. A reaction was conducted in the following manner: A Crawford Bomb was dried in a vacuum oven and a pellet weighing 1.7466 grams and measuring 0.377" thick, 0.386" wide, and 0.488" long of the above compressed stoichiometric mixture of sodium azide and ammonium perchlorate was placed inside the bomb. The system was purged and then pressurized with helium to 870 p.s.i. The volume of the bomb was approximately 20 in.^{3}. The pellet was ignited with a Nichrome wire. After a delay of about 0.26 seconds the pressure rose to 1458 p.s.i. in 0.27 seconds and then declined very slowly. Analysis of the gas exclusive of the helium showed:

	Mole percent
Nitrogen	67
Oxygen	30.0
Nitrous oxide	1.7
Water	2.5
Ammonia	[1] None

[1] By IR and mass spectrograph.

The residue in the bomb had a pH of 7.0 and contained chloride. It is evident that the gas composition was close

to that expected from the theoretical stoichiometric reaction to form nitrogen and oxygen in a 2:1 molar ratio.

EXAMPLE 2

A dried mixture of 65 parts ground sodium azide (particule size 10–100 micron) and 117.5 parts of ground ammonium perchlorate (particle size 5–250 micron) and 3.65 parts of iron oxide (particle size 1–3 micron) was pressed using a rectangular mold until almost theoretical density was reached. The resulting compressed product was sawed into squares 0.337 x 0.386 x 0.488 in. Upon initiation with a Nichrome wire in a Crawford Bomb under similar conditions but using nitrogen as gas, as shown in Example 1, the material decomposed as shown in Table IV producing the theoretical predicted gases.

EXAMPLE 3

An intimate dried stoichiometric mixture of finely ground sodium azide, and finely ground ammonium perchlorate, particle size of 5–19 micron in both, was pressed in a tablet press to form pills of ½ inch in diameter and ⅛ inch thick. The tablets had a density of 1.78 gm./cm.^{3}. These tablets were exposed to air at room temperature. No weight gain due to absorption of moisture was recorded after 24 hours.

EXAMPLE 4

An intimate dried mixture of finely ground sodium azide and finely ground ammonium perchlorate, particle size of 5–19 micron in both, as produced in Example 3, was safety tested. The results on the blended powder show that the material is not particularly sensitive to impact, friction or elevated temperature.

EXAMPLE 5

A saturated aqueous solution of sodium azide and a saturated aqueous solution of ammonium perchlorate in stoichiometric ratio were sprayed into a vacuum chamber whereby the solvent was rapidly evaporated and the sodium azide and ammonium perchlorate crystals were formed in very small particle size. The dried mixture was then collected and compressed to the desired shape. The density of the product was 1.77 gm./cm.^{3} and behave in its chemical reaction exactly as the material produced in Example 1.

EXAMPLE 6

An intimate mixture of 19.8 parts finely ground hydrazine sulphate and 30.2 parts finely ground barium nitrate was safety tested and compression molded. Its impact sensitivity (50% point) was 55.6 cm. (2 kilogram weight). It did not ignite in the rotary friction test at 4000 grams load and 3000 r.p.m. In the DTA an abrupt exotherm with ignition occurred at 270° F. The density of the tablet was 2.0 gm./cm.^{3}.

As has been pointed out hereinabove, the chemical reactions must produce a high exotherm so that the gas development is completed in a short time similar to that of a combustion process. The exotherm calculations of the series of reactions shown in Table I above are presented in the following Table II wherein the equation numbers correspond with the same numbered equations in Table I.

