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(54) **METAL COMPLEXES FOR USE AS GAS
GENERANTS**

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(57) **ABSTRACT**

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Gas generating compositions and methods for their use are provided. Metal complexes are used as gas generating compositions. These complexes are comprised of a metal cation template, a neutral ligand containing hydrogen and nitrogen, and sufficient oxidizing anion to balance the charge of the complex. The complexes are formulated such that when the complex combusts, nitrogen gas and water vapor is produced. Specific examples of such complexes include metal nitrite ammine, metal nitrate ammine, and metal perchlorate ammine complexes, as well as hydrazine complexes. A binder and co-oxidizer can be combined with the metal complexes to improve crush strength of the gas generating compositions and to permit efficient combustion of the binder. Such gas generating compositions are adaptable for use in gas generating devices, such as automobile air bags.

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Related U.S. Application Data

(63) Continuation of application No. 09/025,345, filed on Feb. 18, 1998, which is a continuation-in-part of application No. 08/184,456, filed on Jan. 19, 1994, now abandoned.

METAL COMPLEXES FOR USE AS GAS GENERANTS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application is a continuation of application Ser. No. 09/025,345, filed Feb. 18, 1998, pending, which is a continuation-in-part of copending U.S. patent application Ser. No. 08/184,456, filed Jan. 19, 1994, titled "Metal Complexes For Use As Gas Generants," which is incorporated herein by reference.

BACKGROUND OF THE INVENTION

[0002] Field of the Invention: The present invention relates to complexes of transition metals or alkaline earth metals which are capable of combusting to generate gases. More particularly, the present invention relates to providing such complexes which rapidly oxidize to produce significant quantities of gases, particularly water vapor and nitrogen.

[0003] Gas generating chemical compositions are useful in a number of different contexts. One important use for such compositions is in the operation of "air bags." Air bags are gaining in acceptance to the point that many, if not most, new automobiles are equipped with such devices. Indeed, many new automobiles are equipped with multiple air bags to protect the driver and passengers.

[0004] In the context of automobile air bags, sufficient gas must be generated to inflate the device within a fraction of a second. Between the time the car is impacted in an accident, and the time the driver would otherwise be thrust against the steering wheel, the air bag must fully inflate. As a consequence, nearly instantaneous gas generation is required.

[0005] There are a number of additional important design criteria that must be satisfied. Automobile manufacturers and others have set forth the required criteria which must be met in detailed specifications. Preparing gas generating compositions that meet these important design criteria is an extremely difficult task. These specifications require that the gas generating composition produce gas at a required rate. The specifications also place strict limits on the generation of toxic or harmful gases or solids. Examples of restricted gases include carbon monoxide, carbon dioxide, NO_x , SO_x and hydrogen sulfide.

[0006] The gas must be generated at a sufficiently and reasonably low temperature so that an occupant of the car is not burned upon impacting an inflated air bag. If the gas produced is overly hot, there is a possibility that the occupant of the motor vehicle may be burned upon impacting a just deployed air bag. Accordingly, it is necessary that the combination of the gas generant and the construction of the air bag isolates automobile occupants from excessive heat. All of this is required while the gas generant maintains an adequate burn rate.

[0007] Another related but important design criteria is that the gas generant composition produces a limited quantity of particulate materials. Particulate materials can interfere with the operation of the supplemental restraint system, present an inhalation hazard, irritate the skin and eyes, or constitute a hazardous solid waste that must be dealt with after the operation of the safety device. In the absence of an accept-

able alternative, the production of irritating particulates is one of the undesirable, but tolerated aspects of the currently used sodium azide materials.

[0008] In addition to producing limited, if any, quantities of particulates, it is desired that at least the bulk of any such particulates be easily filterable. For instance, it is desirable that the composition produce a filterable slag. If the reaction products form a filterable material, the products can be filtered and prevented from escaping into the surrounding environment.

[0009] Both organic and inorganic materials have been proposed as possible gas generants. Such gas generant compositions include oxidizers and fuels which react at sufficiently high rates to produce large quantities of gas in a fraction of a second.

[0010] At present, sodium azide is the most widely used and currently accepted gas generating material. Sodium azide nominally meets industry specifications and guidelines. Nevertheless, sodium azide presents a number of persistent problems. Sodium azide is highly toxic as a starting material, since its toxicity level as measured by oral rat LD_{50} is in the range of 45 mg/kg. Workers who regularly handle sodium azide have experienced various health problems such as severe headaches, shortness of breath, convulsions, and other symptoms.

[0011] In addition, no matter what auxiliary oxidizer is employed, the combustion products from a sodium azide gas generant include caustic reaction products such as sodium oxide, or sodium hydroxide. Molybdenum disulfide or sulfur has been used as oxidizers for sodium azide. However, use of such oxidizers results in toxic products such as hydrogen sulfide gas and corrosive materials such as sodium oxide and sodium sulfide. Rescue workers and automobile occupants have complained about both the hydrogen sulfide gas and the corrosive powder produced by the operation of sodium azide-based gas generants.

[0012] Increasing problems are also anticipated in relation to disposal of unused gas-inflated supplemental restraint systems, e.g. automobile air bags, in demolished cars. The sodium azide remaining in such supplemental restraint systems can leach out of the demolished car to become a water pollutant or toxic waste. Indeed, some have expressed concern that sodium azide might form explosive heavy metal azides or hydrazoic acid when contacted with battery acids following disposal.

[0013] Sodium azide-based gas generants are most commonly used for air bag inflation, but with the significant disadvantages of such compositions many alternative gas generant compositions have been proposed to replace sodium azide. Most of the proposed sodium azide replacements, however, fail to deal adequately with all of the criteria set forth above.

[0014] It will be appreciated, therefore, that there are a number of important criteria for selecting gas generating compositions for use in automobile supplemental restraint systems. For example, it is important to select starting materials that are not toxic. At the same time, the combustion products must not be toxic or harmful. In this regard, industry standards limit the allowable amounts of various gases and particulates produced by the operation of supplemental restraint systems.

[0015] It would, therefore, be a significant advance to provide compositions capable of generating large quantities of gas that would overcome the problems identified in the existing art. It would be a further advance to provide a gas generating composition which is based on substantially nontoxic starting materials and which produces substantially nontoxic reaction products. It would be another advance in the art to provide a gas generating composition which produces very limited amounts of toxic or irritating particulate debris and limited undesirable gaseous products. It would also be an advance to provide a gas generating composition which forms a readily filterable solid slag upon reaction.

[0016] Such compositions and methods for their use are disclosed and claimed herein.

BRIEF SUMMARY OF THE INVENTION

[0017] The present invention is related to the use of complexes of transition metals or alkaline earth metals as gas generating compositions. These complexes are comprised of a metal cation and a neutral ligand containing hydrogen and nitrogen. One or more oxidizing anions are provided to balance the charge of the complex. Examples of typical oxidizing anions which can be used include nitrates, nitrites, chlorates, perchlorates, peroxides, and superoxides. In some cases the oxidizing anion is part of the metal cation coordination complex. The complexes are formulated such that when the complex combusts, a mixture of gases containing nitrogen gas and water vapor are produced. A binder can be provided to improve the crush strength and other mechanical properties of the gas generant composition. A co-oxidizer can also be provided primarily to permit efficient combustion of the binder. Importantly, the production of undesirable gases or particulates is substantially reduced or eliminated.

[0018] Specific examples of the complexes used herein include metal nitrite amines, metal nitrate amines, metal perchlorate amines, metal nitrite hydrazines, metal nitrate hydrazines, metal perchlorate hydrazines, and mixtures thereof. The complexes within the scope of the present invention rapidly combust or decompose to produce significant quantities of gas.

[0019] The metals incorporated within the complexes are transition metals, alkaline earth metals, metalloids, or lanthanide metals that are capable of forming ammine or hydrazine complexes. The presently preferred metal is cobalt. Other metals which also form complexes with the properties desired in the present invention include, for example, magnesium, manganese, nickel, titanium, copper, chromium, zinc, and tin. Examples of other usable metals include rhodium, iridium, ruthenium, palladium, and platinum. These metals are not as preferred as the metals mentioned above, primarily because of cost considerations.

[0020] The transition metal cation or alkaline earth metal cation acts as a template at the center of the coordination complex. As mentioned above, the complex includes a neutral ligand containing hydrogen and nitrogen. Currently preferred neutral ligands are NH_3 and N_2H_4 . One or more oxidizing anions may also be coordinated with the metal cation. Examples of metal complexes within the scope of the present invention include $\text{Cu}(\text{NH}_3)_4(\text{NO}_3)_2$ (tetraamminecopper (II) nitrate),

$\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3$ (trinitrotri-aminocobalt (III)), $\text{Co}(\text{NH}_3)_6(\text{ClO}_4)_3$ (hexaamminecobalt (III) perchlorate), $\text{Co}(\text{NH}_3)_6(\text{NO}_3)_3$ (hexaamminecobalt (III) nitrate), $\text{Zn}(\text{N}_2\text{H}_4)_3(\text{NO}_3)_2$ (tris-hydrazine zinc nitrate), $\text{Mg}(\text{N}_2\text{H}_4)_2(\text{ClO}_4)_2$ (bis-hydrazine magnesium perchlorate), and $\text{Pt}(\text{NO}_2)_2(\text{NH}_2\text{NH}_2)_2$ (bis-hydrazine platinum(II) nitrite).

[0021] It is within the scope of the present invention to include metal complexes which contain a common ligand in addition to the neutral ligand. A few typical common ligands include: aquo (H_2O), hydroxo (OH), carbonato (CO_3), oxalate (C_{2O_4}), cyano (CN), isocyanato (NC), chloro (Cl), fluoro (F), and similar ligands. The metal complexes within the scope of the present invention are also intended to include a common counter ion, in addition to the oxidizing anion, to help balance the charge of the complex. A few typical common counter ions include: hydroxide (OH^-), chloride (Cl^-), fluoride (F), cyanide (CN^-), carbonate (CO_3^{-2}), phosphate (PO_4^{-3}), oxalate ($\text{C}_2\text{O}_4^{-2}$), borate (BO_4^{-5}), ammonium (NH_4^+), and the like.

[0022] It is observed that metal complexes containing the described neutral ligands and oxidizing anions combust rapidly to produce significant quantities of gases. Combustion can be initiated by the application of heat or by the use of conventional igniter devices.

DETAILED DESCRIPTION OF THE INVENTION

[0023] As discussed above, the present invention is related to gas generant compositions containing complexes of transition metals or alkaline earth metals. These complexes are comprised of a metal cation template and a neutral ligand containing hydrogen and nitrogen. One or more oxidizing anions are provided to balance the charge of the complex. In some cases the oxidizing anion is part of the coordination complex with the metal cation. Examples of typical oxidizing anions which can be used include nitrates, nitrites, chlorates, perchlorates, peroxides, and superoxides. The complexes can be combined with a binder or mixture of binders to improve the crush strength and other mechanical properties of the gas generant composition. A co-oxidizer can be provided primarily to permit efficient combustion of the binder.

