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0000005-9 3 January 2000 (03.01.2000) SE For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.
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WO 01/49637 A1

(54) Title: METHOD OF PRODUCING GAS-OPERATED VEHICLE SAFETY DEVICES AND THE PYROTECHNIC GAS-GENERATING SUBSTANCES PRODUCED USING THE METHOD

(57) Abstract: The present invention refers to a method of manufacturing a new general type of pyrotechnic gas-generating substance for gas operated vehicle safety devices such as airbags, belt tensioners, and also to the gas-generating substances produced in accordance with this method. The main characteristic of the gas-generating substances in accordance with the invention is that they consist of a salt composition consisting of at least one fuel selected from a group containing such dinitromethane based salts whose base substituent is selected from guanidine, guanyl urea or ammonium and at least one oxygen generating substance selected from a group consisting of the metals Li, Na, K, Mg, Ca and Sr based oxygen-rich salts whose oxygen component consists of one of the substituents NO<sub>3</sub>, NO<sub>2</sub>, ClO<sub>3</sub>, ClO<sub>4</sub> or dinitromethane.

## Case 3821

Method of producing gas-operated vehicle safety devices and the pyrotechnic gas-generating substances produced using the method

The pyrotechnic gas-generating substance in an airbag device is intended to quickly fill the cloth bag with gas so that it provides a shock absorbent protection between the passenger and the interior of the vehicle. The function and safety of the airbag and the surrounding environment set a number of requirements for the pyrotechnic gas-generating substance and the gas that is generated. The same requirements are set for the pyrotechnic gas-generating substances in other gas-operated vehicle safety devices such as belt tensioners, inflatable neck protectors etc.

The gas generated in all such vehicle safety applications shall not therefore contain hot solid particles which could burn through the main system components, the gas filled cloth bags and injure passengers or place the entire function of the safety device at risk. The most common pyrotechnic gas-generating substances used at present in the form of different sodium azide compositions, do not entirely fulfil these requirements and for this reason extra reinforced cloth bags are used in combination with these gas-generating substances in order to stop solid particles formed at the combustion of sodium azide. The necessity of this extra reinforcement results in each such vehicle safety device having a greater weight and volume than would otherwise be required by the intended function.

The environmental requirements for the pyrotechnic gas-generating substances used for this purpose stipulate that these substances shall not create gas compounds which contain toxic gases in quantities that are injurious to the health. The toxic gases which primarily could be relevant in this context are nitrous compounds,  $\text{NO}_x$  and carbon monoxide as these are formed by the combustion of gas-generating substances. If chlorine is included in the gas-generating substance, hydrochloric acid is also formed.

Furthermore, it is also required of a gas-generating pyrotechnic substance in a gas-operated vehicle safety device that this substance shall have a high degree of

efficiency which means that it shall give a large amount of gas per weight or volume unit gas-generating substance. As regards sodium azide compositions, these do not have a specially high degree of efficiency insofar as gas is generated by only approximately 40% of the solid substance. This low degree of efficiency has the result that when sodium azide is used as the gas-generating substance, it is difficult to fulfil the vehicle manufacturers' requirements of low weight and small volume for the vehicle components in question.

Another requirement for these pyrotechnic gas-generating substances is that all shall be thermally stable and not be affected by the very high temperatures which can prevail in a vehicle panel in hot climates. Nitro-cellulose is one example of a substance that does not fulfil this requirement but which would otherwise be conceivable, and which is at present used for this purpose despite giving the vehicle safety device in question a limited service life.

Besides the requirements stated above, to ensure satisfactory function the pyrotechnic gas-generating substance used in the vehicle safety products must fulfil several requirements concerning own burning characteristics. The ideal pyrotechnic gas-generating substance used for this purpose shall have a high rate of combustion which is not influenced by pressure and/or temperature. In this respect, sodium azide compositions are ideal substances but as already stated these substances have several disadvantages.

Another group of substances which are gas-generating during combustion and have been tested in vehicle safety parts are nitramine-based propellant compositions such as RDX which for example is used in compounds with cellulose acetyl butyrate. One disadvantage of the nitramine based propellant is however that its combustion rate is very pressure dependent. In a pressure which is too low, burning ceases completely while in a too high pressure it changes to an explosion. It has been possible to counteract these disadvantages as is demonstrated in USA patent 5695216, by constructing powerful enclosures for the gas generating substance and fitting these enclosures with pressure reliefs, but although this functions well it means that the construction is burdened with extra parts and higher costs.

Another specific type of pyrotechnic gas-generating substance which is well adapted to airbag devices is the compound guanidine dinitramide which is easily produced from guanidine and ammonium dinitramide and is described in the Swedish patent application 9804611-3.