TABLE II.—EXOTHERM CALCULATIONS

	Mole weight of composition	ΔH kcal.				Δn (Gases)	
		H_2O (l.)		H_2O (g.)		Per mole [H_2O (g.)/H_2O (l.)]	Per 100 g. [H_2O (g.)/H_2O (l.)]
		Mole	Gram	Mole	Gram		
1	182.512	−168.655	−.924	−147.601	−.808	5/3	2.739/1.643
2	186.496	−78.025	−.418	−56.915	−.305	5/3	2.681/1.608
3	268.128	−364.06	−1.357	−332.29	−1.239	5.5/2.5	2.051/.932
4	300.128	−81.180	−.270	−49.474	−.164	6.5/3.5	2.165/1.167
5	138.489	−72.595	−.524	−51.528	−.372	3.5/1.5	2.527/1.083
6	154.489	−46.955	−.303	−25.772	−.166	4/2	2.589/1.294
7	435.471	−443.765	−1.019	−380.62	−.874	11/5	2.526/1.148
8	744.711	−976.09	−1.315	−912.23	−1.229	14/8	1.887/1.078
9	575.751	−913.88	−1.587	−850.60	−1.447	10/4	1.736/0.694
10	1,079,352	−1,691.6	−1.567	−1,502.0	−1.391	26/8	2.408/0.741
11	156.512	−203.575	−1.300	−171.905	−1.098	4.5/1.5	2.875/.958
12	207.43	----------	−1.635	−333.19	−1.635	1/1	.482/.482
13	312.99	−205.22	−.656	−163.14	−.521	8/4	2.556/1.278
14	341.01	----------	----------	----------	----------	9/5	----------
15	202.61	−81.58	−.403	60.54	−.299	5/3	2.470/1.483
16*	391.51	−86.50	−.221	−54.94	−.140	6.5/3.5	1.660/.894
17	274.97	−89.60	−.326	−58.04	−.211	6.5/3.5	2.364/1.273
18	190.50	----------	----------	----------	----------	2/0	----------
19	231.80	−291.50	−1.258	−280.98	−1.212	1.5/0.5	.647/.216
20	239.54	----------	−1.343	−321.74	−1.343	1.5/1.5	.626/.626
21	286.82	----------	−1.122	−321.74	−1.122	1.5/1.5	.523/.523

* Actual products may be $BaO + SO_2 + 1/2\ O_2$.

In the above table, the expression "ΔH" means difference of heat; the term "kcal" means kilocalories (eigher by mole or by gram); and the expression "Δn (gases)" signifies number of moles of gas.

The exotherm calculations in Table II show that the reactions indeed produce heat. Considering equation 1, for example, it is seen that 182.512 grams, which is equal to 1 mole of the composition, produces 168.655 kilocalories per mole, assuming that the water is produced as a liquid. In the event the water be produced as a gas, the same mole of the composition produces 147.601 kilocalories per mole. These figures further show that for every gram of the composition there is produced .924 kilocalories in the event the water is produced as a liquid, and .808 kilocalories in the event the water is produced as a gas. With regard to the number of moles of gas produced by equation 1, 182.512 grams of the composition produce 5 moles of gas in the case of the water being produced as a gas, and only 3 moles of gas in the case of water being produced as a liquid. Considering 100 grams instead of 182.512 grams, the number of moles produced at 2.739 for the water produced as a gas and 1.643 for the water produced as a liquid.

The significance of the slanted lines between the numbers of a pair is that the number of the pair at the left represents the gaseous phase and the number at the right indicates the liquid phase. Referring again to the data for equation 1, the expression 5/3 means 5 in the case of gas and 3 in the case of liquid; and 2.739/1.643 means 2.739 moles of gas and 1.643 moles when condensed. These figures show how an air bag collapses after it has been inflated by a gas-producing reaction according to equation 1. It is desired to create a large number of moles of gas and not too much heat.

The numbers for the remaining equations in Table II have their significance similar to that stated for the numbers for equation 1.

The rapidity of the chemical reaction can be increased or influenced by the use of catalysts and catalysts may be selected which promote or decrease the rate of the decomposition of the oxidizer chemicals used in the composition. Typical catalysts for promoting the decomposition of ammonium perchlorate when it is used as an oxidizer are iron oxides, chromium salts and the like.

