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(54) Title: NON-AMMONIUM NITRATE BASED GENERANTS

(57) Abstract: This disclosure is directed to an airbag gas generant formulation optimized for hybrid airbag inflators, and an airbag inflator, an airbag, an airbag module comprising same, and a method of inflating an airbag using the airbag gas generant.



WO 2019/143784 A1

Non-Ammonium Nitrate Based Generants

This application claims the priority and benefit of US provisional application 62/618,269 filed January 17, 2018, entitled "Airbag Propellant", which is incorporated herein by reference in its entirety.

Background

With ammonium nitrate based generants becoming unacceptable for usage in automotive airbag inflator applications regardless whether they are used in pyrotechnic or hybrid type inflators, alternate or non-ammonium nitrate containing generants are highly desirable. Even in a hybrid inflator where the generant is stored in a high-pressure inert gas atmosphere making moisture intrusion nearly impossible, ammonium nitrate based generants are still considered unacceptable.

Brief Summary

One aspect of this disclosure is directed to a gas generant formulation. The gas generant may be used as an airbag gas generant formulation. This document discloses a number of gas generant formulations and it is understood that "formulation" or "the formulation" unless otherwise stated, may refer to any gas generant formulation(s) or airbag gas generant formulation(s) of this document. That is any non-ammonium nitrate based generants of this disclosure.

The airbag gas generant formulation (see, e.g., as claimed) can be optimized for airbag inflators, specifically hybrid airbag inflators. One aspect is an airbag gas generant formulation comprising the following: 40 wt% to 50 wt% strontium nitrate; 35 wt% to 45 wt% nitroguanidine; 3 wt% to 7 wt% potassium perchlorate; 3 wt% to 6 wt% w/w polyvinyl alcohol; and 2 wt% to 6 wt% w/w strontium oxalate. In this case, the ingredients may be adjusted to reach 100 wt% without any additional ingredients. Alternatively, in any aspects of this disclosure, where the ingredients do not add up to 100 wt%, a filler may be used to adjust the ingredients to 100 wt%.

Unless otherwise specified, wt% refers to "weight percent" which is the weight of one chemical relative to the weight of the total airbag gas generant formulation. Where the wt% is less than 100%, an optional filler known to one of ordinary skill in the art may be added. For

example, the filler can be an inert filler such as clay, chalk, and the like. Inert filler refers to a chemical or ingredient that does not react with the other ingredients in the formulation in an environment where the formulation is usually found. Such an environment may be, for example, in an airbag inflator, in a warehouse, or in a car. Each of these locations may be subjected to the conditions expected of an airbag inflator, of a car or of a warehouse which include subfreezing to very hot conditions of a car, for example, in the sun and in a desert.

The gas generant formulations and airbag gas generant formulations of the disclosure has many desirable properties. One aspect is directed to a formulation which has at least one property selected from the group consisting of: a gas yield of greater than 1.57 grams of per cubic centimeter (g/cc); a constant volume flame temperature of 2700°K to 2800°K; and an overall oxygen balance of the formulation -2% to +2%. In a preferred aspect, the formulation comprises two of these properties. In another preferred aspect, the formulation comprises all of these properties.

One aspect relates to an airbag gas generant formulation wherein the formulation comprises 48.2 wt% strontium nitrate; 36.8 wt% nitroguanidine; 5 wt% potassium perchlorate; 5 wt% strontium oxalate; and 5 wt% polyvinyl alcohol.

Another aspect relates to any of the formulations in this disclosure wherein the formulation further comprises 1wt% to 5wt% cupric oxide as a burning rate modifier. As an example, the airbag gas generant formulation may comprise 44.1 wt% strontium nitrate; 39.9 wt% nitroguanidine; 5 wt% potassium perchlorate; 4 wt% strontium oxalate; 4 wt% polyvinyl alcohol; and 3 wt% cupric oxide.

In another aspect, the airbag gas generant formulation can further comprise 2 wt% to 6wt% Kaolin. The kaolin may be for slag formation and as a coolant. In another aspect, the airbag gas generant formulation can further comprise 2 wt% to 6 wt% aluminum oxide. The aluminum oxide may be for slag formation and as a coolant. In another aspect, the airbag gas generant formulation can further comprise 2 wt% to 6 wt% silicon dioxide. The silicon dioxide may be for slag formation and as a coolant. As another aspect, the airbag gas generant formulation can further comprise 2 wt% to 6% wt% of at least one ingredient. The one

ingredient may be one, two, or all three of the following: kaolin; aluminum oxide; and silicon dioxide.