Guanidine dinitramide can be used for this purpose either in pure form or together with other gas forming or oxygen producing substances such as guanyl urea dinitramide with the help of which the combustion and gas forming rates of the pyrotechnic substance can be adjusted to individual requirements.

An important advantage of guanidine dinitramide and compounds in which it is the main component is that these substances themselves contain both oxidisers and fuel. It is therefore in principle a mono-propellant that does not require any additions or access to the oxygen in the air for its own combustion.

As already referred to above it is stated in the Swedish patent application that guanidine dinitramide's combustion rate and thereby the gas generation rate of the substance can be adjusted by the inclusion of other gas-generating or oxygen producing substances such as guanyl urea dinitramide.

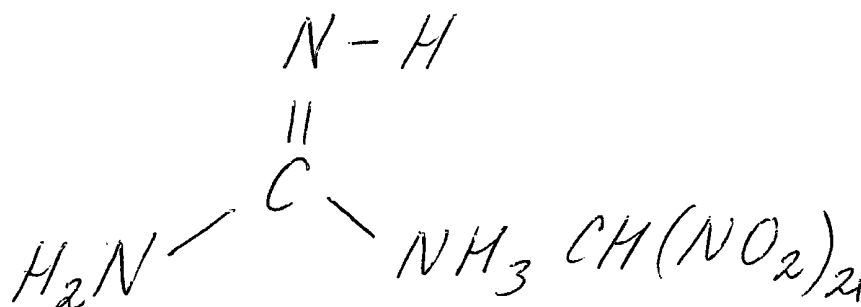
An original idea which in time led to the present invention was that if guanidine dinitramide and guanyl urea dinitramide are good gas-generating substances for vehicle safety devices, the corresponding dinitromethanes should also have the same characteristic. It was not however so simple as these dinitromethanes do not function as complete mono-propellants.

Our efforts to find better gas-generating substances for vehicle safety devices resulted however in the present invention in accordance with which we use as the gas-generating pyrotechnic substance salt compounds consisting of at least one fuel selected from a group including such dinitromethane-based salts whose main characteristic is that they include a nitrogen-rich powerful base with a  $P_{ka}$  for the protonised base  $>9$  and at least one oxygen generator selected from a group including oxygen-rich salts based on one of the metals Li, Na, K, Mg, Ca or Sr and

whose oxygen-rich component consists of one of the substituents  $\text{NO}_3$ ,  $\text{NO}_2$ ,  $\text{ClO}_3$ ,  $\text{ClO}_4$  or dinitromethane.

As regards the fuel component base substituent we have found that it should preferably be guanidine, guanyl urea or ammonium.

An example of a suitable fuel component in accordance with the invention is therefore guanidine dinitromethane which has the following chemical formula:



These components should then be combined in such quantities that provide an oxygen balanced final product with the desired combustion characteristics. The previously known substances for this purpose, guanidine dinitramide and guanyl urea dinitramide, can then be added in the quantities required to the substances which are gas-generating at combustion in order to obtain the desired combustion rate.

An example of a gas-generating substance with a suitable combustion rate for certain gas operated vehicle safety devices is one containing approximately 70% by weight guanidine dinitromethane as fuel and approximately 30% by weight potassium dinitromethane as oxygen generator.

As is the case with guanidine dinitramide and guanyl urea dinitramide compounds proposed previously, the metal salt and dinitromethane based gas-generating substances cause such a small degree of smoke formation that an activated airbag device does not risk being mistaken for a fire in the vehicle as has been the case with earlier types of airbag device for example those containing azides as gas-generating substances.

All of the gas-generating substances proposed are pressed to tablets with good structural strength at least if they have a small quantity of binder which should then preferably not exceed 10% by weight.

In accordance with the present invention, the substances in question have the advantage that when they have served as potential gas-generating substances in vehicle safety devices, which hopefully have not been used in active operation, they can be easily recycled by means of recrystallisation and used as gas-generating substances in other or similar products.

Although at present in all manufacture of chemical substances it is required for environmental reasons to consider how these new products can be recovered and re-used, none of the gas-generating substances used at present in vehicle safety devices can be easily recovered when they have served out their service life but not been put into active use. As vehicle safety devices are by nature products which preferably are not put into practical operation one can expect that the number of unused gas-generating substances which must be taken care of when the vehicles are scrapped will increase at the same rate as such safety devices are installed in the range of new vehicles.

Sodium azide which is used extensively in vehicle safety devices today is therefore in practice always used in the form of a composition in which  $\text{Fe}_2\text{O}_3$  and silicate are included and at present there is no plan for the recycling of sodium azide. Sodium azide is furthermore extremely toxic and for this reason one can see no possibility other than destruction as soon as possible after the vehicle safety device in which it is included has completed its service life. Nor is not possible to re-use nitro-cellulose as the substance is unstable and is consequently degraded with the passage of time. The only practical method of destruction is to remove the nitro-cellulose from the scrapped products and incinerate it as in the case of sodium azide.

