A relatively low temperature nitrogen gas generating composition containing (A) metallic azides and (B) reactants therefor, such as, the metallic sulfides, metallic iodides, organic iodides, organic chlorides, metallic oxides and sulfur.

39 Claims, No Drawings
3,741,585

LOW TEMPERATURE NITROGEN GAS GENERATING COMPOSITION

BACKGROUND OF THE INVENTION

1. Field of the Invention
The invention relates to nitrogen gas generating composition which is capable of generating nitrogen gas at relatively low temperatures such as from 200°F to 1,000°F. More particularly this invention relates to a relatively low temperature nitrogen gas generating composition for inflating passenger vehicle crash bags. This composition comprises (A) metallic oxides and (B) reagents therefor, such as, the metallic oxides, metallic sulfides, metallic iodides, organic iodides, organic chlorides and sulfur.

2. Description of the Prior Art
A need arose for a nitrogen gas generating composition which could be used for inflating certain devices in a very short time. Inflatable structures such as various recreational equipment and inflatable furniture can be filled manually by an air pump. However, the inflatable structures such as emergency crash bags for protecting the life of passengers of automobiles, trains, airplanes, ships etc., must be inflated in a very short period of time with a non-toxic, non-flammable gas. Furthermore, the temperature of the reaction must be sufficiently low enough so that the gas produced and directed into a crash bag can be retained in the bag. The gas in the bag must be at least retained long enough to cool to a temperature so that if the gas does escape, it will not burn the passengers.

In the past such devices used for inflating the above type structures were systems using compressed gas stored in cylinders. However, the response time of these devices for inflating passenger protective crash bags etc., was too slow for uses such as in automobile, train, and airplane crash bags which require an inflating time of approximately 0.040 seconds. For example, it is well known that if a medium size automobile, with a 2 ft. clearance between the rear seat and the back of the front seat, collided into a solid wall at approximately 30 m.p.h., a passenger in the back seat will come into contact with the back of the front seat in approximately 0.0435 seconds.

The older type compressed gas crash inflation devices have a number of other disadvantages. (1) They are bulky and difficult to package neatly in places such as in steering columns of automobiles. (2) Automobile manufacturers regard containers of compressed gas, especially ones equipped with explosive opening devices being hazards when used on automobile assembly lines. (3) These compressed gas type inflation devices may present a hazard during shipping, storing or when handling. Also these devices may tend to be unreliable because of the danger of leakage, especially after several years of being attached to an automobile. (4) The pressure within the container can be dangerously increased by high ambient temperatures. In view of the above problems, the relatively low temperature nitrogen gas generating composition of this invention is considered to be a much superior source of gas for the inflation of such devices are automobile, train, airplane and ship passenger protective type crash bags.

The use of the composition of this invention in devices such as automobile crash bags has a number of advantages. This composition can be contained in a much smaller package than compressed gas. Also this composition should remain reliable for a much longer period of time. Another important advantage is that this composition is relatively insensitive to temperature changes and shock. Therefore, it is considered to be much safer than the compressed gas type inflation device.

The gases produced by the gas generating compositions for use in passenger carrying vehicles, as mentioned above, must be low in temperature and non-toxic because of the danger of a rupture occurring in the crash bags upon inflation and harming the passengers if the gases are toxic or high in temperature. Also the source of the gas must be such that the crash bag is inflated within about 0.040 seconds after a collision signal is received. As mentioned earlier, in the older gas generating devices, which were used to inflate crash bags, the response time was much too slow. Therefore, gas generating compositions with the necessary response time were developed. However, the reaction temperatures of these compositions were approximately 2,500°F. These reaction temperatures were much too high.

In the past various types of inflatable devices have been used extensively by the armed forces for inflating landing pads for helicopters and floatation equipment such as rafts, boats, escape ladders, etc. Recently, it has been proposed to inflate these devices by utilizing gases generated from gas generating compositions. An improvement was made in the prior art over the above mentioned gas generating compositions. These gas generating compositions were reacted in the presence of liquid carbon dioxide resulting in the hot gases heating the liquid carbon dioxide which was converted into a gas which in turn cooled the reaction temperature of the gases produced by the gas generating composition. However, this cooling system was not a complete success. One of the difficulties encountered in the above type system was that the combustion gases and the coolants did not mix uniformly particularly when the gas generation composition was first ignited. This resulted in producing hot spots in the mixing chamber of the apparatus which would burn out or weaken the structural elements of the device to be inflated. Other coolants were tried. It has been proposed to use alcohol or other suitable liquid materials having a high latent heat of vaporization to further reduce the temperature of the gases. None of these systems have been completely successful.