Vehicles may include a variety of airbags that can deploy during vehicle impacts to absorb energy from occupants of the vehicles during the impact. The airbag may be a component of an airbag module comprising an airbag inflator in communication with the airbag for inflating the airbag from an uninflated position to an inflated position.

One aspect is directed to an airbag inflator comprising an airbag gas generant formulation described in this disclosure.

Another aspect is directed to an airbag module or airbag comprising an airbag gas generant formulation described in this disclosure.

Another aspect is directed to a method of inflating an airbag. The method comprises the steps of igniting an airbag gas generant of any airbag gas generant formulation described in this disclosure to generate a gas; and inflating an airbag with the gas.

Detailed Description

This disclosure describes non-ammonium nitrate based generants that are optimized as a replacement and improvement for ammonium nitrate based hybrid inflator generants.

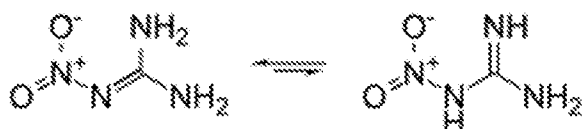
Hybrid inflators contain both stored gas and pyrotechnic materials. In some hybrid inflator designs the stored gas vessel contains both high-pressure gas and pyrotechnic materials. In hybrid inflators the pyrotechnic materials are used for gas generation and heating of the stored gas. Ammonium nitrate based generants worked well due to their high gas yield and relatively high combustion temperature compared to that needed for a pyrotechnic inflator. Ammonium nitrate based hybrid generants were formulated near stoichiometric such that they did not generant unacceptable levels of carbon monoxide or nitrogen oxide compounds; they had oxygen balances near zero. In this type of hybrid inflator the stored gas is inert. Some hybrid inflator designs use a highly negative oxygen balance formulation that generate carbon monoxide (CO) and hydrogen (H₂) requiring oxygen to be added to the stored gas to combust the CO and H₂ to CO₂ and H₂O, respectively. Such a formulation is described in

U.S. Patent 7,942,990. The formulation described here requires no oxygen to be included in the stored gas.

Ammonium nitrate based generants also have a high gas yield to volume of solid generant. For example, the ammonium nitrate based generants described in U.S. Patents 5,850,053 and 6,136,113 have a theoretical density of 1.66 g/cc with a gas yield of 1.57 grams of gas per cubic centimeter (cc) of solid generant. These formulations have a constant pressure flame temperature of 2240K and a constant volume flame temperature of 2700°K. For a replacement generant to work in the same hybrid inflator, it is preferred to have the same or equivalent gas yield per solid volume and flame temperatures.

Due to the preceding constraints of high gas yields per volume of solid gas generant and non-ammonium nitrate containing generants, this makes metal containing oxidizers and high-density fuels attractive. These types of generants have a lower gas yield per weight but due to having a high solid density can produce the same amount of gas per solid volume as the ammonium nitrate based generants. It is also desirable for a gas generant to use commonly available or lowest cost ingredients. For pyrotechnic inflators, the fuel of choice today is guanidine nitrate (GN). Example 1 shows GN with various oxidizers. As this example shows when GN is used as the fuel, the 1.57 grams of gas per cc solid generant cannot be met.

The following chemicals components recited in the claims are individually well-known to one of ordinary skill in the art. They include at least strontium nitrate ($\text{Sr}(\text{NO}_3)_2$); potassium perchlorate (KClO_4); polyvinyl alcohol; strontium oxalate (SrC_2O_4); cupric oxide (CuO); Kaolin; aluminum oxide (Al_2O_3); and silicon dioxide (SiO_2). Nitroguanidine ($(\text{NH}_2)_2\text{CNNO}_2$) or $\text{NO}_2\text{NHC(=NH)NH}_2$ is commercially available and also well-known. It exists in two tautomeric forms, as a nitroimine (left) or a nitroamine (right).



In solution and in the solid state, the nitroimine form predominates (resonance stabilized).

Incorporation by Reference

All publications, patent applications, and patents mentioned anywhere in this disclosure are hereby incorporated by reference in their entirety as if each individual publication or patent was specifically and individually indicated to be incorporated by reference. In case of conflict, the present application, including any definitions herein, will control.

Examples

Example 1: Experiments on various formulations

Example 1: Gas Mass per Volume of Solid Generant with Guanidine Nitrate, -1% Oxygen Balance				
Oxidizer	% Oxidizer	% GN	% PVA Binder	Grams Gas per cc Solid Generant
Sr(NO ₃) ₂	39.4	60.6		1.46
Sr(NO ₃) ₂	49.1	46.9	4	1.45
BCN	44.9	55.1		1.48
KClO ₄	34.8	65.2		1.37
KClO ₄	44.8	55.2	4	1.35

Table 1 lists some fuels used or proposed to be used in airbag gas generants. In order to meet the criteria of 1.57 grams of gas per cc of solid volume low-density ingredients in general like guanidine nitrate can be rejected as a candidate. Also, fuels with a high oxygen demand like 5-aminotetrazole can be rejected due to the low gas yield of such a system with a metal-containing oxidizer.