[0024] Metal complexes which include at least one common ligand in addition to the neutral ligand are also included within the scope of the present invention. As used herein, the term common ligand includes well known ligands used by inorganic chemists to prepare coordination complexes with metal cations. The common ligands are preferably polyatomic ions or molecules, but some monoatomic ions, such as halogen ions, may also be used. Examples of common ligands within the scope of the present invention include aquo (H_2O), hydroxo (OH), perhydroxo (O_2H), peroxy (O_2), carbonate (CO_3), oxalato (C_2O_4), carbonyl (CO), nitrosyl (NO), cyano (CN), isocyanato (NC), isothiocyanato (NCS), thiocyanato (SCN), chloro (Cl), fluoro (F), amido (NH_2), imido (NH), sulfato (SO_4), phosphate (PO_4), ethylenediaminetetraacetic acid (EDTA), and similar ligands. See, F. Albert Cotton and Geoffrey Wilkinson, *Advanced Inorganic Chemistry*, 2nd ed., John Wiley & Sons, pp. 139-142, 1966 and James E. Huheey, *Inorganic Chemistry*, 3rd ed., Harper & Row, pp. A-97-A-107, 1983, which are incorporated herein by reference. Persons skilled in the art will appreciate

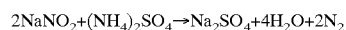
that suitable metal complexes within the scope of the present invention can be prepared containing a neutral ligand and another ligand not listed above.

[0025] In some cases, the complex can include a common counter ion, in addition to the oxidizing anion, to help balance the charge of the complex. As used herein, the term common counter ion includes well known anions and cations used by inorganic chemists as counter ions. Examples of common counter ions within the scope of the present invention include hydroxide (OH⁻), chloride (Cl⁻), fluoride (F⁻), cyanide (CN⁻), thiocyanate (SCN⁻), carbonate (CO₃²⁻), sulfate (SO₄²⁻), phosphate (PO₄³⁻), oxalate (C₂O₄²⁻), borate (BO₄³⁻), ammonium (NH₄⁺), and the like. See, Whitten, K. W., and Gailey, K. D., *General Chemistry*, Saunders College Publishing, p. 167, 1981 and James E. Huheey, *Inorganic Chemistry*, 3rd ed., Harper & Row, pp. A-97-A-103, 1983, which are incorporated herein by reference.

[0026] The gas generant ingredients are formulated such that when the composition combusts, nitrogen gas and water vapor are produced. In some cases, small amounts of carbon dioxide or carbon monoxide are produced if a binder, co-oxidizer, common ligand or oxidizing anion contain carbon. The total carbon in the gas generant composition is carefully controlled to prevent excessive generation of CO gas. The combustion of the gas generant takes place at a rate sufficient to qualify such materials for use as gas generating compositions in automobile air bags and other similar types of devices. Importantly, the production of other undesirable gases or particulates is substantially reduced or eliminated.

[0027] Complexes which fall within the scope of the present invention include metal nitrate amines, metal nitrite amines, metal perchlorate amines, metal nitrite hydrazines, metal nitrate hydrazines, metal perchlorate hydrazines, and mixtures thereof. Metal ammine complexes are defined as coordination complexes including ammonia as the coordinating ligand. The ammine complexes can also have one or more oxidizing anions, such as nitrite (NO₂⁻), nitrate (NO₃⁻), chlorate (ClO₃⁻), perchlorate (ClO₄), peroxide (O₂²⁻), and super-oxide (O₂⁻), or mixtures thereof, in the complex. The present invention also relates to similar metal hydrazine complexes containing corresponding oxidizing anions.

[0028] It is suggested that during combustion of a complex containing nitrite and ammonia groups the nitrite and ammonia groups undergo a diazotization reaction. This reaction is similar, for example, to the reaction of sodium nitrite and ammonium sulfate, which is set forth as follows:



[0029] Compositions such as sodium nitrite and ammonium sulfate in combination have little utility as gas generating substances. These materials are observed to undergo metathesis reactions which result in unstable ammonium nitrate. In addition, most simple nitrite salts have limited stability.

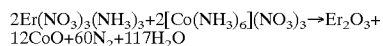
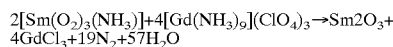
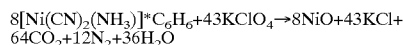
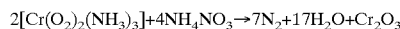
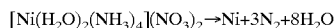
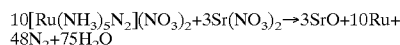
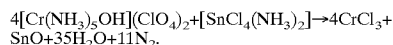
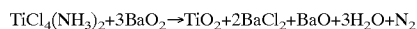
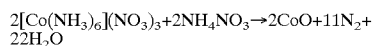
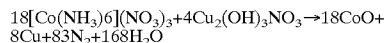
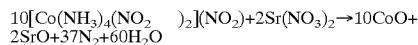
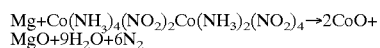
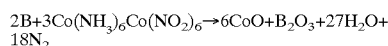
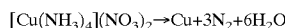
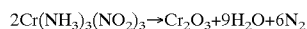
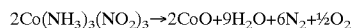
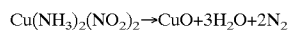
[0030] In contrast, the metal complexes used in the present invention are stable materials which, in certain instances, are capable of undergoing the type of reaction set forth above. The complexes of the present invention also produce reaction products which include desirable quantities of nontoxic gases such as water vapor and nitrogen. In addition, a stable

metal, or metal oxide slag is formed. Thus, the compositions of the present invention avoid several of the limitations of existing sodium azide gas generating compositions.

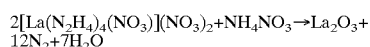
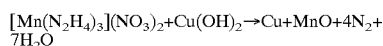
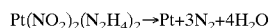
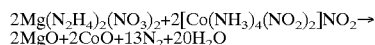
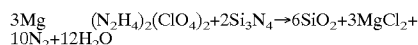
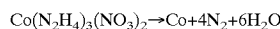
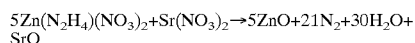
[0031] Any transition metal, alkaline earth metal, metalloid, or lanthanide metal which is capable of forming the complexes described herein is a potential candidate for use in these gas generating compositions. However, considerations such as cost, reactivity, thermal stability, and toxicity may limit the most preferred group of metals.

[0032] The presently preferred metal is cobalt. Cobalt forms stable complexes which are relatively inexpensive. In addition, the reaction products of cobalt complex combustion are relatively nontoxic. Other preferred metals include magnesium, manganese, copper, zinc, and tin. Examples of less preferred but usable metals include nickel, titanium, chromium, rhodium, iridium, ruthenium, and platinum.

[0033] A few representative examples of ammine complexes within the scope of the present invention, and the associated gas generating decomposition reactions are as follows:



[0034] A few representative examples of hydrazine complexes within the scope of the present invention, and related gas generating reactions are as follows:



[0035] While the complexes of the present invention are relatively stable, it is also simple to initiate the combustion reaction. For example, if the complexes are contacted with a hot wire, rapid gas producing combustion reactions are observed. Similarly, it is possible to initiate the reaction by means of conventional igniter devices. One type of igniter device includes a quantity of B/KNO₃ granules or pellets which is ignited, and which in turn is capable of igniting the compositions of the present invention. Another igniter device includes a quantity of Mg/Sr(NO₃)₂/nylon granules.

[0036] It is also important to note that many of the complexes defined above undergo "stoichiometric" decomposition. That is, the complexes decompose without reacting with any other material to produce large quantities of nitrogen and water, and a metal or metal oxide. However, for certain complexes it may be desirable to add a fuel or oxidizer to the complex in order to assure complete and efficient reaction. Such fuels include, for example, boron, magnesium, aluminum, hydrides of boron or aluminum, carbon, silicon, titanium, zirconium, and other similar conventional fuel materials, such as conventional organic binders. Oxidizing species include nitrates, nitrites, chlorates, perchlorates, peroxides, and other similar oxidizing materials. Thus, while stoichiometric decomposition is attractive because of the simplicity of the composition and reaction, it is also possible to use complexes for which stoichiometric decomposition is not possible.

[0037] As mentioned above, nitrate and perchlorate complexes also fall within the scope of the invention. A few representative examples of such nitrate complexes include: Co(NH₃)₆(NO₃)₃, Cu(NH₃)₄(NO₃)₂, [Co(NH₃)₅(NO₃)(NO₃)₂], [Co(NH₃)₅(NO₂)(NO₃)₂], [Co(NH₃)₅(H₂O)(NO₃)₂]. A few representative examples of perchlorate complexes within the scope of the invention include: [Co(NH₃)₆(ClO₄)₃], [Co(NH₃)₅(NO₂)(ClO₄)], [Mg(N₂H₄)₂](ClO₄)₂.

[0038] Preparation of metal nitrite or nitrate ammine complexes of the "present invention is described in the literature. Specifically, reference is made to Hagel et al., "The Triamines of Cobalt (III). I. Geometrical Isomers of Trinitrotriamminecobalt (III)," *9 Inorganic Chemistry*, 1496 (June 1970); G. Pass and H. Sutcliffe, *Practical Inorganic Chemistry*, 2nd Ed., Chapman & Hull, New York, 1974; Shibata et al., "Synthesis of Nitroammine—and Cyanoamminecobalt (III). Complexes With Potassium Tricarbonatocobaltate(III) as the Starting Material," *3 Inorganic Chemistry* 1573 (November 1964); Wieghardt et al., " μ -Carboxylatodim- μ -hydroxo-bis [triamminecobalt (III)] Complexes," *23 Inorganic Synthesis* 23 (1985); Laing, "mer- and fac- [Co(NH₃)₃(NO₂)₃]: Do They Exist?" *62 J. Chem Educ.*, 707 (1985); Siebert, "Isomere des Trinitrotriamminecobalt (III)," *441 Z. Anorg. Allg. Chem.* 47 (1978); all of which are incorporated herein by this reference. Transition metal perchlorate ammine complexes are synthesized by similar methods. As mentioned above, the ammine complexes of the present invention are generally stable and safe for use in preparing gas generating formulations.

[0039] Preparation of metal perchlorate, nitrate, and nitrite hydrazine complexes is also described in the literature. Specific reference is made to Patil et al., "Synthesis and Characterization of Metal Hydrazine Nitrate, Azide, and Perchlorate Complexes," *12 Synthesis and Reactivity In Inorganic and Metal Organic Chemistry*, 383 (1982); Klyichnikov et al., "Preparation of Some Hydrazine Compounds of Palladium," *13 Russian Journal of Inorganic Chemistry*, 416 (1968); Klyichnikov et al., "Conversion of Mononuclear

Hydrazine Complexes of Platinum and Palladium Into Binuclear Complexes," *36 Ukr. Khim. Zh.*, 687 (1970).