One of the objects of the present invention is the use of a low temperature nitrogen gas generating composition for the inflation of passenger protective crash bags for use in passenger carrying vehicles. More particularly these protective crash bags have been installed in the dash of automobiles and have been designed to inflate rapidly and automatically in order to protect the occupants of the vehicle in the event of a collision. Apparatus for use in automobiles of this general nature are known in the prior art. For example, U.S. Pat. No. 3,336,045 describes a cushion device which is inflated by use of a solid fuel gas generator using an undesigned gas generating composition. Also, U.S. Pat. No. 3,450,414 discloses a cushion device which is inflated by a non-flammable gaseous material such as dichlorodifluoromethane and similar type gases which are contained in a sealed container. Also as mentioned earlier, there are numerous designs for inflating crash bags for passenger carrying vehicles where the source of gas for
inflating the bags is contained in cylinders under pressure and is released by an explosive device which is activated when the vehicle is involved in a collision. These devices have also not been entirely successful.

SUMMARY OF THE INVENTION

It is the object of this invention to provide a relatively low temperature nitrogen gas generating composition. Particularly, a relatively low temperature nitrogen generating composition for use as a gas generant in the inflation of passenger protective crash bags for use in passenger carrying vehicles. The nitrogen gas generating composition's reaction temperature must be sufficiently low so that the temperature created by the reaction will not be above approximately 200° to 1,000° F.

Also the gases generated must be non-toxic.

The term relatively low temperature as used in the context of this invention means a gas temperature between approximately 200° and 1,000° F. These temperatures are considered low reaction temperatures when compared to the reaction temperatures of presently known nitrogen gas generating compositions which have reaction temperatures approximately 2,000° to 3,000° F.

Another object of the invention is to provide a gas generating composition which has a very fast response rate for inflating the crash bags. For example, the inflation time required in automobile passenger protective crash bags is approximately 0.040 seconds.

More particularly, the object of the invention is to provide a source of inert and non-toxic gas for automobile crash bags. This source of gas must be reliable for long periods of time, nonhazardous during prolonged storage, non-toxic, possess a relatively low reaction temperature, and possess the capability of being produced in sufficient quantities in order to inflate automobile passenger protective crash bags in 0.040 seconds.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Devices which may be inflated by use of this invention include inflatable passenger protective crash bags for use in passenger carrying vehicles, inflatable boats, rafts, escape ladders, etc. This invention is especially useful in the inflation of shock-absorbing, flexible, inflatable passenger protective crash bags for use in automobiles. Automobile crash bags of this general type are disclosed in U.S. Pat. Nos. 3,450,414, 2,834,609 and 3,573,885.

Gas generators which may be utilized by this invention may be of the type disclosed in copending application entitled "Gas Generators" by F. E. Schneider, Ser. No. 47,788 incorporated herein by reference. Also other similar type gas generators which may be utilized are of the type disclosed in U.S. Pat. No. 3,117,424 incorporated herein by reference.

The objectives of the invention are accomplished by reacting (A) metallic azide, more particularly alkali metal azides, alkaline earth metal azides or an aluminum azide with an (B) reactant therefor, such as, the metallic oxides, metallic sulfides, metallic iodides, organic iodides, organic chlorides or sulfur in order to produce nitrogen gas very rapidly at relatively low temperatures.

The (A) azides useful in the practice of the present invention are the alkali metal azides, alkaline earth metal azides and aluminum azides.

The preferred alkali metal azides are lithium azide, sodium azide and potassium azide. The most preferred alkali metal azide is sodium azide.

The preferred alkaline earth metal azides are calcium azide, barium azide, and magnesium azide. The most preferred alkaline earth metal azide is magnesium azide.