The flame temperature of compositions tend to increase with fuel heat-of-formation so generants containing HMX and RDX tend to have high flame temperatures; besides HMX and RDX generants are sensitive and tend to fall under export control laws. So candidates like HMX and RDX are not considered as being viable; they also would require significant amounts of coolant (flame temperature reducing material) to be added to such a formulation. Of the two other ingredients listed in Table 1, AZODN while being the ideal fuel is not commercially available so the preferred fuel is nitroguanidine.

Table 1			
Fuel	Density (g/cc)	Oxygen Balance %	Heat of Formation (kcal/kg)
HMX	1.91	-21.61	60.54
RDX	1.816	-21.61	75.64
Nitroguanidine	1.77	-30.75	-216.97
Azodicarbonamidine Dinitrate (AZODN)	1.70	-13.33	-366.

5-Aminotetrazole	1.65	-65.83	587.77
Guanidine Nitrate	1.436	-26.21	-746.21

Table 2 lists oxidizers that have been used or proposed to be used in airbag gas generant formulations.

Table 2					
Oxidizer	Density (g/cc)	Oxygen Balance %	Percent Post Combustion Condensable	Heat of Formation (kcal/kg)	Gas Yield Density (g/cc)
Strontium Nitrate	2.986	37.8	48.96	-1104.76	1.524
Basic Copper Nitrate (BCN)	3.394	29.98	52.93	-866.	1.598
Potassium Perchlorate (KP)	2.52	46.19	53.81	-742.	1.164
Potassium Nitrate (KN)	2.109	39.56	68.35	-1169.	0.667
Sodium Nitrate + Ammonium Perchlorate (SNAP)	2.069	39.51	28.86	-901.	1.472
Strontium Nitrate + Ammonium Perchlorate (SRAP)	2.334	35.82	35.5	-840.	1.505

Example 2: Measurements of experimental results

Example 2 lists -1% oxygen balance two-component systems with oxidizers from Table 2 combined with nitroguanidine; PSAN-GN formulations are also listed for comparison purposes. Potassium nitrate-nitroguanidine formulations have a low gas yield making them unable to meet the 1.57g/cc requirement. Potassium perchlorate and ammonium perchlorate containing formulations tend to have too high of a combustion temperature. Strontium nitrate and BCN are the remaining oxidizers to be considered.

Example 2:
-1% O/B Constant Volume Flame Temperature at
0.08 loading volume (cc-solid / cc-total volume)

Oxidizer	Oxidizer %	Fuel	Fuel %	Gas Yield Density (g/cc)	Const. Vol. Flame Temp (K)
PSAN (AN-KP-GN Eutectic)	50.8	GN	49.2	1.543	2693
PSAN AN-KN-GN Eutectic)	52.9	GN	47.1	1.542	2623
Strontium Nitrate	43.4	NQ	56.6	1.693	3057
BCN	49.0	NQ	51.0	1.712	2645
Potassium Perchlorate	38.7	NQ	61.3	1.584	3344
Potassium Nitrate	42.3	NQ	57.7	1.350	2776
SNAP	42.3	NQ	57.7	1.655	3223
SRAP	44.7	NQ	55.3	1.669	3236

Airbag generants have to be cost competitive so these formulations preferably use low-bulk-density (LBD) nitroguanidine which consists of long fibers which do not thermal cycle well. As mentioned in the literature LBD needs to be ground. Patent 6,547,900 describes a method using vibratory ball-mills to break up the Nitroguanidine needles. It is preferred to have minimal grinding of the NQ to break up the needle bundles plus the addition of polyvinyl alcohol (PVA) as a binder allows NQ formulations to withstand thermal cycling and heat age environment conditioning. PVA is a preferred binder because it is water soluble. Binders that require organic solvents to dissolve them can add high production costs to the generant.

While a two oxidizer combination of strontium nitrate and BCN with NQ and PVA can achieve an ideal flame temperature, BCN and PVA do not heat age well together. Since PVA is the preferred binder, this eliminates BCN as a candidate. The general replacement generant formulation for an ammonium nitrate formulation is strontium nitrate, nitroguanidine, and polyvinyl alcohol as the binder plus a coolant to reduce the combustion temperature. In examples 3 through 8 various combinations of strontium nitrate and NQ with PVA as a binder are shown. These combinations all meet the minimum gas weight per volume of solid generant and flame temperature.