[0040] The described complexes can be processed into usable granules or pellets for use in gas generating devices. Such devices include automobile air bag supplemental restraint systems. Such gas generating compositions will comprise a quantity of the described complexes and preferably, a binder and a co-oxidizer. The compositions produce a mixture of gases, principally nitrogen and water vapor, upon decomposition or burning. The gas generating device will also include means for initiating the burning of the composition, such as a hot wire or igniter. In the case of an automobile air bag system, the system will include the compositions described above; a collapsed, inflatable air bag; and means for igniting said gas-generating composition within the air bag system. Automobile air bag systems are well known in the art.

[0041] Typical binders used in the gas generating compositions of the present invention include binders conventionally used in propellant, pyrotechnic and explosive compositions including, but not limited to, lactose, boric acid, silicates including magnesium silicate, polypropylene carbonate, polyethylene glycol, naturally occurring gums such as guar gum, acacia gum, modified celluloses and starches (a detailed discussion of such gums is provided by C. L. Mantell, *The Water-Soluble Gums*, Reinhold Publishing Corp., 1947, which is incorporated herein by reference), polyacrylic acids, nitrocellulose, polyacrylamide, polyamides, including nylon, and other conventional polymeric binders. Such binders improve mechanical properties or provide enhanced crush strength. Although water immiscible binders can be used in the present invention, it is currently preferred to use water soluble binders. The binder concentration is preferably in the range from 0.5 to 12% by weight, and more preferably from 2% to 8% by weight of the gas generant composition.

[0042] Applicants have found that the addition of carbon such as carbon black or activated charcoal to gas generant compositions improves binder action significantly perhaps by reinforcing the binder and thus, forming a micro-composite. Improvements in crush strength of 50% to 150% have been observed with the addition of carbon black to compositions within the scope of the present invention. Ballistic reproducibility is enhanced as crush strength increases. The carbon concentration is preferably in the range of 0.1% to 6% by weight, and more preferably from 0.3 to 3% by weight of the gas generant composition.

[0043] The co-oxidizer can be a conventional oxidizer such as alkali, alkaline earth, lanthanide, or ammonium perchlorates, chlorates, peroxides, nitrites, and nitrates, including for example, Sr(NO₃)₂, NH₄ClO₄, KNO₃, and (NH₄)₂Ce(NO₃)₆.

[0044] The co-oxidizer can also be a metal containing oxidizing agent such as metal oxides, metal hydroxides, metal peroxides, metal oxide hydrates, metal oxide hydroxides, metal hydrous oxides, and mixtures thereof, including those described in U.S. Pat. No. 5,439,537 issued Aug. 8, 1995, titled "Thermite Compositions for Use as Gas Generants," which is incorporated herein by reference. Examples of metal oxides include, among others, the oxides of copper, cobalt, manganese, tungsten, molybdenum, and iron, such as CuO, Co₂O₃, Co₃O₄, CoFe₂O₄, Fe₂O₃, MoO₃, Bi₂MoO₆, and Bi₂O₃. Examples of metal hydroxides include, among others, Fe(OH)₃, Co(OH)₃, Co(OH)₂, Ni(OH)₂, Cu(OH)₂, and Zn(OH)₂. Examples of

metal oxide hydrates and metal hydrous oxides include, among others, $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$, $\text{SnO}_2 \cdot x\text{H}_2\text{O}$, and $\text{MoO}_3 \cdot \text{H}_2\text{O}$. Examples of metal oxide hydroxides include, among others, $\text{CoO}(\text{OH})_2$, $\text{FeO}(\text{OH})_2$, $\text{MnO}(\text{OH})_2$ and $\text{MnO}(\text{OH})_3$.

[0045] The co-oxidizer can also be a basic metal carbonate such as metal carbonate hydroxides, metal carbonate oxides, metal carbonate hydroxide oxides, and hydrates and mixtures thereof and a basic metal nitrate such as metal hydroxide nitrates, metal nitrate oxides, and hydrates and mixtures thereof including those oxidizers described in U.S. Pat. No. 5,429,691, titled "Thermite Compositions for use as Gas Generants." which is incorporated herein by reference.

[0046] Table 1, below, lists examples of typical basic metal carbonates capable of functioning as co-oxidizers in the compositions of the present invention:

TABLE 1

Basic Metal Carbonates
$\text{Cu}(\text{CO}_3)_{1-x}\text{Cu}(\text{OH})_{2x}$, e.g., $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ (malachite)
$\text{Co}(\text{CO}_3)_{1-x}(\text{OH})_{2x}$, e.g., $2\text{Co}(\text{CO}_3) \cdot 3\text{Co}(\text{OH})_2 \cdot \text{H}_2\text{O}$
$\text{Co}_x\text{Fe}_y(\text{CO}_3)_z(\text{OH})_2$, e.g., $\text{Co}_{0.69}\text{Fe}_{0.34}(\text{CO}_3)_{0.2}(\text{OH})_2$
$\text{Na}_3[\text{Co}(\text{CO}_3)_3] \cdot 3\text{H}_2\text{O}$
$\text{Zn}(\text{CO}_3)_{1-x}(\text{OH})_{2x}$, e.g., $\text{Zn}_2(\text{CO}_3)(\text{OH})_2$
$\text{Bi}_x\text{Mg}_y(\text{CO}_3)_z(\text{OH})_d$, e.g., $\text{Bi}_2\text{Mg}(\text{CO}_3)_2(\text{OH})_4$
$\text{Fe}(\text{CO}_3)_{1-x}(\text{OH})_{2x}$, e.g., $\text{Fe}(\text{CO}_3)_{0.12}(\text{OH})_{2.76}$
$\text{Cu}_x\text{Zn}_y(\text{CO}_3)_{1-x-y}(\text{OH})_{2z}$, e.g., $\text{Cu}_{1.54}\text{Zn}_{0.46}(\text{CO}_3)(\text{OH})_2$
$\text{Co}_x\text{Cu}_y(\text{CO}_3)_{1-x-y}(\text{OH})_{2z}$, e.g., $\text{Co}_{0.46}\text{Cu}_{0.51}(\text{CO}_3)_{0.43}(\text{OH})_{1.1}$
$\text{Ti}_x\text{Bi}_y(\text{CO}_3)_z(\text{OH})_d(\text{H}_2\text{O})_c$, e.g., $\text{Ti}_3\text{Bi}_4(\text{CO}_3)_2(\text{OH})_2\text{O}_9(\text{H}_2\text{O})_2$ ($\text{BiO})_2\text{CO}_3$

[0047] Table 2, below, lists examples of typical basic metal nitrates capable of functioning as co-oxidizers in the compositions of the present invention:

TABLE 2

Basic Metal Nitrates
$\text{Cu}_2(\text{OH})_3\text{NO}_3$ (gerhardite)
$\text{Co}_2(\text{OH})_3\text{NO}_3$
$\text{Cu}_x\text{Co}_y(\text{OH})_z\text{NO}_3$, e.g., $\text{CuCo}(\text{OH})_3\text{NO}_3$
$\text{Zn}_2(\text{OH})_3\text{NO}_3$
$\text{Mn}(\text{OH})_2\text{NO}_3$
$\text{Fe}(\text{NO}_3)_n(\text{OH})_{3-n}$, e.g., $\text{Fe}_4(\text{OH})_{11}\text{NO}_3 \cdot 2\text{H}_2\text{O}$
$\text{Mo}(\text{NO}_3)_2\text{O}_2$
$\text{BiONO}_3 \cdot \text{H}_2\text{O}$
$\text{Ce}(\text{OH})(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$

[0048] In certain instances it will also be desirable to use mixtures of such oxidizing agents in order to enhance ballistic properties or maximize filterability of the slag formed from combustion of the composition.

[0049] The present compositions can also include additives conventionally used in gas generating compositions, propellants, and explosives, such as burn rate modifiers, slag formers, release agents, and additives which effectively remove NO_x . Typical burn rate modifiers include Fe_2O_3 , $\text{K}_2\text{B}_{12}\text{H}_{12}$, Bi_2MoO_6 , and graphite carbon powder or fibers. A number of slag forming agents are known and include, for example, clays, talcs, silicon oxides, alkaline earth oxides, hydroxides, oxalates, of which magnesium carbonate, and magnesium hydroxide are exemplary. A number of additives and/or agents are also known to reduce or eliminate the oxides of nitrogen from the combustion products of a gas generant composition, including alkali metal salts and complexes of tetrazoles, aminotetrazoles, triazoles and related nitrogen heterocycles of which potassium aminotetrazole, sodium carbonate and potassium carbonate are exemplary. The composition can also include materials which facilitate the release of the composition from a mold such as graphite, molybdenum sulfide, calcium stearate, or boron nitride.

[0050] Typical ignition aids/burn rate modifiers which can be used herein include metal oxides, nitrates and other compounds such as, for instance, Fe_2O_3 , $\text{K}_2\text{B}_{12}\text{H}_{12}$, H_2O , $\text{BiO}(\text{NO}_3)$, Co_2O_3 , CoFe_2O_4 , CuMoO_4 , Bi_2MoO_6 , MnO_2 , $\text{Mg}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$, and NH_4NO_3 . Coolants include magnesium hydroxide, cupric oxalate, boric acid, aluminum hydroxide, and silicotungstic acid. Coolants such as aluminum hydroxide and silicotungstic acid can also function as slag enhancers.

[0051] It will be appreciated that many of the foregoing additives may perform multiple functions in the gas generant formulation such as a co-oxidizer or as a fuel, depending on the compound. Some compounds may function as a co-oxidizer, burn rate modifier, coolant, and/or slag former.

[0052] Several important properties of typical hexaamminecobalt (III) nitrate gas generant compositions within the scope of the present invention have been compared with those of commercial sodium azide gas generant compositions. These properties illustrate significant differences between conventional sodium azide gas generant compositions and gas generant compositions within the scope of the present invention. These properties are summarized below:

Property	Typical Invention Range	Typical Sodium Azide
Flame Temperature	1850–2050° K.	1400–1500° K.
Gas Fraction of Generant	0.65–0.85	0.4–0.45
Total Carbon Content in Generant	0–3.5%	trace
Burn Rate of Generant at 1000 psi	0.10–0.35 ips	1.1–1.3 ips
Surface Area of Generant	2.0–3.5 cm ² /g	0.8–0.85 cm ² /g
Charge Weights in Generator	30–45 g	75–90 g

[0053] The term "gas fraction of generant" means the weight fraction of gas generated per weight of gas generant. Typical hexaamminecobalt (III) nitrate gas generant compositions have more preferred flame temperatures in the range from 1850° K to 1900° K, gas fraction of generant in the range from 0.70 to 0.75, total carbon content in the generant in the range from 1.5% to 3.0% burn rate of generant at 1000 psi in the range from 0.2 ips to 0.35 ips, and surface area of generant in the range from 2.5 cm²/g to 3.5 cm²/g.

