



(11) Publication number: **0 543 026 A1**

(12) **EUROPEAN PATENT APPLICATION**  
**published in accordance with Art.**  
**158(3) EPC**

(21) Application number: **92917388.8**

(51) Int. Cl.<sup>5</sup>: **C06D 5/06**

(22) Date of filing: **28.05.92**

(86) International application number:  
**PCT/JP92/00697**

(87) International publication number:  
**WO 92/21636 (10.12.92 92/31)**

(30) Priority: **28.05.91 JP 123662/91**

(43) Date of publication of application:  
**26.05.93 Bulletin 93/21**

(84) Designated Contracting States:  
**DE FR GB**

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(54) **GAS GENERATING AGENT.**

(57) A gas generating agent comprising: (A) at least one alkali metal salt of chloric or perchloric acid, and (B) an organic compound composed of carbon, hydrogen and oxygen and/or a metal salt of an organic acid composed of carbon, hydrogen and oxygen, and characterized in that the molar fraction of oxygen and that of carbon dioxide contained in the formed gas meet a relation represented by the following equation (I): (mol. fraction of oxygen)/(mol. fraction of oxygen) + (mol. fraction of carbon dioxide)] = 0.01 – 0.5.

**EP 0 543 026 A1**

Background of the InventionField of the Invention

5 The present invention relates to a gas generant which is used in an air bag apparatus for securing the safety of an occupant(s) against the shock caused by a car crash and which is harmless to human bodies.

Description of the Related Art

10 The gas generant used in such an air bag apparatus according to the prior art is mainly constituted of a mixture of an alkali metal azide and an alkaline earth metal azide with a metallic oxide, a chlorate, sulfur, a metallic sulfide or the like, and the gas generated therefrom is nitrogen. Further, sodium azide is now widely used as the alkali metal azide.

Most of the air bag apparatuses now set in cars use a gas generant as described above comprising sodium azide as a main raw material and are mounted on a steering wheel to protect a driver. At the instant of a car crash, the gas generant generates pure nitrogen gas, which inflates the air bag to thereby secure the safety of the driver. Thereafter, the pure nitrogen gas is speedily discharged from the air bag to the inside of the car through a vent hole provided in the air bag. In this case, it does not occur a problem with regard to occurrence of any physiological injuries due to the oxygen deficiency in the car, because the volume of the air bag is about 60 l or less. However, it seemed that air bag apparatuses for an passenger's seat and rear seats may be set in addition to one for a driver's seat, and that air bag apparatuses for absorbing the shock caused by a side crash may also be set in the near future. An attempt to cope with this situation solely by means of an air bag using pure nitrogen gas alone necessitates a large amount of pure nitrogen gas, and there is the possibility that a problem such as the occurrence of physiological injuries due to the oxygen deficiency in the car becomes clear.

Sodium azide is easily decomposed in the atmosphere to generate hydrazoic acid which is volatile and explosive. The hydrazoic acid is easily reacted with a metal such as copper, lead and the like present around to form an extremely unstable substance which ignites or explodes by friction or a crash. In the air bag apparatus using sodium azide, of course, the sodium azide is placed in a hermetically sealed state so as to be out of contact with the atmosphere. Thus, the air bag apparatus is constituted so as not to form the unstable substance described above when it is set in a car. Nevertheless, there is still disadvantage that the gas generant comprising sodium azide must be handled with care in an explosion proof facility in the preparation, storage and disposal of the gas generant itself and in the preparation or disposal of the air bag apparatus using the gas generant.

Further, such an air bag apparatus uses, for example, copper oxide, sulfur or the like as an oxidizing agent for combusting the sodium azide, so that a mist of sodium oxide or sodium sulfide is formed and discharged during the combustion. In the air bag apparatus which is currently used, the mist can be sufficiently removed by the use of a filter, by which the problem such as occurrence of any physiological injuries does not occur. However, the air bag apparatus has another problem that the weight and volume of the gas generator must be increased in order to enhance the performances of the filter.

In order to avoid the above-described problem that sodium azide forms an unstable substance, there have been disclosed a gas generant which comprises an oxahydroxamic acid and poly(vinyl lower alkyl ether) (Japanese Patent Publication - B No. 7873/1966); one which comprises a bitetrazole compound as a main component (Japanese Patent Publication - B Nos. 6156/1989 and 6157/1989); and one which comprises nitroorotic acid as a main component (Japanese Patent Publication - A No. 184590/1990). However, these gas generants are in danger of generating a gas containing, as by-products, a cyanide compound, nitrogen oxide, carbon monoxide, etc., which are causative of a problem such as the physiological injuries due to the by-products when many air bag apparatuses are set in the car. Further, the principal ingredients of the above gas generants are more expensive than sodium azide and do not satisfy all of the requirements as a gas generant. Most of the gases which is generated from the gas generants comprising a nitrogen-containing compound as a principal ingredient are pure nitrogen, so that there is the possibility that a problem such as the occurrence of physiological injuries due to the oxygen deficiency in the car becomes clear when a large amount of the gas generant is used, which is same as the case where the gas generant comprising sodium azide as the principal ingredient is employed.

