

EUROPEAN QUALIFYING EXAMINATION 2015

Paper B(Ch)

Chemistry

This paper comprises:

- | | |
|--|---------------------|
| * Patent application | 2015/B(Ch)/EN/1-7 |
| * Communication | 2015/B(Ch)/EN/8-9 |
| * Document D1 | 2015/B(Ch)/EN/10-11 |
| * Document D2 | 2015/B(Ch)/EN/12 |
| * Letter from the applicant
(including new set of claims) | 2015/B(Ch)/EN/13-14 |



Patent application

Airbag composition

[001] Airbags are used to protect drivers and passengers in automobiles. An airbag system contains a gas-generating composition and is activated when a sensor detects a collision. The gas-generating composition has to produce a large amount of clean gas in a short time (50 ms or less).

[002] The composition needs to be stable for the lifetime of the automobile without loss of activity. During this time the composition will be exposed to a wide variety of temperatures.

[003] The gas-generating compositions are in the form of pellets containing fuel particles and particles of an oxidant.

[004] Organic nitrogen compounds can be used as the fuel in airbags. We use tetrazole, aminotetrazole, nitrotetrazole, nitroaminotetrazole and triazole as the fuel, because we have found that only these compounds are sufficiently stable in our compositions.

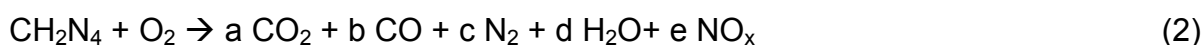
[005] The oxidants are chlorates, perchlorates or nitrates. These oxidants are added as the alkali metal or alkaline earth metal salts. After reaction these compounds are converted to oxides. These oxides are harmful for the environment and can be toxic.

[006] The following reactions take place when the airbag is activated:

Oxidant (e.g. strontium nitrate):



This oxygen formed will then react with the fuel. In the reaction equation tetrazole is shown (CH_2N_4).



[007] As mentioned above, the oxides formed, such as strontium oxide (SrO) in equation (1), can be harmful for the human body and/or for the environment. Measures should therefore be taken to avoid that the oxides are released. In most airbag systems the oxides are converted to an easily collectable slag.

[008] The temperatures during the combustion are so high that the oxides formed tend to melt. In order to avoid this problem, slag forming agents need to be added to the composition. These slag forming agents help to produce a solid with a melting point above the reaction temperature of the airbag composition.

[009] We have now found a way to increase the percentage of the oxides converted into slag by the use of a carbide or a nitride as the slag forming agent.

[010] Carbides or nitrides of boron, aluminium or silicon can be used in the present invention. Carbides or nitrides of silicon or aluminium are preferred because the silicates and aluminates that are formed are particularly easy to collect.

[011] The slag formation can be further improved by the addition of a secondary slag forming agent. These additives can help optimise the slag formation. These secondary slag forming agents are selected from oxides or hydroxides of titanium or aluminium. When carbides are used as primary slag forming agents hydrotalcites are very useful secondary slag forming agents. Hydrotalcites (HTC) are layered double hydroxides of formula $\text{Mg}_6\text{Al}_2(\text{CO}_3)(\text{OH})_{16}\cdot 4\text{H}_2\text{O}$. Hydrotalcites are a very specific form of clays. This combination, in addition, seems to have an effect on the level of noxious gases produced, probably due to the adsorptive properties of the hydrotalcite.



[012] In its most general form, the present invention therefore provides gas-generating compositions comprising at least a fuel component, an oxidant and a slag forming agent. Additionally the composition usually contains a water-soluble polymer for helping to shape the composition and a lubricant to further improve the formability. All of the components used are commercially available.

[013] The fuel component is present in an amount of 20 to 50 wt.% of the gas-generating composition. When the amount of fuel is below 20 wt.% the amount of gas produced is not sufficient. On the other hand, if the amount of fuel is above 50 wt.% a complete combustion of the fuel cannot be achieved.

[014] The fuel particles must have a size of 5 to 80 μm . Outside this range the composition is not suitable for use in airbags.

[015] The oxidant is a nitrate, a chlorate or a perchlorate of an alkali metal or an alkaline earth metal. Mixtures of these oxidants can also be used. The oxidant is present in an amount of 30 to 70 wt.% of the gas-generating composition. Of these known oxidants nitrates are preferred because they do not release chlorine-containing compounds.

[016] The slag forming agent as a whole should be present in an amount of 10 to 20 wt.% of the gas-generating composition. If a secondary slag forming agent is present this must be added in a weight ratio of 1:5 to 5:1 with respect to the nitride or the carbide to have any effect.