Because $\text{Sr}(\text{NO}_3)_2$ – NQ formulations can have low burning rates potassium perchlorate (KP) and copper(II) oxide (CuO) or combinations thereof can be added to increase the burning rate. Examples 6 through 8 show cases where KP and CuO are included in the formulation. These cases also meet the gas yield and flame temperature requirements for a hybrid inflator application. Potassium perchlorate and CuO both act as burning rate catalysts.

Examples 3-8: Additional formulations and their experimental results

Example	Strontium Nitrate	NQ	Strontium Oxalate	PVA	KP	CuO	Gas Yield Density (g/cc)	Const. Vol. Flame Temp (K)
3	53.9%	36.6%	4.5%	5%			1.585	2716.
4	51.6%	39.4%	5.0%	4%			1.594	2700.
5	49.4%	42.6%	5.5%	3%			1.608	2700.
6	45.8%	39.7%	5.5%	4%	5%		1.575	2708.
7	43.7%	40.8%	5.5%	4%	6%		1.574	2720.
8	43.9%	39.6%	4.5%	4%	5%	3.0	1.587	2720.

While the invention has been described in connection with what is presently considered to be the most practical and preferred embodiments, it is to be understood that the invention is not to be limited to the disclosed embodiments, but on the contrary, is intended to cover various modifications and equivalent arrangements included within the spirit and scope of the appended claims.

Claims

1. An airbag gas generant formulation optimized for hybrid airbag inflators, the formulation comprising:
 - 40 wt% to 50 wt% strontium nitrate;
 - 35 wt% to 45 wt% nitroguanidine;
 - 3 wt% to 7 wt% potassium perchlorate;
 - 3 wt% to 6 wt% w/w polyvinyl alcohol; and
 - 2 wt% to 6 wt% w/w strontium oxalate.
2. The airbag gas generant formulation of claim 1 which has at least one property selected from the group consisting of:
 - a gas yield of greater than 1.57 grams of per cubic centimeter (g/cc);
 - a constant volume flame temperature of 2700°K to 2800°K; and
 - an overall oxygen balance of the formulation -2% to +2%.
3. The airbag gas generant formulation of claim 1, wherein the formulation comprises
 - 48.2 wt% strontium nitrate;
 - 36.8 wt% nitroguanidine;
 - 5 wt% potassium perchlorate;
 - 5 wt% strontium oxalate; and
 - 5 wt% polyvinyl alcohol.
4. The airbag gas generant formulation of claim 1, wherein the formulation further comprises
 - 1wt% to 5wt% cupric oxide as a burning rate modifier.
5. The airbag gas generant formulation of claim 4 wherein the formulation is
 - 44.1 wt% strontium nitrate;
 - 39.9 wt% nitroguanidine;

- 5 wt% potassium perchlorate;
 - 4 wt% strontium oxalate;
 - 4 wt% polyvinyl alcohol; and
 - 3 wt% cupric oxide.
6. The airbag gas generant formulation of claim 1 which further comprises 2 wt% to 6wt% Kaolin for slag formation and as a coolant.
 7. The airbag gas generant formulation of Claim 1 which further comprises 2 wt% to 6 wt% aluminum oxide for slag formation and as a coolant.
 8. The airbag gas generant formulation of Claim 1 which further comprises 2 wt% to 6 wt% silicon dioxide for slag formation and as a coolant.
 9. The airbag gas generant formulation of Claim 1 which further comprises 2 wt% to 6% wt% of at least one selected from the group consisting of:
 - kaolin;
 - aluminum oxide; and
 - silicon dioxide.
 10. The airbag gas generant formulation of Claim 1 which does not contain oxygen as a stored gas.
 11. An inflator for an airbag comprising the airbag gas generant formulation of claim 1 wherein the inflator does not contain oxygen as a stored gas.
 12. A method for inflating an airbag comprising the steps of
 - igniting the airbag gas generant formulation of claim 1 to generate a gas; and
 - inflating the airbag with the gas.

13. The method of claim 12 wherein the igniting step does not involve igniting oxygen as a stored gas.

INTERNATIONAL SEARCH REPORT

International application No

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A. CLASSIFICATION OF SUBJECT MATTER
 INV. C06D5/06
 ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
 C06D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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A	US 6 527 886 B1 (YAMATO YO [JP] ET AL) 4 March 2003 (2003-03-04) example 1 -----	1-13
A	US 2004/025991 A1 (CANTERBERRY JB [US] ET AL) 12 February 2004 (2004-02-12) example 1; table 1 -----	1-13



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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