Up to this time, there have been disclosed a composition comprising a nitrate or a perchlorate as an oxidizing agent and an organic polymer consisting of carbon, hydrogen and oxygen (U.S. Patent No. 3837942) and a composition comprising such an oxidizing agent and a metallic salt of an organic acid consisting of carbon, hydrogen and oxygen (U.S. Patent No. 4214438). These compositions contain the

oxidizing agent in an amount exceeding the stoichiometrically necessary one in order to prevent the generation of carbon monoxide, so that the gaseous component generated therefrom is composed only of water vapor and carbon dioxide. However, the prime object of these U.S. patents is to prevent the generation of carbon monoxide, so that the amount of the oxidizing agent used is nearly equivalent to the stoichiometrically necessary one. Accordingly, there is the possibility that a problem such as the occurrence of physiological injuries due to the oxygen deficiency in the car becomes clear when many air bag apparatuses are set in the car, which is same as the case where the sodium azide is employed.

The present invention aims at providing an inexpensive and harmless gas generant which can be easily handled in the preparation, storage and disposal thereof and in the preparation or disposal of the air bag apparatus without the necessity for any special handling manner unlike alkali metal azides and which is used for inflating an air bag with a gas which does not cause the physiological injuries due to oxygen deficiency or by-products even when many air bag apparatuses are set in the car.

#### Description of the Invention

##### Summary of the Invention

The present inventors have extensively studied on the influence of carbon dioxide on a human body and have found that the gas generated from the gas generant of the present invention can maintain an oxygen partial pressure in carbon dioxide like in the air, so that it can be used for inflating an air bag in safety without causing any trouble due to oxygen deficiency. The present invention has been accomplished on the basis of this finding.

Namely, the present invention relates to a gas generant for an air bag apparatus comprising (A) one of alkali metal salts of chloric or perchloric acid or a mixture of two or more of them and (B) an organic compound consisting of carbon, hydrogen and oxygen and/or a metallic salt of an organic acid consisting of carbon, hydrogen and oxygen, characterized in that the value which is related to the molar fractions of oxygen and carbon dioxide in the gas generated and which is calculated by the following formula (I):

$$\frac{(\text{molar fraction of oxygen})}{(\text{molar fraction of oxygen}) + (\text{molar fraction of carbon dioxide})} \dots (I)$$

lies within a range of 0.01 to 0.5, and to a gas generant which may further contain 1 to 6% of a combustion modifier to be able to control the time taken for inflating an air bag within a suitable range.

When the value calculated by the formula:

$$\frac{(\text{molar fraction of oxygen})}{(\text{molar fraction of oxygen}) + (\text{molar fraction of carbon dioxide})} \dots (I)$$

is less than 0.01, it is unfavorable because there are the possibilities that a problem such as the occurrence of physiological injuries due to the oxygen deficiency in the car becomes clear and that a problem such as the physiological injuries to a human body due to the carbon dioxide occurs when many air bag apparatuses are set in the car. On the contrary, when this value exceeds 0.5, the combustion temperature will be so high that there is the possibility of burning the air bag, unfavorably. It is still preferable that the value be from 0.1 to 0.3.

According to the present invention, it is possible that a low-temperature gas which does not form any nitrogen oxide harmful to a human body is generated by using a composition comprising (A) an oxidizing agent comprising sodium or potassium salt of chloric or perchloric acid, (B) a fuel component of an organic compound free from any nitrogen atom in its molecule and consisting of carbon, hydrogen and oxygen and/or a fuel component of a metallic salt of an organic acid consisting of carbon, hydrogen and oxygen and, if necessary, a combustion modifier component, even when the composition contains an excess of the oxidizing agent, that is, the composition generate a gas containing oxygen.

Regarding the oxidizing agent, the use of a perchlorate is advantageous from the standpoint of lowering the temperature of the gas generated, because the perchlorate generates less heat in its thermal decomposition and gives oxygen at a higher ratio.

The fuel component is preferably an organic compound consisting of carbon, hydrogen and oxygen and generating a low heat of combustion, such as oxalic acid, cellulose acetate and the like. The combustion modifier is used for the purpose of controlling the reaction rate and completing the reaction in the combustion reaction of the gas generant and is preferably carbon and an oxide of iron, nickel, etc., a ferrocene compound or a metallic salt of a nonnitrogenous organic acid such as formic acid, oxalic acid and the like.