The substances now suggested are however unified and stable and are also easy to recrystallize. Should degradation have taken place to any extent these products can still be re-used following recrystallization. In recrystallization, all the possible degradable products are washed away and the recrystallized product is completely

comparable with newly manufactured products. This capability to recover and re-use gas-generating products in scrapped vehicle safety devices of this type is of course a great environmental advantage compared with the azides and nitro-cellulose propellants normally used at present which also must be destroyed by incineration while the previously mentioned nitramine propellant can be recovered by recrystallization.

The invention in its different parts has been defined in the following patent claims and a principle diagram which shows the combustion/pressure graph for the product in accordance with the invention compared with sodium azide compositions used at present, and a general sodium propellant is shown in the enclosed figure.

From these plots it can be seen that the products in accordance with the invention generally have the same low pressure dependence for combustion rate as the sodium compositions used at present and that both these product groups differ on this point from most other propellants. (Nitro-cellulose has combustion plots that are almost the same as those for nitramine propellants). The figures also show that the products in accordance with the invention have a combustion rate which is greater than the sodium azide compositions in present use.

The present invention therefore makes available a gas-generating product which is adapted to the purpose and has a high combustion rate and low pressure dependence which together mean that it is possible to make cheaper airbag devices and that these do not need to withstand great overpressure and that they can be loaded with larger propellant tablets than has been possible previously as the products in accordance with the invention will never require extreme combustion areas.

## PATENT CLAIMS

1. Method of manufacturing gas-operated vehicle safety devices such as airbags, belt tensioners, inflatable neck cushions and equivalent, in which the chemicals used in the gas-generating substance in the event the device is not subjected to active use and following the removal of the original installation at the time of the end of its normal use, can be recovered, **w h e r e i n** the gas-generating pyrotechnic substance used consists of salt compositions consisting of at least one fuel selected from a group containing such dinitromethane based salts whose main characteristic is that they include a nitrogen rich powerful base with a Pka for the protonised base >9 and at least one oxygen generating substance selected from a group consisting of the metals Li, Na, K, Mg, Ca and Sr based oxygen rich salts whose oxygen component consists of one of the substituents NO<sub>3</sub>, NO<sub>2</sub>, ClO<sub>3</sub>, ClO<sub>4</sub> or dinitromethane.
2. Method in accordance with Claim 1 **w h e r e i n** guanidine, guanyl urea or ammonium is selected as the fuel component base substituent.
3. Pyrotechnic gas-generating substance for gas operated vehicle safety devices such as airbags, belt tensioners etc manufactured in accordance with either Claim 1 or 2 **w h e r e i n** the substance consists of salt composition consisting of at least one fuel selected from a group containing such dinitromethane based salts whose main characteristic is that they include a nitrogen rich powerful base with a Pka for the protonised base >9 and at least one oxygen generating substance selected from a group consisting of the metals Li, Na, K, Mg, Ca and Sr based oxygen rich salts whose oxygen component consists of one of the substituents NO<sub>3</sub>, NO<sub>2</sub>, ClO<sub>3</sub>, ClO<sub>4</sub> or dinitromethane.
4. Pyrotechnic gas-generating substance **w h e r e i n** the base substituent of the fuel component consists of guanidine, guanyl urea or ammonium.



5. Pyrotechnic gas-generating substance in accordance with Claim 4 **w h e r e i n** it includes several of the different fuel and oxygen generating substances stated in Claims 1-4 and which together form the gas generating substance.

6. Pyrotechnic gas-generating substance in accordance with Claims 1-5 **w h e r e i n** at least one of the compounds guanide dinitramide or guanyl urea dinitramide is included as well as one out of each group of the fuels and oxygen generating substances defined in Claims 1-5.