[0054] The gas generating compositions of the present invention are readily adapted for use with conventional hybrid air bag inflator technology. Hybrid inflator technology is based on heating a stored inert gas (argon or helium) to a desired temperature by burning a small amount of propellant. Hybrid inflators do not require cooling filters used with pyrotechnic inflators to cool combustion gases, because hybrid inflators are able to provide a lower temperature gas. The gas discharge temperature can be selectively changed by adjusting the ratio of inert gas weight to propellant weight. The higher the gas weight to propellant weight ratio, the cooler the gas discharge temperature.

[0055] A hybrid gas generating system comprises a pressure tank having a rupturable opening, a pre-determined amount of inert gas disposed within that pressure tank; a gas generating device for producing hot combustion gases and having means for rupturing the rupturable opening; and means for igniting the gas generating composition. The tank has a rupturable opening which can be broken by a piston when the gas generating device is ignited. The gas generating device is configured and positioned relative to the pressure tank so that hot combustion gases are mixed with and heat the inert gas. Suitable inert gases include, among others, argon, helium and mixtures thereof. The mixed and heated gases exit the pressure tank through the opening and ultimately exit the hybrid inflator and deploy an inflatable bag or balloon, such as an automobile air bag.

[0056] Preferred embodiments of the invention yield combustion products with a temperature greater than about 1800° K, the heat of which is transferred to the cooler inert gas causing a further improvement in the efficiency of the hybrid gas generating system.

[0057] Hybrid gas generating devices for supplemental safety restraint application are described in Frantom, Hybrid Airbag Inflator Technology, *Airbag Int'l Symposium on Sophisticated Car Occupant Safety, Systems*, (Weinbrenner-Saal, Germany, Nov. 2-3, 1992).

EXAMPLES

[0058] The present invention is further described in the following non-limiting examples. Unless otherwise stated, the compositions are expressed in weight percent.

Example 1

[0059] A quantity (132.4 g) of Co(NH₃)₃(NO₂)₃, prepared according to the teachings of Hagel et al., "The Triamines of Cobalt (III). 1. Geometrical Isomers of Trinitrotriamminecobalt (III)," 9 *Inorganic Chemistry* 1496 (June 1970), was slurried in 35 mL of methanol with 7 g of a 38 percent by weight solution of pyrotechnic grade vinyl acetate/vinyl alcohol polymer resin commonly known as VAAR dissolved

in methyl acetate. The solvent was allowed to partially evaporate. The paste-like mixture was forced through a 20-mesh sieve, allowed to dry to a stiff consistency, and forced through a sieve yet again. The granules resulting were then dried in vacuo at ambient temperature for 12 hours. One-half inch diameter pellets of the dried material were prepared by pressing. The pellets were combusted at several different pressures ranging from 600 to 3,300 psig. The burning rate of the generant was found to be 0.237 inches per second at 1,000 psig with a pressure exponent of 0.85 over the pressure range tested.

Example 2

[0060] The procedure of Example 1 was repeated with 100 g of Co(NH₃)₃(NO₂)₃ and 34 g of 12 percent by weight solution of nylon in methanol. Granulation was accomplished via 10- and 16-mesh screens followed by air drying. The burn rate of this composition was found to be 0.290 inches per second at 1,000 psig with a pressure exponent of 0.74.

Example 3

[0061] In a manner similar to that described in Example 1, 400 g of Co(NH₃)₃(NO₂)₃ was slurried with 219 g of a 12 percent by weight solution of nitrocellulose in acetone. The nitrocellulose contained 12.6 percent nitrogen. The solvent was allowed to partially evaporate. The resulting paste was forced through an 8-mesh sieve followed by a 24-mesh sieve. The resultant granules were dried in air overnight and blended with sufficient calcium stearate mold release agent to provide 0.3 percent by weight in the final product. A portion of the resulting material was pressed into ½-inch diameter pellets and found to exhibit a burn rate of 0.275 inches per second at 1,000 psig with a pressure exponent of 0.79. The remainder of the material was pressed into pellets ⅜-inch diameter by 0.07-inch thickness on a rotary tablet press. The pellet density was determined to be 1.88 g/cc. The theoretical flame temperature of this composition was 2,358° K and was calculated to provide a gas mass fraction of 0.72.

Example 4

[0062] This example discloses the preparation of a reusable stainless steel test fixture used to simulate driver's side gas generators. The test fixture, or simulator, consisted of an igniter chamber and a combustion chamber. The igniter chamber was situated in the center and had 24, 0.10 inch diameter ports exiting into the combustion chamber. The igniter chamber was fitted with an igniter squib. The igniter chamber wall was lined with 0.001 inch thick aluminum foil before -24/+60 mesh igniter granules were added. The outer combustion chamber wall consisted of a ring with nine exit ports. The diameter of the ports was varied by changing rings. Starting from the inner diameter of the outer combustion chamber ring, the combustion chamber was fitted with a 0.004 inch aluminum shim, one wind of 30 mesh stainless steel screen, four winds of a 14 mesh stainless steel screen, a deflector ring, and the gas generant. The generant was held intact in the combustion chamber using a "donut" of 18 mesh stainless steel screen. An additional deflector ring was placed around the outside diameter of the outer combustion chamber wall. The combustion chamber was fitted with a pressure port. The simulator was attached to either a 60 liter

tank or an automotive air bag. The tank was fitted with pressure, temperature, vent, and drain ports. The automotive air bags have a maximum capacity of 55 liters and are constructed with two ½ inch diameter vent ports. Simulator tests involving an air bag were configured such that bag pressures were measured. The external skin surface temperature of the bag was monitored during the inflation event by infrared radiometry, thermal imaging, and thermocouple.

Example 5

[0063] Thirty-seven and one-half grams of the ⅛-inch diameter pellets prepared as described in Example 3 were combusted in an inflator test device vented into a 60 L collection tank as described in Example 4, with the additional incorporation of a second screened chamber containing 2 winds of 30 mesh screen and 2 winds of 18 mesh screen. The combustion produced a combustion chamber pressure of 2,000 psia and a pressure of 39 psia in the 60 L collection tank. The temperature of the gases in the collection tank reached a maximum of 670° K at 20 milliseconds. Analysis of the gases collected in the 60 L tank showed a concentration of nitrogen oxides (NO_x) of 500 ppm and a concentration of carbon monoxide of 1,825 ppm. Total expelled particulate as determined by rinsing the tank with methanol and evaporation of the rinse was found to be 1,000 mg.

Example 6

[0064] The test of Example 4 was repeated except that the 60 L tank was replaced with a 55 L vented bag as typically employed in driver side automotive inflator restraint devices. A combustion chamber pressure of 1,900 psia was obtained with a full inflation of the bag occurring. An internal bag pressure of 2 psig at peak was observed at approximately 60 milliseconds after Ignition. The bag surface temperature was observed to remain below 83° C. which is an improvement over conventional azide-based inflators, while the bag inflation performance is quite typical of conventional systems.

Example 7

[0065] The nitrate salt of copper tetraammine was prepared by dissolving 116.3 g of copper (II) nitrate hemipentahydrate in 230 mL of concentrated ammonium hydroxide and 50 mL of water. Once the resulting warm mixture had cooled to 40° C, one liter of ethanol was added with stirring to precipitate the tetraammine nitrate product. The dark purple-blue solid was collected by filtration, washed with ethanol, and air dried. The product was confirmed to be Cu(NH₃)₄(NO₃)₂ by elemental analysis. The burning rate of this material as determined from pressed 1/2-inch diameter pellets was 0.18 inches per second at 1,000 psig.

Example 8

[0066] The tetraammine copper nitrate prepared in Example 7 was formulated with various supplemental oxidizers and tested for burning rate. In all cases, 10 g of material were slurried with approximately 10 mL of methanol, dried, and pressed into 1/2-inch diameter pellets. Burning rates were measured at 1,000 psig, and the results are shown in the following table.

Copper Tetraammine Nitrate	Oxidizer	Burn Rate (ips)
88%	CuO (6%) Sr(NO ₃) ₂ (6%)	0.13
92%	Sr(NO ₃) ₂ (8%)	0.14
90%	NH ₄ NO ₃ (10%)	0.25
78%	Bi ₂ O ₃ (22%)	0.10
85%	SrO ₂ (15%)	0.18

Example 9

[0067] A quantity of hexaamminecobalt (III) nitrate was prepared by a replacing ammonium chloride with ammonium nitrate in the procedure for preparing of hexaamminecobalt (III) chloride as taught by G. Pass and H. Sutcliffe, *Practical Inorganic Chemistry*, 2nd Ed., Chapman & Hull, New York, 1974. The material prepared was determined to be [Co(NH₃)₆](NO₂)₃ by elemental analysis. A sample of the material was pressed into ½-inch diameter pellets and a burning rate of 0.26 inches per second measured at 2,000 psig.

Example 10

[0068] The material prepared in Example 9 was used to prepare three lots of gas generant containing hexaamminecobalt (III) nitrate as the fuel and ceric ammonium nitrate as the co-oxidizer. The lots differ in mode of processing and the presence or absence of additives. Burn rates were determined from ½ inch diameter burn rate pellets. The results are summarized below:

Formulation	Processing	Burn Rate
12% (NH ₄) ₂ [Ce(NO ₃) ₆]	Dry Mix	0.19 ips at 1690 psi
88% [Co(NH ₃) ₆](NO ₃) ₃		0.20 ips
12% (NH ₄) ₂ [Ce(NO ₃) ₆]	Mixed with	at 1690 psi
88% [Co(NH ₃) ₆](NO ₃) ₃	35% MeOH	0.20 ips
18% (NH ₄) ₂ [Ce(NO ₃) ₆]	Mixed with	at 1690 psi
81% [Co(NH ₃) ₆](NO ₃) ₃	10% H ₂ O	0.20 ips
1% Carbon Black		

Example 11

[0069] The material prepared in Example 9 was used to prepare several 10-g mixes of generant compositions utilizing various supplemental oxidizers. In all cases, the appropriate amount of hexaamminecobalt (III) nitrate and co-oxidizer(s) were blended into approximately 10 mL of methanol, allowed to dry, and pressed into ½-inch diameter pellets. The pellets were tested for burning rate at 1,000 psig, and the results are shown in the following table.

Hexaamminecobalt (III) Nitrate	Co-oxidizer	Burning Rate @ 1,000 psig
60%	CuO (40%)	0.15
70%	CuO (30%)	0.16
83%	CuO (10%) Sr(NO ₃) ₂ (7%)	0.13

-continued

Hexaamminecobalt (III) Nitrate	Co-oxidizer	Burning Rate @ 1,000 psig
88%	Sr(NO ₃) ₂ (12%)	0.14
70%	Bi ₂ O ₃ (30%)	0.10
83%	NH ₄ NO ₃ (17%)	0.15

Example 12

[0070] Binary compositions of hexaamminecobalt (III) nitrate ("HACN") and various supplemental oxidizers were blended in 20 gram batches. The compositions were dried for 72 hours at 200° F. and pressed into ½-inch diameter pellets. Burn rates were determined by burning the ½ inch pellets at different pressures ranging from 1000 to 4000 psi. The results are shown in the following table.