Another preferred azide is aluminum azide.

The amount of (A) azides is from about 25 to 95 percent by weight based on the total weight of the composition, preferably from about 30 to 70 percent by weight.

The (B) reactants for the azides of this invention are the metallic sulfides, metallic iodides, organic iodides, organic chlorides, metallic oxides and sulfur. The preferred metallic sulfides are antimony trisulfide, bismuth sulfide, ferrous sulfide, stannous sulfide, tungsten disulfide, aluminum sulfide and molybdenum disulfide. The most preferred metallic sulfides are aluminum sulfide, molybdenum disulfide and ferrous sulfide. The most particularly preferred of the metallic sulfides is molybdenum disulfide and ferrous sulfide.

The preferred metallic iodides are antimony triiodide, bismuth triiodide, ferrous iodide and stannic iodide.

The preferred organic iodides are carbon tetraiodide and iodofrom. The most preferred organic iodide is carbon tetraiodide.

The preferred organic chlorides are hexachloroethane, hexachlorobenzene and perchloropentacyclocdecane. The most preferred organic chloride is perchloropentacyclocdecane.

The preferred metallic oxides are molybdenum trioxide, tungsten trioxide, lead dioxide and vanadium pentoxide. The most particularly preferred of the metallic oxides is vanadium pentoxide.

The preferred amount of the (B) reactants of this invention is from about 1 to 75 percent by weight based on the total amount of the composition, more preferably from about 30 to 60 percent.

A preferred relatively low temperature nitrogen gas generating composition of this invention is from about 30 to 75 percent preferably 60 to 70 percent sodium azide, from about 25 to 45 percent preferably 30 to 40 percent molybdenum disulfide and from about 0.5 to 30 percent preferably 1 to 20 percent sulfur. The most preferred relatively low temperature nitrogen gas generating composition of this invention is from about 25 to 90 percent preferably 30 to 70 percent sodium azide, from about 30 to 70 percent preferably 40 to 60 percent vanadium pentoxide and from about 0.5 to 7.0 percent preferably 1 to 5 percent molybdenum disulfide.

In the relatively low temperature nitrogen gas generating composition the ingredients are simply mixed together for approximately one-half hour with a common dry powder blender. After mixing this material, it is then pelletized in a common pressure type pelleting forming small pellets. These small pellets are then placed into a gas generator of a type which is suitable for inflating passenger vehicle crash bags. This gas generator should contain a chamber in which the pellets are to be ignited and burned in order to generate the gas. Also the gas generator should contain an ignition means to ignite the pellets inside the chamber and a discharge orifice in order to discharge the gas from the
chamber into an inflatable crash bag or collection chamber. Gas generators of the type which may be used are described in a pending application entitled "Gas Generators" by F. E. Schenier, Ser. No. 47,788 previously mentioned and incorporated herein by reference. Also other gas generators of the type which may be used are described in U.S. Pat. No. 3,117,424 mentioned previously. However, other similar type gas generators may be used.

After placing the pellets into the gas generator the composition is ignited. Any general type ignition system may be used. However, there are two types of ignition systems preferred. The first of these systems is a regular boron and potassium nitrate ignition system which is a hot particle type ignition. The second type ignition system is a sodium azide and sulfur ignition system which is a hot gas type ignition.

In order to point out more fully the invention in its practical aspects, the following illustrative examples are given of the practice of the invention for preparing the sub-combinations and combinations of the ingredients used in their various phases.

Examples 1 through 13 as shown in Table 1 demonstrate, (1) the amount of pressure which was generated by the various compositions in the gas generator unit, (2) upon ignition, the time in seconds required for the gas being produced to reach a maximum pressure in a collection chamber, (3) the pressure in the collection chamber after 200 milliseconds have elapsed, (4) the number of millimoles of gas produced per gram of the gas generating composition ignited, and (5) the maximum temperature in degrees Fahrenheit of the gas produced by the reaction.