[017] The process for making the composition is straightforward, although some precautions need to be taken. The ingredients are ground to the intended particle size and are then mixed together. It is important that the mixture is homogeneous because inhomogeneity may lead to instability of the composition. Devices for such mixing are well-known to the person skilled in the art. Merely as an example the Batch Muller[®] mixer is mentioned. The homogeneous mixture is then pressed into pellets.



[018] The pressing needs to last for at least 5 minutes when the mixture contains hydrotalcite. The choice of the type of pelletiser is not crucial for the process. Finally the pellets are heat treated at a temperature between 80 and 120°C for at least 10 hours to make them more resistant to ageing. Below 80°C the treatment is not effective and above 120°C decomposition of the pellets may take place. In case a secondary slag forming agent is used it is essential that the slag forming agents are first mixed and then the other ingredients are added.

Examples

[019] A large number of compositions were prepared in order to show the benefits of the present invention. All compositions use 36 wt.% fuel, 52 wt.% oxidant and 12 wt.% slag forming agent. When a secondary slag forming agent was used, it was used in a 1:1 weight ratio with respect to the primary slag forming agent. The total amount of slag forming agent was always 12 wt.% in the examples.

[020] The active ingredients all have an average particle size of 30 µm. The ingredients were mixed together with 0.4 wt.% polyvinyl alcohol as a water-soluble polymer and 0.6 wt.% stearic acid as a lubricant in a Batch Muller[®] mixer. These ingredients were pressed for 5 minutes into a cylindrically shaped pellet having a height of 2 mm and a diameter of 2 mm and then heat treated at 100°C for 12 hours. When pressing pellets from compositions containing hydrotalcite it turned out to be essential to press for at least 5 minutes. Otherwise, stable pellets could not be obtained. After this heat treatment, the pellets were tested in a tank test vessel in which the amount of gas produced per unit of time was measured. Furthermore, an analysis of the composition of the gases produced was made and the amount of collected slag was measured.



[021] In Table 1 several parameters are presented that indicate the efficiency of the compositions. The time of filling the standard volume of the tank to a pressure of 5 bar is a measure for the speed of gas generation. The amount of collected slag is weighed and is compared with the theoretical amount of slag that could be formed. The percentage of slag is the amount of oxides converted into a slag. Table 2 gives an indication of concentrations of noxious gases generated by the compositions.

Table 1: Time for gas generation and efficiency of slag collection in airbag compositions

Example	Fuel	Oxidant	Slag forming agent	Further additive	Time to generate standard amount of gas (ms)	Percentage of collected slag
1	tetrazole	$\text{Sr}(\text{NO}_3)_2$	SiC	none	45.1	87
2	tetrazole	$\text{Sr}(\text{NO}_3)_2$	Si_3N_4	none	46.7	86
3	tetrazole	$\text{Sr}(\text{NO}_3)_2$	SiC	TiO_2	43.2	91
4	tetrazole	$\text{Sr}(\text{NO}_3)_2$	SiC	HTC	42.7	93
5	tetrazole	$\text{Sr}(\text{NO}_3)_2$	Si_3N_4	TiO_2	44.1	90
Comparative 1	tetrazole	$\text{Sr}(\text{NO}_3)_2$	none	none	41.0	49
Comparative 2	tetrazole	$\text{Sr}(\text{NO}_3)_2$	none	TiO_2	42.5	48
Comparative 3	tetrazole	$\text{Sr}(\text{NO}_3)_2$	none	HTC	42.8	46



Table 2: Analysis of noxious gases (CO, NO_x) in airbag compositions

Example	Fuel	Oxidant	Slag forming agent	Further additive	CO (ppm)	NO _x (ppm)
1	tetrazole	Sr(NO ₃) ₂	SiC	none	2000	140
2	tetrazole	Sr(NO ₃) ₂	Si ₃ N ₄	none	2200	140
3	tetrazole	Sr(NO ₃) ₂	SiC	TiO ₂	2100	110
4	tetrazole	Sr(NO ₃) ₂	SiC	HTC	1400	80
5	tetrazole	Sr(NO ₃) ₂	Si ₃ N ₄	TiO ₂	2300	110
Comparative 1	tetrazole	Sr(NO ₃) ₂	none	none	4000	320
Comparative 2	tetrazole	Sr(NO ₃) ₂	none	TiO ₂	4000	320
Comparative 3	tetrazole	Sr(NO ₃) ₂	none	HTC	2500	180

In the tables the molecular formulae and abbreviations have the following meaning:
 Sr(NO₃)₂ is strontium nitrate; SiC is silicon carbide; Si₃N₄ is silicon nitride; TiO₂ is titanium dioxide and HTC is hydrotalcite.