Composition	R _b (ips) at X psi				Temp. ° K.
	1000	2000	3000	4000	
HACN 100/0	0.19	0.28	0.43	0.45	1856
HACN/CuO 90/10	0.26	0.35	0.39	0.44	1861
HACN/Ce(NH ₄) ₂ (NO ₃) ₆ 88/12,	0.16	0.22	0.30	0.38	—
HACN/Co ₂ O ₃ 90/10	0.10	0.21	0.26	0.34	1743
HACN/Co(NO ₃) ₂ , 6H ₂ O 90/10	0.13	0.22	0.35	0.41	1865
HACN/V ₂ O ₅ 85/15	0.12	0.16	0.21	0.30	1802
HACN/Fe ₂ O ₃ 75/25	0.12	0.12	0.17	0.23	1626
HACN/Co ₃ O ₄ 81.5/18.5	0.13	0.20	0.25	0.30	1768
HACN/MnO ₂ 80/20	0.11	0.17	0.22	0.30	—
HACN/Fe(NO ₃) ₂ , 9H ₂ O 90/10	0.14	0.22	0.31	0.48	—
HACN/Al(NO ₃) ₂ , 6H ₂ O 90/10	0.10	0.18	0.26	0.32	1845
HACN/Mg(NO ₃) ₂ , 2H ₂ O 90/10	0.16	0.24	0.32	0.39	2087

Example 13

[0071] A processing method was devised for preparing small parallelepipeds ("pps.") of gas generant on a laboratory scale. The equipment necessary for forming and cutting the pps. included a cutting table, a roller and a cutting device. The cutting table consisted of a 9 inch×18 inch sheet of metal with 0.5 inch wide paper spacers taped along the length-wise edges. The spacers had a cumulative height 0.043 inch. The roller consisted of a 1 foot long, 2 inch diameter cylinder of teflon. The cutting device consisted of a shaft, cutter blades and spacers. The shaft was a ¼ inch bolt upon which a series of seventeen ¾ inch diameter, 0.005 inch thick stainless steel washers were placed as cutter blades. Between each cutter blade, four ⅔ inch diameter, 0.020 inch thick brass spacer washers were placed and the series of washers were secured by means of a nut. The repeat distance between the circular cutter blades was 0.085 inch.

[0072] A gas generant composition containing a water-soluble binder was dry-blended and then 50-70 g batches

were mixed on a Spex mixer/mill for five minutes with sufficient water so that the material when mixed had a dough-like consistency.

[0073] A sheet of velostat plastic was taped to the cutting table and the dough ball of generant mixed with water was flattened by hand onto the plastic. A sheet of polyethylene plastic was placed over the generant mix. The roller was positioned parallel to the spacers on the cutting table and the dough was flattened to a width of about 5 inches. The roller was then rotated 90 degrees, placed on top of the spacers, and the dough was flattened to the maximum amount that the cutter table spacers would allow. The polyethylene plastic was peeled carefully off the generant and the cutting device was used to cut the dough both lengthwise and widthwise.

[0074] The velostat plastic sheet upon which the generant had been rolled and cut was unfastened from the cutting table and placed lengthwise over a 4 inch diameter cylinder in a 135° F. convection oven. After approximately 10 minutes, the sheet was taken out of the oven and placed over a ½ inch diameter rod so that the two ends of the plastic sheet formed an acute angle relative to the rod. The plastic was moved back and forth over rod so as to open up the cuts between the parallelepipeds ("pps."). The sheet was placed widthwise over the 4 inch diameter cylinder in the 135° F. convection oven and allowed to dry for another 5 minutes. The cuts were opened between the pps. over the ½ inch diameter rod as before. By this time, it was quite easy to detach the pps. from the plastic. The pps. were separated from each other further by rubbing them gently in a pint cup or on the screens of a 12 mesh sieve. This method breaks the pps. into singlets with some remaining doublets. The doublets were split into singlets by use of a razor blade. The pps. were then placed in a convection oven at 165-225° F. to dry them completely. The crush strengths (on edge) of the pps. thus formed were typically as great or greater than those of ⅓ diameter pellets with a ¼ inch convex radius of curvature and a 0.070 inch maximum height which were formed on a rotary press. This is noteworthy since the latter are three times as massive.

Example 14

[0075] A gas generating composition was prepared utilizing hexaamminecobalt (III) nitrate, [(NH₃)₆Co](NO₃)₃, powder (78.07%, 39.04 g), ammonium nitrate granules (19.93%, 9.96 g), and ground polyacrylamide, MW 15 million (2.00%, 1.00 g). The ingredients were dry-blended in a Spex mixer/mill for one minute. Deionized water (12% of the dry weight of the formulation, 6 g) was added to the mixture which was blended for an additional five minutes on the Spex mixer/mill. This resulted in material with a dough-like consistency which was processed into parallelepipeds (pps.) as in Example 13. Three additional batches of generant were mixed and processed similarly. The pps. from the four batches were blended. The dimensions of the pps. were 0.052 inch×0.072 inch×0.084 inch. Standard deviations on each of the dimensions were on the order of 0.010 inch. The average weight of the pps. was 6.62 mg. The bulk density, density as determined by dimensional measurements, and density as determined by solvent displacement were determined to be 0.86 g/cc, 1.28 g/cc, and 1.59 g/cc, respectively. Crush strengths of 1.7 kg (on the narrowest edge) were measured with a standard deviation of 0.7 kg. Some of the pps. were pressed into ½ inch diameter pellets weighing

approximately three grams. From these pellets the burn rate was determined to be 0.13 ips at 1000 psi with a pressure exponent of 0.78.

Example 15

[0076] A simulator was constructed according to Example 4. Two grams of a stoichiometric blend of Mg/Sr(NO₃)₂/nylon igniter granules were placed into the igniter chamber. The diameter of the ports exiting the outer combustion chamber wall were $\frac{3}{16}$ inch. Thirty grams of generant described in Example 14 in the form of parallelepipeds were secured in the combustion chamber. The simulator was attached to the 60 L tank described in Example 4. After ignition, the combustion chamber reached a maximum pressure of 2300 psia in 17 milliseconds, the 60 L tank reached a maximum pressure of 34 psia and the maximum tank temperature was 640° K. The NO_x, CO and NH₃ levels were 20, 380, and 170 ppm, respectively, and 1600 mg of particulate were collected from the tank.

Example 16

[0077] A simulator was constructed with the exact same igniter and generant type and charge weight as in Example 15. In addition the outer combustion chamber exit port diameters were identical. The simulator was attached to an automotive safety bag of the type described in Example 4. After ignition, the combustion chamber reached a maximum pressure of 2000 psia in 15 milliseconds. The maximum pressure of the inflated air bag was 0.9 psia. This pressure was reached 18 milliseconds after ignition. The maximum bag surface temperature was 67° C.

Example 17

[0078] A gas generating composition was prepared utilizing hexaamminecobalt (III) nitrate powder (76.29%, 76.29 g), ammonium nitrate granules (15.71%, 15.71 g, Dynamit Nobel, granule size: <350 micron), cupric oxide powder formed pyrometallurgically (5.00%, 5.00 g) and guar gum (3.00%, 3.00 g). The ingredients were dry-blended in a Spex mixer/mill for one minute. Deionized water (18% of the dry weight of the formulation, 9 g) was added to 50 g of the mixture which was blended for an additional five minutes on the Spex mixer/mill. This resulted in material with a dough-like consistency which was processed into parallelepipeds (pps.) as in Example 13. The same process was repeated for the other 50 g of dry-blended generant and the two batches of pps. were blended together. The average dimensions of the blended pps. were 0.070 inch×0.081 inch×0.088 inch. Standard deviations on each of the dimensions were on the order of 0.010 inch. The average weight of the pps. was 9.60 mg. The bulk density, density as determined by dimensional measurements, and density as determined by solvent displacement were determined to be 0.96 g/cc, 1.17 g/cc, and 1.73 g/cc, respectively. Crush strengths of 5.0 kg (on the narrowest edge) were measured with a standard deviation of 2.5 kg. Some of the pps. were pressed into $\frac{1}{2}$ inch diameter pellets weighing approximately three grams. From these pellets the burn rate was determined to be 0.20 ips at 1000 psi with a pressure exponent of 0.67.

Example 18

[0079] A simulator was constructed according to Example 4. One gram of a stoichiometric blend of Mg/Sr(NO₃)₂/

nylon and two grams of slightly over-oxidized B/KNO₃ igniter granules were blended and placed into the igniter chamber. The diameter of the ports exiting the outer combustion chamber wall were 0.166 inch. Thirty grams of generant described in Example 17 in the form of parallelepipeds were secured in the combustion chamber. The simulator was attached to the 60 L tank described in Example 4. After ignition, the combustion chamber reached a maximum pressure of 2540 psia in 8 milliseconds, the 60 L tank reached a maximum pressure of 36 psia and the maximum tank temperature was 600° K. The NO_x, CO, and NH₃ levels were 50, 480, and 800 ppm, respectively, and 240 mg of particulate were collected from the tank.

Example 19

[0080] A simulator was constructed with the exact same igniter and generant type and charge weight as in Example 18. In addition the outer combustion chamber exit port diameters were identical. The simulator was attached to an automotive safety bag of the type described in Example 4. After ignition, the combustion chamber reached a maximum pressure of 2700 psia in 9 milliseconds. The maximum pressure of the inflated air bag was 2.3 psig. This pressure was reached 30 milliseconds after ignition. The maximum bag surface temperature was 73° C.

Example 20

[0081] A gas generating composition was prepared utilizing hexaamminecobalt (III) nitrate powder (69.50%, 347.5 g), copper (II) trihydroxy nitrate, [Cu₂(OH)₃NO₃], powder (21.5%, 107.5 g), 10 micron RDX (5.00%, 25 g), 26 micron potassium nitrate (1.00%, 5 g) and guar gum (3.00%, 3.00 g). The ingredients were dry-blended with the assistance of a 60 mesh sieve. Deionized water (23% of the dry weight of the formulation, 15 g) was added to 65 g of the mixture which was blended for an additional five minutes on the Spex mixer/mill. This resulted in material with a dough-like consistency which was processed into parallelepipeds (pps.) as in Example 13. The same process was repeated for two additional 65 g batches of dry-blended generant and the three batches of pps. were blended together. The average dimensions of the pps. were 0.057 inch×0.078 inch×0.084 inch. Standard deviations on each of the dimensions were on the order of 0.010 inch. The average weight of the pps. was 7.22 mg. The bulk density, density as determined by dimensional measurements, and density as determined by solvent displacement were determined to be 0.96 g/cc, 1.23 g/cc, and 1.74 g/cc, respectively. Crush strengths of 3.6 kg (on the narrowest edge) were measured with a standard deviation of 0.9 kg. Some of the pps. were pressed into 1/2 inch diameter pellets weighing approximately three grams. From these pellets the burn rate was determined to be 0.27 ips at 1000 psi with a pressure exponent of 0.51.