The ingredients of the Example 1 through 13, which were in a powdered form, were simply mixed together for approximately one-half hour in a gallon container using a paint shaker type mixer. This material was then pelletized in a standard pressure type pelletizer in order to make small pellets of the gas generating composition. These pellets were then put into a gas generator of the type described previously and ignited. The ignition gases were directed into an evacuated collection chamber with a volume of approximately 7.6 liters. The pressure of the gas versus the time required to reach this pressure in the collection chamber was measured and recorded. Also a measurement was made of the total pressure reached in the collection chamber. Also, the temperature of the gases as they came out of the generator and into the collection chamber were measured.

The invention is illustrated but not limited by the following examples in which the parts are by weight unless otherwise specified.

### Table I

<table>
<thead>
<tr>
<th>Example No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium Azide</td>
<td>80.3</td>
<td>90.0</td>
<td>64.0</td>
<td>65.5</td>
<td>69.6</td>
<td>52.1</td>
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<tr>
<td>Sulfur</td>
<td>19.7</td>
<td>10.0</td>
<td>1.0</td>
<td>4.0</td>
<td>2.0</td>
<td></td>
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<tr>
<td>Molybdenum sulfide</td>
<td>25.0</td>
<td>30.5</td>
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<td></td>
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<tr>
<td>Ferrous sulfide</td>
<td>28.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lead dioxide</td>
<td>47.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Generator maximum pressure (psia)</td>
<td>1467</td>
<td>1797</td>
<td>1292</td>
<td>2050</td>
<td>1322</td>
<td>1582</td>
</tr>
<tr>
<td>Action time (sec) to achieve max. pressure in collection chamber</td>
<td>0.085</td>
<td>0.026</td>
<td>0.039</td>
<td>0.047</td>
<td>0.080</td>
<td>0.028</td>
</tr>
<tr>
<td>Pressure (psia) at 0.02 sec. in collection chamber</td>
<td>27.8</td>
<td>27.8</td>
<td>17.7</td>
<td>15.4</td>
<td>17.6</td>
<td>16.1</td>
</tr>
<tr>
<td>Millimoles of gas per gram of material</td>
<td>23.6</td>
<td>26.04</td>
<td>23.8</td>
<td>21.6</td>
<td>27.4</td>
<td>15.7</td>
</tr>
<tr>
<td>Max. temp. of gas in collection chamber</td>
<td>866°F</td>
<td>813°F</td>
<td>343°F</td>
<td>296°F</td>
<td>232°F</td>
<td>611°F</td>
</tr>
</tbody>
</table>

### Example 13

- Sodium azide: 58.8
- Carbon tetraiodide: 66.7
- Molybdenum trioxide: 59.6
- Sodium azide: 50.4, 46.9, 40.5
- Molybdenum disulfide: 2.0, 2.0
- Pressure (psia) at 0.02 sec. in collection chamber: 3803, 1691, 3282, 2273, 1952, 3525, 3265
- Pressure (psia) at 0.02 sec. in collection chamber: 50, 51, 45, 70, 30, 29, 42
- Max. temp. of gas in collection chamber: 98°F, 86°F, 65°F, 64°F, 58°F, 51°F, 49°F

We claim:

1. A nitrogen gas generating composition which upon ignition generates nitrogen gas at a temperature in the range of from about 200°F to about 1,000°F, said composition consisting essentially of an effective gas generating amount of

   a. from about 25 to 95 percent by weight of azides selected from the group consisting of alkali metal azides, alkaline earth metal azides, and aluminum azides and

   b. from about 1 to 75 percent by weight of reactants selected from the group consisting of antimony triiodide, bismuth sulfide, ferrous sulfide, sannous sulfide, tungsten disulfide, aluminum sulfide, molybdenum disulfide, antimony trioxide, bismuth trioxide, ferrous iodide, stannic iodide, carbon tetraiodide, iodoform, hexachloroethane, hexachlorobenzene, perchloropentacetylodenec acid, molybdenum trioxide, tungsten trioxide, lead dioxide, vanadium dioxide, and sulfur or mixtures thereof.

2. The composition as in claim 1 wherein the amount of (A) azides present is from about 30 to 70 percent by weight based on the total weight of the composition.

3. The composition as in claim 1 wherein the amount of (B) reactants present is from about 30 to 60 percent by weight based on the total weight of the composition.