Decomposition rates for typical equations are given in Table III as follows:

TABLE III.—DECOMPOSITION RATES

Material	Pressure, p.s.i.a.	Rate, in./sec.
NH_4ClO_4/NaN_3	1,000	1.75
	2,000	2.70
$NH_4ClO_4/NaN_3 + 2\% Fe_2O_3$	1,000	1.75
	2,000	2.55

A pressure test in respect to equation 1 revealed results set forth in Table IV as follows:

TABLE IV.—PRESSURE TESTS

Material	Weight, grams	Pressure, p.s.i.a. 1st	Pressure, p.s.i.a. Peak	Pressure, p.s.i.a. Final	Pressure increase, p.s.i.a. Observed	Pressure increase, p.s.i.a. Predicted
NH_4ClO_4/NaN_3	1.569	2,450	3,215	2,470	20	20

This test was performed in a 29.24 cubic inch bomb filled with nitrogen with initial (1st) and final temperatures at 73±0.5° F.

Besides the measurement of the actual rate of decomposition in the chemical reaction producing safe gases, other safety tests indicate the decomposition of matter is not hazardous. This is shown in the DTA (Differential Thermal Analysis) data, the impact sensitivity data, and the friction sensitivity data of Table V below which indicates that the safe handling of this composition of matter is also proven.

TABLE V.—SUMMARY OF DATA ON GAS GENERANTS

Material	Safety tests: Impact sensitivity [1] (50% point), cm./2 kg.	Safety tests: Rotary friction [2] load, grams/velocity, r.p.m.	DTA: Temp., ° F.	DTA: Observation
NH_4ClO_4/NaN_3	24	4,000/6,000 negative	469	Endotherm.
			638	Do.
			685	Exotherm.
			791	Do.
$NH_4ClO_4/NaN_3 + 2\% Fe_2O_3$	16.5	4,000/3,000 negative, 4,000/7,000 positive.	460	Endotherm.
			603	Exotherm.
			642	Do.

[1] RDX control 32.
[2] Typical solid propellant control 2,080–2,200 gram load at 3,000 r.p.m.

It is understood that the oxidizing agents used in the reactions described herein may be mixtures of any two or more of the oxidizers, and likewise the reducing agents used in the reactions may be mixtures of any two or more of the reducers.

The compositions of matter described herein can be used in various applications. Besides the use as a gas augmentor producing non-toxic gases in air bag applications, there are other uses envisaged. For example, those compositions of matter which produce oxygen in the decomposition reaction would be suitable in devices for emergency oxygen generation. Such emergency oxygen generators are life savers in space applications, in mine disasters, in submarine applications, or any other application in which oxygen is being used to sustain life. The reaction temperature and the hot gases formed in the decomposition make these compositions of matter suitable in applications of solid rocket motors, as turbo starter initiators for jet engines, in gas generators where gases are needed on command, such as in steering of missiles, ships and other transportation vehicles. Rapid gas generation is also desired in application of emergency brakes and in military applications such as flares or incendiary devices.

We claim:

1. A carbon-free composition of matter capable of yielding gaseous products non-toxic to humans, upon combustion of the composition said composition consisting essentially of a stoichiometric mixture of at least two different compounds, at least one of which is an oxidizing agent selected from the group consisting of ammonium perchlorate, sodium nitrite, sodium nitrate, sodium chlorate, bariumnitrate, potassium perchlorate, and at least one of which is a reducing agent selected from the group consisting of sodium azide, sodium nitrite, hydrazine sulphate, hydroxyzamine hydrochloride, sodium nitride, silicon nitride, sodium amide, magnesium nitride, sodium peroxide, sodium hyponitrite, potassium nitrite, titanium hydride, zirconium hydride, magnesium hydride, and calcium nitride.

2. A composition of matter which upon combustion yields non-toxic to human gaseous products, which composition consists essentially of a stoichiometrix mixture of an oxidizer compound ammonium perchlorate and a reducing agent selected from the group consisting of sodium azide, sodium nitrite, sodium nitride, silicon nitride, sodium amide, magnesium nitride, sodium peroxide, sodium hyponitrite, potassium nitrite, and calcium nitride.

3. A composition of matter which upon combustion yields non-toxic to humans gaseous products, which composition consists essentially of a stoichiometric mixture of an oxidizer compound sodium nitrite and a reducing agent selected from the group consisting of hydrazine sulfate and hydroxylamine hydrochloride.