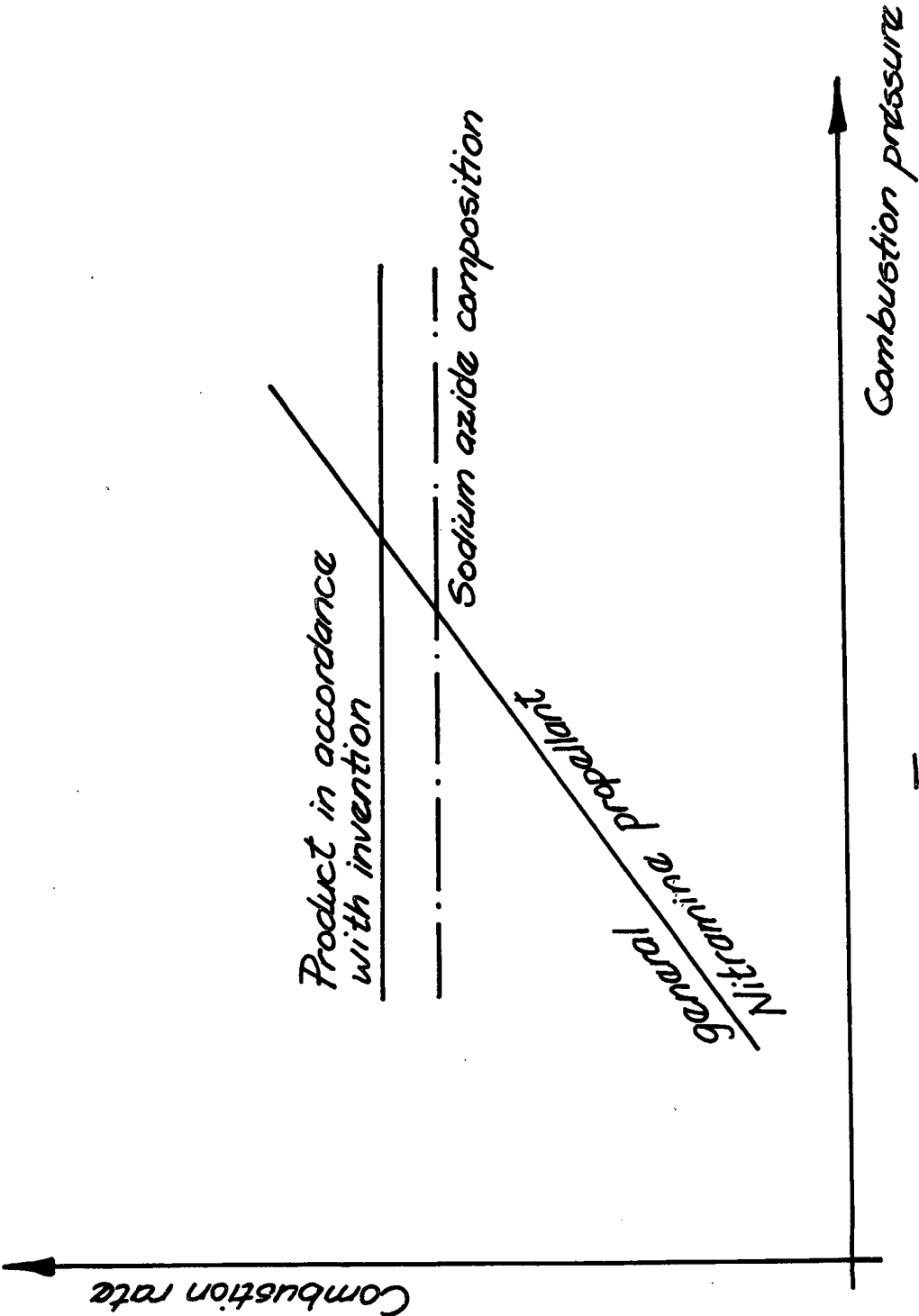


Fig.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/SE 01/00001

## A. CLASSIFICATION OF SUBJECT MATTER

IPC7: C06D 5/06, C06B 25/34, C06B 31/00, C01B 21/082  
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)

IPC7: C01B, C06B, C06D

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

SE,DK,FI,NO classes as above

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

QUESTEL; EDOC, WPIL, STN:REG.CA, DIALOG: DIALINDEX

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 9855428 A1 (FÖRSVARETS FORSKNINGSANSTALT), 10 December 1998 (10.12.98), claim 5  -- -----	2,4-6



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

"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)

"O" document referring to an oral disclosure, use, exhibition or other means

"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

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"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

"&amp;" document member of the same patent family

Date of the actual completion of the international search

5 April 2001

Date of mailing of the international search report

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# INTERNATIONAL SEARCH REPORT

International application No.  
**PCT/SE01/00001**

## Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
  
2. ☒ Claims Nos.: **1, 3**  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:  
  
**See extra sheet**
  
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
  
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

### Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.  
☐ No protest accompanied the payment of additional search fees.

Present claims 1 and 3 relate to gas generators for vehicle safety equipment defined inter alia by reference to the following parameter:

Pka for the protonised base >9

The use of this parameter in the present context is considered to lead to a lack of clarity within the meaning of Article 6 PCT. It is impossible to compare the parameter the applicant has chosen to employ with what is set out in the prior art. The lack of clarity is such as to render a meaningful complete search impossible. Consequently, the search has been restricted to claims 2 and 4-6.

### Information on patent family members

International application No.

PCT/SE 01/00001

Form PCT/ISA/210 (patent family annex) (July 1998)