The present invention relates to a gas generant for inflating an air bag, which is prepared by preparing a mixture comprising a nitrogen-free chlorate, a nitrogen-free fuel component consisting of carbon, hydrogen and oxygen and, if necessary, a combustion modifier and processing the mixture.

The gas generant composition of the present invention can be prepared by pulverizing each of the oxidizing agent, the fuel component and, if necessary, the combustion modifier and mixing the obtained powders with each other by the dry or wet process. When the powder mixture thus prepared is placed under the circumstances of suffering vibration for a long time, it is separated owing to the specific gravity difference among the powders to bring about a variation in the combustion properties. Therefore, the powder mixture may be granulated or may be compressed into a tablet or pellet by a conventional process. Although the particle size of the gas generant composition is not particularly limited, it is preferred in the case of requiring rapid combustion that the particle size be 10  $\mu\text{m}$  or below.

The gas generant composition of the present invention can be used in a state packed in a common gas generator according to the prior art, which is constituted of a reaction chamber which is used for packing gas generant pellets and an ignition charge, and a filtration chamber fitted with a metal screen, glass cloth or ceramic paper, etc., for separating and collecting the mist contained in the gas generated.

#### Effect of the Invention

The gas generant of the present invention is harmless to human bodies. Further, the gas generant is safe because the combustion product therefrom is composed of a gaseous component consisting of oxygen, carbon dioxide and water and a mist of an alkali metal chloride and a metallic oxide, such as iron oxide and the like, resulting from the combustion modifier to cause neither physiological injuries due to oxygen deficiency nor those due to the by-products such as nitrogen compounds and does not contain any harmful mist such as sodium oxide or sodium sulfide, etc. Therefore, the air bag apparatus using the gas generant of the present invention does not need to enhance the performance of the filter unlike the commercially available air bag apparatus of the prior art as described above. Thus, the gas generant of the present invention contributes to the reduction of the weight and volume of the gas generator.

The fuel component according to the present invention is non-explosive and therefore need not be handled in a special manner unlike alkali metal azides in the preparation, storage and disposal of the gas generant.

#### Example

The present invention will now be described more specifically by referring to the following Examples, though the present invention is not limited by them.

#### Example 1

73 parts by weight of a dry powder of sodium perchlorate and 27 parts by weight of a dry powder of glucose were sufficiently mixed with each other and press-molded into cylindrical pellets having an outer diameter of 7 mm and a thickness of 4 mm. 50 g of the pellets were packed into a gas generator for a driver's seat and the gas generator was actuated in a 60-l pressure tank to determine the relationship between the pressure and time. The results are as follows:

0.6 atm after 30 msec, and

0.8 atm after 50 msec.

Further, the gas generated was analyzed for composition. The results are as follows:

oxygen	14% by volume
carbon dioxide	42% by volume
water	43% by volume
nitrogen oxide	not detected
nitrogen	not detected
carbon monoxide	not detected

With respect to the above gas composition,

$$\begin{aligned}
 & \frac{\text{(molar fraction of oxygen)}}{\text{(molar fraction of oxygen)} + \text{(molar fraction of carbon dioxide)}} \\
 &= \frac{14}{14 + 42} \\
 &= 0.25
 \end{aligned}$$

#### Example 2

73 parts by weight of a dry powder of sodium perchlorate, 27 parts by weight of a dry powder of glucose and 2 parts by weight of a dry powder of iron oxide were sufficiently mixed with each other and press-molded into cylindrical pellets having an outer diameter of 7 mm and a thickness of 4 mm. 50 g of the pellets were packed into a gas generator for a driver's seat and the gas generator was actuated in a 60-l pressure tank to determine the relationship between the pressure and time. The results are as follows:

0.9 atm after 30 msec, and

1.1 atm after 50 msec.

Further, the gas generated was analyzed for composition. The results are as follows:

oxygen	14% by volume
carbon dioxide	42% by volume
water	43% by volume
nitrogen oxide	not detected
nitrogen	not detected
carbon monoxide	not detected

With respect to the above gas composition,

$$\begin{aligned}
 & \frac{\text{(molar fraction of oxygen)}}{\text{(molar fraction of oxygen)} + \text{(molar fraction of carbon dioxide)}} \\
 &= \frac{14}{14 + 42} \\
 &= 0.25
 \end{aligned}$$

### Example 3

75 parts by weight of a dry powder of sodium perchlorate and 25 parts by weight of a dry powder of cellulose triacetate were sufficiently mixed with each other and press - molded into cylindrical pellets having an outer diameter of 7 mm and a thickness of 4 mm. 50 g of the pellets were packed into a gas generator for a driver's seat and the gas generator was actuated in a 60 - l pressure tank to determine the relationship between the pressure and time. The results are as follows:

0.8 atm after 30 msec, and

1.0 atm after 50 msec.