Example 21

[0082] A simulator was constructed according to Example 4. 1.5 grams of a stoichiometric blend of Mg/Sr(NO₃)₂/nylon and 1.5 grams of slightly over-oxidized B/KNO₃ igniter granules were blended and placed into the igniter chamber. The diameter of the ports exiting the outer combustion chamber wall were 0.177 inch. Thirty grams of generant described in Example 20 in the form of parallelepipeds were secured in the combustion chamber. The

simulator was attached to the 60 L tank described in Example 4. After ignition, the combustion chamber reached a maximum pressure of 3050 psia in 14 milliseconds. The NO_x , CO, and NH_3 levels were 25, 800, and 90 ppm, respectively, and 890 mg of particulate were collected from the tank.

Example 22

[0083] A gas generating composition was prepared utilizing hexaamminecobalt (III) nitrate powder (78.00%, 457.9 g), copper (II) trihydroxy nitrate powder (19.00%, 111.5 g), and guar gum (3.00%, 17.61 g). The ingredients were dry-blended and then mixed with water (32.5% of the dry weight of the formulation, 191 g) in a Baker-Perkins pint mixer for 30 minutes. To a portion of the resulting wet cake (220 g), 9.2 additional grams of copper (II) trihydroxy nitrate and 0.30 additional grams of guar gum were added as well as 0.80 g of carbon black (Monarch 1100). This new formulation was blended for 30 minutes on a Baker-Perkins mixer. The wet cake was placed in a ram extruder with a barrel diameter of 2 inches and a die orifice diameter of $\frac{3}{32}$ inch (0.09038 inch). The extruded material was cut into lengths of about one foot, allowed to dry under ambient conditions overnight, placed into an enclosed container holding water in order to moisten and thus soften the material, chopped into lengths of about 0.1 inch and dried at 165° F. The dimensions of the resulting extruded cylinders were an average length of 0.113 inches and an average diameter of 0.091 inches. The bulk density, density as determined by dimensional measurements, and density as determined by solvent displacement were 0.86 g/cc, 1.30 g/cc, and 1.61 g/cc, respectively. Crush strengths of 2.1 and 4.1 kg were measured on the circumference and axis, respectively. Some of the extruded cylinders were pressed into $\frac{1}{2}$ inch diameter pellets weighing approximately three grams. From these pellets the burn rate was determined to be 0.22 ips at 1000 psi with a pressure exponent of 0.29.

Example 23

[0084] Three simulators were constructed according to Example 4. 1.5 grams of a stoichiometric blend of $\text{Mg}/\text{Sr}(\text{NO}_3)_2/\text{nylon}$ and 1.5 grams of slightly over-oxidized B/KNO_3 igniter granules were blended and placed into the igniter chambers. The diameter of the ports exiting the outer combustion chamber wall were 0.177 inch, 0.166 inch, and 0.152 inch, respectively. Thirty grams of generant described in Example 22 in the form of extruded cylinders were secured in each of the combustion chambers. The simulators were, in succession, attached to the 60 L tank described in Example 4. After ignition, the combustion chambers reached a maximum pressure of 1585, 1665, and 1900 psia, respectively. Maximum tank pressures were 32, 34, and 35 psia, respectively. The NO_x levels were 85, 180, and 185 ppm whereas the CO levels were 540, 600, and 600 ppm, respectively. NH_3 levels were below 2 ppm. Particulate levels were 420, 350, and 360 mg, respectively.

Example 24

[0085] The addition of small amounts of carbon to gas generant formulations have been found to improve the crush strength of parallelepipeds and extruded pellets formed as in Example 13 or Example 22. The following table summarizes the crush strength enhancement with the addition of carbon

to a typical gas generant composition within the scope of the present invention. All percentages are expressed as weight percent:

TABLE 3

Crush Strength Enhancement with Addition of Carbon					
% HACN	% CTN	% Guar	% Carbon	Form	Strength
65.00	30.00	5.00	0.00	EP	2.7 kg
64.75	30.00	4.50	0.75	EP	5.7 kg
78.00	19.00	3.00	0.00	pps.	2.3 kg
72.90	23.50	3.00	0.60	pps.	5.8 kg
78.00	19.00	3.00	0.00	EP	2.3 kg
73.00	23.50	3.00	0.50	EP	4.1 kg

HACN = hexaamminecobalt (III) nitrate, $[(\text{NH}_3)_6\text{Co}](\text{NO}_3)_3$ (Thiokol)

CTN = copper (II) trihydroxy nitrate, $[\text{Cu}_2(\text{OH})_3\text{NO}_3]$ (Thiokol)

Guar = guar gum (Aldrich)

Carbon = "Monarch 1100" carbon black (Cabot)

EP = extruded pellet (see Example 22)

pps. = parallelepipeds (see Example 13)

strength = crush strength of pps. or extruded pellets in kilograms.

Example 25

[0086] Hexaamminecobalt (III) nitrate was pressed into four gram pellets with a diameter of $\frac{1}{2}$ inch. One half of the pellets were weighed and placed in a 95° C oven for 700 hours. After aging, the pellets were weighed once again. No loss in weight was observed. The burn rate of the pellets held at ambient temperature was 0.16 ips at 1000 psi with a pressure exponent of 0.60. The burn rate of the pellets held at 95° C. for 700 hours was 0.15 at 1000 psi with a pressure exponent of 0.68.

Example 26

[0087] A gas generating composition was prepared utilizing hexaamminecobalt (III) nitrate powder (76.00%, 273.6 g), copper (II) trihydroxy nitrate powder (16.00%, 57.6 g), 26 micron potassium nitrate (5.00%, 18.00 g), and guar gum (3.00%, 10.8 g). Deionized water (24.9% of the dry weight of the formulation, 16.2 g) was added to 65 g of the mixture which was blended for an additional five minutes on the Spex mixer/mill. This resulted in material with a dough-like consistency which was processed into parallelepipeds (pps.) as in Example 13. The same process was repeated for the other 50-65 g batches of dry-blended generant and all the batches of pps. were blended together. The average dimensions of the pps. were 0.065 inch \times 0.074 inch \times 0.082 inch. Standard deviations on each of the dimensions were on the order of 0.005 inch. The average weight of the pps. was 7.42 mg. The bulk density, density as determined by dimensional measurements, and density as determined by solvent displacement were determined to be 0.86 g/cc, 1.15 g/cc, and 1.68 g/cc, respectively. Crush strengths of 2.1 kg (on the narrowest edge) were measured with a standard deviation of 0.3 kg. Some of the pps. were pressed into ten, one half inch diameter pellets weighing approximately three grams. Approximately 60 g of pps. and five $\frac{1}{2}$ inch diameter pellets were placed in an oven held at 107° C. After 450 hours at this temperature, 0.25% and 0.41% weight losses were observed for the pps. and pellets, respectively. The remainder of the pps. and pellets were stored under ambient conditions. Burn rate data were obtained from both sets of pellets and are summarized in Table 4.

TABLE 4

<u>Burn Rate Comparison Before and After Accelerated Aging</u>		
Storage Conditions	Burn, Rate at 1000 psi	Pressure Exponent
24-48 Hours @ Ambient	0.15 ips.	0.72
450 Hours @ 107° C.	0.15 ips	0.70

Example 27

[0088] Two simulators were constructed according to Example 4. In each igniter chamber, a blended mixture of 1.5 g of a stoichiometric blend of Mg/Sr(NO₃)₂/nylon and 1.5 grams of slightly over-oxidized B/KNO₃ igniter granules were placed. The diameter of the ports exiting the outer combustion chamber wall in each simulator were 0.177 inch. Thirty grams of ambient aged generant described in Example 26 in the form of parallelepipeds were secured in the combustion chamber of one simulator whereas thirty grams of generant pps. aged at 107° C. were placed in the other combustion chamber. The simulators were attached to the 60 L tank described in Example 4. Test fire results are summarized in Table 5 below.

TABLE 5

<u>Test-Fire Results for Aged Generant</u>							
Aging Temp.	Comb. Press. (psia)	Tank Press. (psia)	Tank Temp. (° K.)	NH ₃ Level (ppm)	CO Level (ppm)	NO _x Level (ppm)	Part. Level (mg)
Amb.	2171	31.9	628	350	500	80	520
107° C.	2080	31.6	629	160	500	100	480

Example 28

[0089] A mixture of 2Co(NH₃)₃(NO₂)₃ and Co(NH₃)₄(NO₂)₂ Co(NH₃)₂(NO₂)₄ was prepared and pressed in a pellet having a diameter of approximately 0.504 inches. The complexes were prepared within the scope of the teachings of the Hagel, et al. reference identified above. The pellet was placed in a test bomb, which was pressurized to 1,000 psi with nitrogen gas.

[0090] The pellet was ignited with a hot wire and burn rate was measured and observed to be 0.38 inches per second. Theoretical calculations indicated a flame temperature of 1805° C. From theoretical calculations, it was predicted that the major reaction products would be solid CoO and gaseous reaction products. The major gaseous reaction products were predicted to be as follows:

Product	Volume %
H ₂ O	57.9
N ₂	38.6
O ₂	3.1

Example 29

[0091] A quantity of Co(NH₃)₃(NO₂)₃ was prepared according to the teachings of Example 1 and tested using

differential scanning calorimetry. It was observed that the complex produced a vigorous exotherm at 200° C.

Example 30

[0092] Theoretical calculations were undertaken for Co(NH₃)₃(NO₂)₃. Those calculations indicated a flame temperature of about 2,000° K and a gas yield of about 1.75 times that of a conventional sodium azide gas generating compositions based on equal volume of generating composition ("performance ratio"). Theoretical calculations were also undertaken for a series of gas generating compositions. The composition and the theoretical performance data is set forth below in Table 6.

TABLE 6

Gas Generant	Ratio	Temp. (C.°)	Perf. Ratio
Co(NH ₃) ₃ (NO ₂) ₃	—	1805	1.74
NH ₄ [Co(NH ₃) ₂ (NO ₂) ₄]	—	1381	1.81
NH ₄ [Co(NH ₃) ₂ (NO ₂) ₄]B	99/1	1634	1.72
Co(NH ₃) ₆ (NO ₃) ₃	—	1585	2.19
[Co(NH ₃) ₅ (NO ₃)](NO ₃) ₂	—	1637	2.00
[Fe(N ₂ H ₄) ₃](NO ₃) ₂ /Sr(NO ₃) ₂	87/13	2345	1.69
[Co(NH ₃) ₆](ClO ₄) ₃ /CaH ₂	86/14	2577	1.29
[Co(NH ₃) ₃ (NO ₂)](NO ₃) ₂	—	1659	2.06

[0093] Performance ratio is a normalized relation to a unit volume of azide-based gas generant. The theoretical gas yield for a typical sodium azide-based gas generant (68 wt. % NaN₃; 30 wt % of MoS₂; 2 wt % of S) is about 0.85 g gas/cc NaN₃ generant.