4. A composition of matter which upon combustion yields non-toxic to humans gaseous products, which composition consists essentially of a stoichiometric mixture of an oxidizer compound sodium nitrate and a reducing agent selected from the group consisting of hydrazine sulfate, and hydroxylamine hydrochloride.

5. A composition of matter which upon combustion yields non-toxic to humans gaseous products, which composition consists essentially of a stoichiometric mixture of an oxidizer compound sodium chlorate and a reducing agent selected from the group consisting of hydrazine sulphate, sodium amide, magnesium nitride, titanium hydride, zirconium hydride, magnesium hydride, and calcium nitride.

6. A composition of matter which upon combustion yields non-toxic to humans gaseous products, which composition consists essentially of a stoichiometric mixture of an oxidizer compound barium nitrate and a reducing agent selected from the group consisting of hydrazine sulphate, hydroxylamine hydrochloride, sodium amide, magnesium nitride, titanium hydride, zirconium hydride, magnesium hydride, and calcium nitride.

7. A composition of matter which upon combustion yields non-toxic to humans gaseous products, which composition consists essentially of a stoichiometric mixture of an oxidizer compound potassium perchlorate and a reducing agent selected from the group consisting of hydrazine sulphate, hydroxylamine hydrochloride, sodium amide, magnesium nitride, titanium hydride, zirconium hydride, magnesium hydride, and calcium nitride.

8. A composition according to claim 1 in which the oxidizing agent is ammonium perchlorate and the reducing agent is sodium azide.

9. A composition according to claim 1 in which the oxidizing agent is ammonium perchlorate and the reducing agent is sodium nitrite.

10. A composition according to claim 1 in which the reducing agent is hydrazine sulphate and the oxidizing agent is sodium nitrite.

11. A composition according to claim 1 in which the oxidizing agent is sodium nitrate and the reducing agent is hydrazine sulphate.

12. A composition according to claim 1 in which the reducing agent is hydroxylamine hydrochloride and the oxidizing agent is sodium nitrite.

13. A composition according to claim 1 in which the reducing agent is hydroxylamine hydrochloride and the oxidizing agent is sodium nitrate.

14. A composition according to claim 1 in which the reducing agent is sodium nitride and the oxidizing agent is ammonium perchlorate.

15. A composition according to claim 1 in which the reducing agent is silicon nitride plus sodium azide and the oxidizing agent is ammonium perchlorate.

16. A composition according to claim 1 in which the reducting agent is silicon nitride plus sodium nitride and the oxidizing agent is ammonium perchlorate.

17. A composition according to claim 1 in which the reducing agent is silicon nitride plus sodium amide and the oxidizing agent is ammonium perchlorate.

18. A composition according to claim 1 in which the reducing agent is sodium amide and the oxidizing agent is ammonium perchlorate.

19. A composition according to claim 1 in which the reducing agent is silicon nitride plus sodium nitride and agent is sodium chlorate.

20. A composition according to claim 1 in which the reducing agent is sodium peroxide and the oxidizing agent is ammonium perchlorate.

21. A composition according to claim 1 in which the reducing agent is sodium hyponitrite and the oxidizing agent is ammonium perchlorate.

22. A composition according to claim 1 in which the reducing agent is potassium nitrite and the oxidizing agent is ammonium perchlorate.

23. A composition according to claim 1 in which the reducing agent is hydrazine sulphate and the oxidizing agent is barium nitrate.

24. A composition according to claim 1 in which the reducing agent is hydrazine hydrochloride and the oxidizing agent is sodium nitrate.

25. A composition according to claim 1 in which the reducing agent is titanium hydride and the oxidizing agent is potassium perchlorate.

26. A composition according to claim 1 in which the reducing agent is zirconium hydride and the oxidizing agent is potassium perchlorate.

27. A composition according to claim 1 in which the reducing agent is magnesium hydride and the oxidizing agent is potassium perchlorate.

28. A composition according to claim 1 in which the reducing agent is calcium nitride and the oxidizing agent is potassium perchlorate.

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