Further, the gas generated was analyzed for composition. The results are as follows:

oxygen	12% by volume
carbon dioxide	43% by volume
water	44% by volume
nitrogen oxide	not detected
nitrogen	not detected
carbon monoxide	not detected

With respect to the above gas composition,

$$\begin{aligned}
 & \frac{(\text{molar fraction of oxygen})}{(\text{molar fraction of oxygen}) + (\text{molar fraction of carbon dioxide})} \\
 &= \frac{12}{12 + 43} \\
 &= 0.21
 \end{aligned}$$

### Example 4

75 parts by weight of a dry powder of sodium perchlorate, 25 parts by weight of a dry powder of cellulose triacetate and 2 parts by weight of a dry powder of iron oxide were sufficiently mixed with each other and press - molded into cylindrical pellets having an outer diameter of 7 mm and a thickness of 4 mm. 50 g of the pellets were packed into a gas generator for a driver's seat and the gas generator was actuated in a 60 - l pressure tank to determine the relationship between the pressure and time. The results are as follows:

0.9 atm after 30 msec, and

1.1 atm after 50 msec.

Further, the gas generated was analyzed for composition. The results are as follows:

oxygen	12% by volume
carbon dioxide	43% by volume
water	44% by volume
nitrogen oxide	not detected
nitrogen	not detected
carbon monoxide	not detected

With respect to the above gas composition,

$$\begin{aligned}
 & \frac{(\text{molar fraction of oxygen})}{(\text{molar fraction of oxygen}) + (\text{molar fraction of carbon dioxide})} \\
 &= \frac{12}{12 + 43} \\
 &= 0.21
 \end{aligned}$$

**Claims**

1. A gas generant for an air bag apparatus comprising (A) one of alkali metal salts of chloric or perchloric acid or a mixture of two or more of them and (B) an organic compound consisting of carbon, hydrogen and oxygen and/or a metallic salt of an organic acid consisting of carbon, hydrogen and oxygen, characterized in that the value which is related to the molar fractions of oxygen and carbon dioxide in the gas generated and which is calculated by the following formula (I):

$$\frac{(\text{molar fraction of oxygen})}{(\text{molar fraction of oxygen}) + (\text{molar fraction of carbon dioxide})} \dots (I)$$

lies within a range of 0.01 to 0.5.

2. The gas generant for an air bag apparatus as set forth in claim 1, characterized in that the value calculated by the formula

$$\frac{(\text{molar fraction of oxygen})}{(\text{molar fraction of oxygen}) + (\text{molar fraction of carbon dioxide})} \dots (I)$$

lies within a range of 0.1 to 0.3.

3. The gas generant for an air bag apparatus as set forth in claims 1 or 2, characterized in that further contains (C) a combustion modifier.

4. The gas generant for an air bag apparatus as set forth in claim 3, characterized in that 1 to 6 % of the combustion modifier is added.

# INTERNATIONAL SEARCH REPORT

International Application No PCT/JP92/00697

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (If several classification symbols apply, indicate all) *		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int. Cl. <sup>5</sup> C06D5/06		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>7</sup>		
Classification System	Classification Symbols	
IPC	C06D5/06	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>8</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT <sup>9</sup></b>		
Category *	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
X	JP, A, 49-74165 (Societe Nationale des Poudres et Explosifs), July 17, 1974 (17. 07. 74), Claim, lines 4 to 9, lower right column, page 1, line 14, lower left column, page 3 to line 4, upper left column, page 4 & FR, B1, 2213254 & US, A, 3964256	1-4
X	JP, A, 49-132208 (Societe Nationale des Poudres et Explosifs), December 18, 1974 (18. 12. 74), Claim, lines 6 to 10, upper right column, page 2, line 12, upper left column to line 17, upper right column, page 3, line 17, lower left column to line 9, lower right column, page 4 & FR, B1, 2190776 & US, A, 3986908	1-4
A	US, A, 3837942 (Specialty Products Development Corporation), September 24, 1974 (24. 09. 74), & JP, A, 48-99310	1-4
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>* Special categories of cited documents: <sup>10</sup></p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"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</p> <p>"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"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</p> <p>"&amp;" document member of the same patent family</p> </div> </div>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
August 14, 1992 (14. 08. 92)	September 8, 1992 (08. 09. 92)	
International Searching Authority	Signature of Authorized Officer	
Japanese Patent Office		