4. The composition as in claim 1 wherein the (A) azides are alkali metal azides selected from the group consisting of lithium azide, sodium azide and potassium azide.

5. The composition as in claim 4 wherein the alkali metal azide is sodium azide.

6. The composition as in claim 1 wherein the (A) azides are alkaline earth metal azides selected from the group consisting of calcium azide, barium azide and magnesium azide.

7. The composition as in claim 6 wherein the alkaline earth metal azide is magnesium azide.

8. The composition as in claim 1 wherein the (A) azide is aluminum azide.

9. The composition as in claim 1 wherein the (B) reactant is aluminum sulfide.

10. The composition as in claim 1 wherein the (B) reactant is molybdenum disulfide.

11. The composition as in claim 1 wherein the (B) reactant is ferrous sulfide.

12. The composition as in claim 1 wherein the (B) reactant is iodoform.

13. The composition as in claim 1 wherein the (B) reactant is carbon tetraiodide.
14. The composition as in claim 1 wherein the (B) reactant is perchloropentacyclodecane.
15. The composition as in claim 1 wherein the (B) reactant is molybdenum trioxide.
16. The composition as in claim 1 wherein the (B) reactant is tungsten trioxide.
17. The composition as in claim 1 wherein the (B) reactant is lead dioxide.
18. The composition as in claim 1 wherein the (B) reactant is vanadium pentoxide.
19. The composition as in claim 1 wherein the (B) reactant is sulfur.
20. In an improved method for inflating a shock-absorbing, flexible, inflatable, passenger protective crash bag for use in a passenger carrying vehicle wherein the improvement comprises generating nitrogen gas at a temperature of from about 200°F. to about 1,000°F. by means of a nitrogen generating composition consisting essentially of an effective amount of
   a. from about 25 to 95 percent by weight of azides selected from the group consisting of alkali metal azides, alkaline earth metal azides and aluminum azides and
   b. from about 1 to 75 percent by weight of reactants selected from the group consisting of antimony tri-sulfide, bismuth sulfide, ferrous sulfide, stannous sulfide, tungsten disulfide, aluminum sulfide, molybdenum disulfide, antimony triiodide, bismuth triiodide, ferrous iodide, stannic iodide, carbon tetraiodide, iodoform, hexachloroethane, hexachloro benzene, perchloropentacyclodecane, molybdenum trioxide, lead dioxide, vanadium dioxide sulfur or mixtures thereof.
21. The method as in claim 20 wherein the amount of (A) azides present is from about 30 to 70 percent by weight based on the total weight of the composition.
22. The method as in claim 20 wherein the amount of (B) reactants present is from about 30 to 60 percent by weight based upon the total weight of the composition.
23. The method as in claim 20 wherein the (A) azides are alkali metal azides selected from the group consisting of lithium azide, sodium azide and potassium azide.
24. The method as in claim 23 wherein the alkali metal azide is sodium azide.
25. The method as in claim 20 wherein the (A) azides are alkaline earth metal azides selected from the group consisting of calcium azide, barium azide and magnesium azide.
26. The method as in claim 25 wherein the alkaline earth metal azide is magnesium azide.
27. The method as in claim 20 wherein the (A) azide is aluminum azide.
28. The method as in claim 20 wherein the (B) reactant is aluminum sulfide.
29. The method as in claim 20 wherein the (B) reactant is molybdenum disulfide.
30. The method as in claim 20 wherein the (B) reactant is ferrous sulfide.
31. The method as in claim 20 wherein the (B) reactant is iodoform.
32. The method as in claim 20 wherein the (B) reactant is carbon tetraiodide.
33. The method as in claim 20 wherein the (B) reactant is hexachloroethane.
34. The method as in claim 20 wherein the (B) reactant is perchloropentacyclodecane.
35. The method as in claim 20 wherein the (B) reactant is molybdenum trioxide.
36. The method as in claim 20 wherein the (B) reactant is tungsten trioxide.
37. The method as in claim 20 wherein the (B) reactant is lead dioxide.
38. The method as in claim 20 wherein the (B) reactant is vanadium pentoxide.
39. The method as in claim 20 wherein (B) reactant is sulfur.