[022] The pellets were also tested for their stability. Under accelerated ageing conditions the pellets of example 4 containing HTC as a secondary slag forming agent were substantially more stable than the other pellets.



Claims

1. Airbag composition comprising,
 - (i) 20 to 50 wt.% of a fuel being selected from the group of tetrazole, aminotetrazole, nitrotetrazole, nitroaminotetrazole and triazole;
 - (ii) 30 to 70 wt.% of an oxidant being selected from alkali metal or alkaline earth metal nitrate, chlorate or perchlorate;
 - (iii) 10 to 20 wt.% of a slag forming agent comprising a carbide or nitride of boron, aluminium or silicon.
2. Airbag composition according to claim 1 in which the slag forming agent comprises a secondary slag forming agent selected from oxides or hydroxides of titanium or aluminium.
3. Airbag composition according to claim 1 in which the composition comprises carbides as slag forming agent and hydrotalcite as a secondary slag forming agent.
4. Airbag composition according to either claim 2 or 3 in which the secondary slag forming agent is added in a weight ratio of 1:5 to 5:1 with respect to the nitride or carbide.
5. Process for making the airbag composition according to any of claims 1 to 4 comprising the steps:
 - (i) mixing the ingredients;
 - (ii) pressing the mixture into pellets;
 - (iii) heat treating the pellets at a temperature between 80 and 120°C for at least 10 hours.
6. Airbag comprising the airbag composition according to any one of claims 1 to 4.



Communication under Art. 94(3) EPC

1. This communication is based on the application as originally filed. Attached documents D1 and D2 are prior art according to Article 54(2) EPC.
2. Reference is made to the following documents; the numbering will be adhered to in the rest of the procedure:

Document D1 (Journal of Automotive Technology, **12**, pages 111-112, 2005)

Document D2 (Journal of Heavy Explosives, **10**, page 2345, 2003)

3. Document D1 discloses an airbag composition comprising a triazole or tetrazole-type compound as fuel, an oxidant and a carbide or nitride as a slag forming agent. Oxides or hydroxides of titanium or aluminium can be added to the slag forming agent in order to improve the slag formation. Paragraph [005] also shows that clays can be used. It would appear that hydrotalcite falls within this definition. The subject-matter of claims 1 to 6 lacks novelty over this disclosure.
4. Document D2 discloses an explosive composition, used for the destruction of buildings. The composition comprises tetrazole, strontium nitrate, silicon carbide and hydrotalcite. The combination of silicon carbide and hydrotalcite makes up about 10 wt.% of the composition. They are used in equal amounts by weight (see paragraph [003]). The subject-matter of claims 1 to 4 is thus not novel.
5. It is clear from paragraph [014] that the particle size of the fuel components must be 5 to 80 μm . This essential feature is missing from claim 1. The requirements of Article 84 EPC are not fulfilled.



6. If the applicant wishes to maintain the application, amended claims taking the above objections into account should be filed. These amended claims would need to satisfy the EPC's requirements with respect to novelty, inventive step, clarity and, where appropriate, unity of invention. They should also not feature any amendments which cause the subject-matter to extend beyond the content of the application as originally filed (Article 123(2) EPC).
7. The letter of reply should set out the difference between the new claims and the prior art disclosed in documents D1 and D2 as well as its significance as regards inventive step. The technical problem underlying the invention compared with the closest prior art and the solution to that problem should emerge clearly from the applicant's arguments.
8. To make it easier to assess whether the amended claims comprise subject-matter which extends beyond the content of the application as filed, the applicant is urged to give an exact indication of the basis in the application as filed for the proposed amendments (Article 123(2) EPC).



Document D1 (Journal of Automotive Technology, 12, pages 111-112, 2005)

Gas-generating compositions for inflating airbags

[001] In airbags it is important to find a balance between fast reaction time when needed and long-term stability when the airbag is not deployed. In addition to this complex balance between stability and fast reaction time, other problems arise when designing gas-generating compositions. A well-known problem is the formation of oxides during the deployment of the airbag. These oxides, usually formed from the oxidant, are harmful to the environment and toxic. Currently these oxides are converted into a solid slag which can easily be collected.

[002] We have now found an improved way of forming slag. We add metal carbides to the airbag composition as slag forming agents. In addition to forming a slag that is easy to collect, the reaction of the carbide with the other components also generates additional gas. This is a huge advantage, because it results in a composition with a higher gas generation per unit of weight of the composition.