Example 31

[0094] Theoretical calculations were conducted on the reaction of [Co(NH₃)₆](ClO₄)₃ and CaH₂ as listed in Table 6 to evaluate its use in a hybrid gas generator. If this formulation is allowed to undergo combustion in the presence of 6.80 times its weight in argon gas, the flame temperature decreases from 2577° C. to 1085° C., assuming 100% efficient heat transfer. The output gases consist of 86.8% by volume argon, 1600 ppm by volume hydrogen chloride, 10.2% by volume water, and 2.9% by volume nitrogen. The total slag weight would be 6.1 % by mass.

Example 32

[0095] Pentaamminecobalt (III) nitrate complexes were synthesized which contain a common ligand in addition to NH₃. Aquopentaamminecobalt (III) nitrate and pentaamminecarbonatocobalt (III) nitrate were synthesized according to *Inorg. Syn.*, vol. 4, p. 171 (1973). Pentaamminehydroxocobalt (III) nitrate was synthesized according to H. J. S. King, *J. Chem. Soc.*, p. 2105 (1925) and O. Schmitz, et al., *Zeit. Anorg. Chem.*, vol. 300, p. 186 (1959). Three lots of gas generant were prepared utilizing the pentaamminecobalt (III) nitrate complexes described above. In all cases guar gum was added as a binder. Copper (II) trihydroxy nitrate, [Cu₂(OH)₃NO₃], was added as the co-oxidizer where needed. Burn rates were determined from ½ inch diameter burn rate pellets. The results are summarized below in Table 7.

TABLE 7

Formulations Containing [Co (NH ₃) ₅ X](NO ₃) _y		
Formulation	% H ₂ O Added	Burn Rate
97.0% [Co(NH ₃) ₅ (H ₂ O)](NO ₃) ₃ 3% guar	27%	0.16 ips at 1000 psi
68.8% [Co(NH ₃) ₅ (OH)](NO ₃) ₂ 28.2% [Cu ₂ (OH) ₃ NO ₃] 3.0% guar	55%	0.14 ips at 1000 psi
48.5 [Co(NH ₃) ₅ (CO ₃)](NO ₃) 48.5% [Cu ₂ (OH) ₃ NO ₃] 3.0% guar	24%	0.06 ips at 4150 psi

SUMMARY

[0096] In summary the present invention provides gas generating materials that overcome some of the limitations of conventional azide-based gas generating compositions. The complexes of the present invention produce nontoxic gaseous products including water vapor, oxygen, and nitrogen. Certain of the complexes are also capable of efficient decomposition to a metal or metal oxide, and nitrogen and water vapor. Finally, reaction temperatures and burn rates are within acceptable ranges.

[0097] The invention may be embodied in other specific forms without departing from its essential characteristics. The described embodiments are to be considered in all respects only as illustrative and not restrictive. The scope of the invention is, therefore, indicated by the appended claims rather than by the foregoing description.

1. A gas generating composition, comprising:

at least one metal complex comprising a metal cation, a hydrazine ligand, and sufficient oxidizing anion to balance the charge of the metal cation, wherein the gas generating composition comprises about 48.5% to less than about 100% by weight of the at least one metal complex.

2. The gas generating composition of claim 1, wherein the at least one metal complex is selected from the group consisting of metal nitrite hydrazines, metal nitrate hydrazines, metal perchlorate hydrazines, and mixtures thereof.

3. The gas generating composition of claim 1, wherein the metal cation is a transition metal, alkaline earth metal, metalloid, or lanthanide metal cation.

4. The gas generating composition of claim 1, wherein the metal cation is selected from the group consisting of cobalt, magnesium, manganese, nickel, titanium, copper, chromium, zinc, tin, rhodium, iridium, ruthenium, palladium and platinum.

5. The gas generating composition of claim 1, wherein the oxidizing anion is selected from the group consisting of nitrate, nitrite, chlorate, perchlorate, peroxide, and superoxide.

6. The gas generating composition of claim 1, wherein the oxidizing anion is free of carbon.

7. The gas generating composition of claim 1, wherein the at least one metal complex comprises at least one common ligand in addition to the hydrazine ligand, wherein the at least one common ligand is selected from the group consisting of aquo (H₂O), hydroxo (OH), perhydroxo (O₂H), peroxy (O₂), carbonato (CO₃), carbonyl (CO), oxalato

(C₂O₄), nitrosyl (NO), cyano (CN), isocyanato (NC), isothiocyanato (NCS), thiocyanato (SCN), amido (NH₂), imido (NH), sulfato (SO₄), chloro (Cl), fluoro (F), phosphato (PO₄), and ethylenediaminetetraacetic acid (EDTA) ligands.

8. The gas generating composition of claim 1, wherein the at least one metal complex includes a common counter ion in addition to the oxidizing anion, wherein the common counter ion is selected from the group consisting of hydroxide (OH⁻), chloride (Cl⁻), fluoride (F⁻), cyanide (CN⁻), thiocyanate (SCN⁻), carbonate (CO₃⁻²), sulfate (SO₄⁻²), phosphate (PO₄⁻³), oxalate (C₂O₄⁻²), borate (BO₄⁻⁵), and ammonium (NH₄⁺) counter ions.

9. The gas generating composition of claim 1, further comprising a co-oxidizer.

10. The gas generating composition of claim 9, wherein the co-oxidizer is selected from the group consisting of alkali perchlorates, alkaline earth perchlorates, lanthanide perchlorates, ammonium perchlorates, alkali chlorates, alkaline earth chlorates, lanthanide chlorates, ammonium chlorates, alkali peroxides, alkaline earth peroxides, lanthanide peroxides, ammonium peroxides, alkali nitrites, alkaline earth nitrites, lanthanide nitrites, ammonium nitrites, alkali nitrates, alkali earth nitrates, lanthanide nitrates, and ammonium nitrates.

11. The gas generating composition of claim 9, wherein the co-oxidizer is selected from the group consisting of metal oxides, metal hydroxides, metal peroxides, metal oxide hydrates, metal oxide hydroxides, metal hydrous oxides, basic metal carbonates, basic metal nitrates, and mixtures thereof.

12. The gas generating composition of claim 9, wherein the co-oxidizer is selected from the group consisting of oxides of copper, cobalt, manganese, tungsten, bismuth, molybdenum, and iron.

13. The gas generating composition of claim 9, wherein the co-oxidizer is selected from the group consisting of CuO, Co₂O₃, Co₃O₄, CoFe₂O₄, Fe₂O₃, MoO₃, Bi₂MoO₆, Bi₂O₃, Fe(OH)₃, Co(OH)₃, Co(OH)₂, Ni(OH)₂, Cu(OH)₂, Zn(OH)₂, Fe₂O₃.xH₂O, SnO₂.xH₂O, MoO₃.H₂O, CoO(OH)₂, FeO(OH)₂, MnO(OH)₂, MnO(OH)₃, CuCO₃.Cu(OH)₂ (malachite), 2Co(CO₃)₂.3Co(OH)₂.H₂O, Co_{0.69}Fe_{0.34}(CO₃)_{0.2}(OH)₂, Na₃[Co(CO₃)₃].3H₂O, Zn₂(CO₃)(OH)₂, Bi₂Mg(CO₃)₂(OH)₄, Fe(CO₃)_{0.12}(OH)_{2.76}, Cu_{1.54}Zn_{0.46}(CO₃)(OH)₂, Co_{0.49}Cu_{0.51}(CO₃)_{0.43}(OH)_{1.1}, Ti₃Bi₄(CO₃)₂(OH)₂O₉(H₂O)₂, (BiO)₂CO₃, Cu₂(OH)₃NO₃, Co₂(OH)₃NO₃, CuCo(OH)₃NO₃, Zn₂(OH)₃NO₃, Zn₂(OH)₂NO₃, Mn(OH)₂NO₃, Fe₄(OH)₁₁NO₃.2H₂O, Mo(NO₃)₂O₂, BiONO₃.H₂O, and Ce(OH)(NO₃)₃.3H₂O.

14. The gas generating composition of claim 9, wherein the co-oxidizer is present in an amount of from 5% to 50% by weight of the gas generating composition.

15. The gas generating composition of claim 1, further comprising a binder.

16. The gas generating composition of claim 15, wherein the binder is selected from the group consisting of naturally occurring gums, polyacrylic acids, and polyacrylamides.

17. The gas generating composition of claim 15, wherein the binder comprises guar gum or acacia gum.

18. The gas generating composition of claim 15, wherein the binder is selected from the group consisting of nitrocellulose, VAAR (vinyl acetate vinyl alcohol resin), and nylon.

19. The gas generating composition of claim 15, wherein the binder has a concentration in the gas generating composition of at least 0.1% by weight.

20. The gas generating composition of claim 15, wherein the binder has a concentration in the gas generating composition from 0.5% to 10% by weight.

21. The gas generating composition of claim 1, wherein the at least one metal complex is $Zn(N_2H_4)_3(NO_3)_2$ (tris-hydrazine zinc nitrate), $Mg(N_2H_4)_2(ClO_4)_2$ (bis-hydrazine magnesium perchlorate), or $Pt(NO_2)_2(NH_2NH_2)_2$ (bis-hydrazine platinum(II) nitrite).

22. The gas generating composition of claim 1, further comprising carbon powder present in an amount from 0.1% to 6% by weight of the gas generating composition.

23. The gas generating composition of claim 1, wherein the gas generating composition is in the form of pellets or granules.

24. The gas generating composition of claim 1, wherein the gas generating composition comprises at least about 60% by weight of the at least one metal complex.

25. The gas generating composition of claim 1, wherein the gas generating composition comprises at least about 65% by weight of the at least one metal complex.

26. The gas generating composition of claim 1, wherein the gas generating composition comprises about 50% to about 80% by weight of the at least one metal complex.

27. The gas generating composition of claim 1, further comprising at least one additive selected from the group consisting of burn rate modifiers, slag formers, release agents, coolants and NO_x reducing agents.

28. A gas generating device, comprising:

a gas generating composition comprising at least one metal complex of a transition metal cation or alkaline earth metal cation, a hydrazine ligand, and sufficient oxidizing anion to balance the charge of the metal cation, such that when the at least one metal complex combusts, a mixture of gases containing nitrogen gas and water vapor is produced; and

an igniter to ignite the gas generating composition.

29. The gas generating device of claim 28, wherein the igniter comprises an igniter composition that includes a mixture of $Mg/Sr(NO_3)_2$ /nylon and B/KNO_3 .

30. An air bag system for a vehicle comprising:

a collapsed, inflatable air bag;

a gas generating device connected to the collapsed, inflatable air bag for inflating the collapsed, inflatable air bag, wherein the gas generating device includes a gas generating composition comprising at least one metal complex of a transition metal cation, a hydrazine ligand, and sufficient oxidizing anion to balance the charge of the transition metal cation; and

an igniter to ignite the gas generating composition.

31. The air bag system of claim 30, wherein the gas generating composition comprises from 48.5% to less than about 100% by weight of the at least one metal complex.

32. The air bag system of claim 30, wherein the gas generating composition comprises the at least one metal complex, at least one member selected from the group consisting of a water-soluble binder and carbon powder in an amount of 0.1% to 6% of the gas generating composition, and less than 50% by weight of an inorganic co-oxidizer.

33. A vehicle equipped with a supplemental restraint system, the supplemental restraint system including an air bag system which comprises:

a collapsed, inflatable air bag;

a gas generating device connected to the collapsed, inflatable air bag for inflating the collapsed, inflatable air bag, wherein the gas generating device contains a gas generating composition comprising at least one metal complex of a transition metal cation, a hydrazine ligand, and sufficient oxidizing anion to balance the charge of the transition metal cation; and

an igniter to ignite the gas generating composition.

34. The vehicle of claim 33, wherein the gas generating composition further comprises at least one of a binder and carbon powder, wherein the crush strength of the gas generating composition is increased compared to the gas generating composition without the carbon powder.

35. The vehicle of claim 33, wherein the gas generating composition comprises about 48.5% by weight to less than 100% by weight of the at least one metal complex.

36. The vehicle of claim 33, wherein the gas generating composition further comprises at least one of a binder and carbon powder in an amount of 0.1% to 6% by weight of the gas generating composition.

37. The vehicle of claim 33, wherein the gas generating composition comprises the at least one metal complex, at least one member selected from the group consisting of a binder and carbon powder in an amount of 0.1 to 6% by weight, a secondary fuel, less than 50% by weight of an inorganic co-oxidizer, and at least one additive selected from the group consisting of burn rate modifiers, slag formers, release agents, coolants, and NO_x reducing agents.

38. A method of inflating an inflatable air bag or balloon comprising:

generating substantially non-toxic gases by combusting an at least essentially azide-free gas generating composition comprising at least one metal complex having a transition metal cation or alkaline earth metal cation and at least one neutral ligand comprised of ammonia, and sufficient oxidizing anion to balance the charge of the metal cation, wherein when the at least essentially azide-free gas generating composition combusts, a substantially non-toxic mixture of gases comprising nitrogen gas and water vapor is produced; and

inflating the inflatable air bag or balloon with the substantially non-toxic mixture of gases.

39. The method of claim 38, wherein the metal cation is selected from the group consisting of manganese, magnesium, cobalt, and zinc.

40. The method of claim 38, wherein the at least essentially azide-free gas generating composition further comprises an oxidizing agent and wherein the oxidizing agent is other than a metal ammonia complex and is at least one member selected from the group consisting of nitrates, nitrites, chlorates, perchlorates, peroxides, and metal oxides.

41. The method of claim 38, wherein the at least essentially azide-free gas generating composition further comprises a fuel.

42. The method according to claim 38, wherein the at least essentially azide-free gas generating composition is in the form of pellets or granules.

43. The method of claim 38, wherein the at least essentially azide-free gas generating composition further comprises a binder in an amount of 0.5 to 12% by weight of the at least essentially azide-free gas generating formulation.

44. The method of claim 43, wherein the binder is selected from the group consisting of naturally occurring gums, polyacrylic acids, and polyacrylamides.

45. The method of claim 43, wherein the binder is selected from the group consisting of nitrocellulose, VAAR, and nylon.

46. The method of claim 43, wherein the binder comprises guar gum or acacia gum.

47. The method of claim 38, wherein the at least essentially azide-free gas generating composition further comprises carbon powder in an amount of 0.1 % to 6% by weight of the at least essentially azide-free gas generating composition.

48. The method of claim 38, wherein the at least essentially azide-free gas generating composition further comprises at least one additive selected from the group consisting of burn rate modifiers, slag formers, release agents, coolants, and NO_x reducing agents.

49. The method of claim 38, wherein the at least essentially azide-free gas generating composition comprises at least about 60% by weight of the at least one metal complex.

50. The method of claim 38, wherein the at least essentially azide-free gas generating composition comprises at least about 65% by weight of the at least one metal complex.

51. The method of claim 38, wherein the at least essentially azide-free gas generating composition comprises at least about 50% by weight but less than 100% by weight of the at least one metal complex.

52. The method of claim 38, wherein the at least essentially azide-free gas generating composition comprises at least about 50% to about 80% by weight of the at least one metal complex.

53. The method of claim 38, wherein combustion of the at least one metal complex is initiated by heat.

54. The method of claim 38, wherein the at least one metal complex is selected from the group consisting of a metal nitrite ammine, a metal nitrate hydrazine, and a metal perchlorate ammine.

55. The method of claim 38, wherein the transition metal cation or the alkaline earth metal cation is selected from the group consisting of magnesium, manganese, nickel, titanium, copper, chromium, zinc, rhodium, iridium, ruthenium, palladium, and platinum.

56. The method of claim 38, wherein the oxidizing anion is selected from the group consisting of nitrate, nitrite, chlorate, perchlorate, peroxide, superoxide, and mixtures thereof.

57. The method of claim 38, wherein the oxidizing anion and the at least one neutral ligand are free of carbon.

58. The method of claim 38, wherein the at least one metal complex includes at least one other common ligand in addition to the at least one neutral ligand and wherein the at least one common ligand is selected from the group con-

sisting of aquo (H_2O), hydroxo (OH), perhydroxo (O_2H), peroxy (O_2), carbonato (CO_3), carbonyl (CO), oxalato (C_2O_4), nitrosyl (NO), cyano (CN), isocyanato (NC), isothiocyanato (NCS), thiocyanato (SCN), amido (NH_2), imido (NH), sulfato (SO_4), chloro (Cl), fluoro (F), phosphato (PO_4), and ethylenediaminetetraacetic acid (EDTA) ligands.

59. The method of claim 38, wherein the at least one metal complex includes a common counter ion in addition to the oxidizing anion and wherein the common counter ion is selected from the group consisting of hydroxide (OH^-), chloride (Cl^-), fluoride (F^-), cyanide (CN^-), thiocyanate (SCN^-), carbonate (CO_3^{-2}), sulfate (SO_4^{-2}), phosphate (PO_4^{-3}), oxalate ($\text{C}_2\text{O}_4^{-2}$), borate (BO_4^{-3}), and ammonium (NH_4^+) counter ions.

60. The method of claim 38, wherein the gas generating composition further comprises a co-oxidizer.

61. The method of claim 60, wherein the co-oxidizer is selected from the group consisting of alkali perchlorates, alkaline earth perchlorates, lanthanide perchlorates, ammonium perchlorates, alkali chlorates, alkaline earth chlorates, lanthanide chlorates, ammonium chlorates, alkali peroxides, alkaline earth peroxides, lanthanide peroxides, ammonium peroxides, alkali nitrites, alkaline earth nitrites, lanthanide nitrites, ammonium nitrites, alkali nitrates, alkali earth nitrates, lanthanide nitrates, and ammonium nitrates.

62. The method of claim 60, wherein the co-oxidizer is selected from the group consisting of metal oxides, metal hydroxides, metal peroxides, metal oxide hydrates, metal oxide hydroxides, metal hydrous oxides, basic metal carbonates, basic metal nitrates, and mixtures thereof.

63. The method of claim 60, wherein the co-oxidizer is selected from the group consisting of oxides of copper, cobalt, manganese, tungsten, bismuth, molybdenum, and iron.

64. The method of claim 60, wherein the co-oxidizer is selected from CuO , Co_2O_3 , Co_3O_4 , CoFe_2O_4 , Fe_2O_3 , MoO_3 , Bi_2MoO_6 , Bi_2O_3 , $\text{Fe}(\text{OH})_3$, $\text{Co}(\text{OH})_3$, $\text{Co}(\text{OH})_2$, $\text{Ni}(\text{OH})_2$, $\text{Cu}(\text{OH})_2$, $\text{Zn}(\text{OH})_2$, $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$, $\text{SnO}_2 \cdot x\text{H}_2\text{O}$, $\text{MoO}_3 \cdot \text{H}_2\text{O}$, $\text{CoO}(\text{OH})_2$, $\text{FeO}(\text{OH})_2$, $\text{MnO}(\text{OH})_2$, $\text{MnO}(\text{OH})_3$, $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ (malachite), $2\text{Co}(\text{CO}_3) \cdot 3\text{Co}(\text{OH})_2 \cdot \text{H}_2\text{O}$, $\text{Co}_{0.69}\text{Fe}_{0.34}(\text{CO}_3)_{0.2}(\text{OH})_2$, $\text{Na}_3[\text{Co}(\text{CO}_3)_3] \cdot 3\text{H}_2\text{O}$, $\text{Zn}_2(\text{CO}_3)(\text{OH})_2$, $\text{Bi}_2\text{Mg}(\text{CO}_3)_2(\text{OH})_4$, $\text{Fe}(\text{CO}_3)_{0.12}(\text{OH})_{2.76}$, $\text{Cu}_{1.54}\text{Zn}_{0.46}(\text{CO}_3)(\text{OH})_2$, $\text{Co}_{0.49}\text{Cu}_{0.51}(\text{CO}_3)_{0.43}(\text{OH})_{1.1}$, $\text{Ti}_3\text{Bi}_4(\text{CO}_3)_2(\text{OH})_2\text{O}_9 \cdot (\text{H}_2\text{O})_2$, $(\text{BiO})_2\text{CO}_3$, $\text{Cu}_2(\text{OH})_3\text{NO}_3$, $\text{Co}_2(\text{OH})_3\text{NO}_3$, $\text{CuCo}(\text{OH})_3\text{NO}_3$, $\text{Zn}_2(\text{OH})_3\text{NO}_3$, $\text{Zn}_2(\text{OH})_2\text{NO}_3$, $\text{Mn}(\text{OH})_2\text{NO}_3$, $\text{Fe}_4(\text{OH})_{11}\text{NO}_3 \cdot 2\text{H}_2\text{O}$, $\text{Mo}(\text{NO}_3)_2\text{O}_2$, $\text{BiONO}_3 \cdot \text{H}_2\text{O}$, and $\text{Ce}(\text{OH})(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$.

65. The method of claim 38, wherein the at least one metal complex is hexaamminecobalt(III) nitrate, $[(\text{NH}_3)_6\text{Co}](\text{NO}_3)_3$ and the co-oxidizer is copper(II) trihydroxy nitrate ($\text{Cu}_2(\text{OH})_3\text{NO}_3$).

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