[003] Many carbides are suitable. Carbides of silicon, boron and aluminium have been found useful. Silicon carbide is a very useful carbide, because the slag formed is a silicate which has turned out to be very easy to collect. Furthermore, we believe that the equivalent nitrides will function in the same way as the carbides.

[004] The carbides are useful with both inorganic and organic fuels. Best results have been obtained for compositions using tetrazole, substituted tetrazole or triazole as fuels. The oxidants used in such compositions are nitrates, chlorates or perchlorates of alkali metals or alkaline earth metals.



[005] The efficiency of the slag collection thanks to the carbides can be improved by adding a compound selected from oxides or hydroxides of titanium or aluminium to the airbag composition. Clays can also be used to obtain the same effect.

[006] The effectiveness of the compositions is shown in the following examples. In the examples a mixture of 35 wt.% fuel, 53 wt.% oxidant and 11 wt.% slag forming agent is prepared. In the case titanium dioxide is used, this is used in a 1:1 ratio with respect to the carbide. The titanium dioxide is mixed with the other slag forming agent before it is mixed with the other components. The total amount of carbide and titanium dioxide then amounts to 11 wt.%. The ingredients all have an average particle size of 50 µm. In order to easily form the mixture into pellets 0.4 wt.% polyvinyl alcohol and 0.6 wt.% of stearic acid are added. These additives are well-known in the technology of making pellets. The ingredients are mixed in a Batch Muller® and then pressed into pellets. In order to improve the stability of the pellets they are subjected to a heat treatment. The heat treatment took place at 100°C and lasted for 15 hours.

[007] The pellets were then tested in a standard airbag testing device. In this device the time to fill a tank of standard size up to a pressure of 5 bar is measured. When the time is less than 50 ms the airbag performance is good. All the compositions in the table below passed this test.

Example	Fuel	Oxidant	Slag forming agent	Further additive	Percentage of collected slag
1	tetrazole	$\text{Sr}(\text{NO}_3)_2$	SiC	none	88
2	tetrazole	$\text{Sr}(\text{NO}_3)_2$	SiC	TiO_2	92
3	amino tetrazole	$\text{Sr}(\text{NO}_3)_2$	SiC	none	93
4	triazole	$\text{Sr}(\text{NO}_3)_2$	SiC	none	93



Document D2 (Journal of Heavy Explosives, 10, pages 2345, 2003)

[001] This document describes an explosive composition that is especially suitable for the demolition of old buildings, because the composition allows for very good control of the explosion. The composition contains a fuel and an oxidant.

[002] A composition for this purpose needs to generate a powerful, targeted shockwave. The fuel therefore needs to be present as large particles. They must be bigger than 1 mm. The large fuel particles will give rise to a very powerful explosion.

[003] We have found that a composition comprising tetrazole as fuel and strontium nitrate as oxidant is very useful. Silicon carbide and hydrotalcite are added to the composition as binder materials to obtain a composition that is mechanically stable. The fuel and oxidant are used in more or less equal amounts. An excess of up to 20 wt.% could ease the start of the explosion. Silicon carbide and hydrotalcite are each present in an amount of around 5 wt.%. The compositions are pressed into cubes having sides of 5 cm length. Small amounts (less than 1 wt.%) of water-soluble polymer or lubricant can be added in order to improve the formability of the composition.

[004] The cubes are tested in an experimental setup that is often used in the state of the art to verify the efficiency of explosive compositions for demolition purposes. The test is fully automated. The time until explosion and the explosive efficiency are measured. The above-described composition in cube form has an average time until explosion of 3 seconds and an explosive efficiency of 83%. This compares well to some commercially available explosives where the time until explosion was 5 seconds and the efficiency was 81%.



Letter from the applicant

Dear Mr. Attorney,

[001] Herewith we send you our instructions after having studied the communication from the European Patent Office you have forwarded to us. We believe there is still clearly patentable subject-matter in the application. We have drafted a new set of claims, which we believe overcomes all objections raised by the examining division. A copy of the claims is attached to this letter.

[002] We have directed claim 1 to an airbag composition that contains hydrotalcite as secondary slag forming agent. The process claim 5 also needed to be amended in view of this change to claim 1.

[003] In the communication from the European Patent Office, the examiner objected to the fact that the particle size of the fuel is not in the claim. We don't understand this objection. We leave it up to you to take action if any is needed.

[004] We have, however, included in claim 1 the subject-matter of original claim 4. We currently believe that these are the only compositions that work.

[005] Our research department will have its annual fishing outing the next few days, so we will not be available for giving you any further instructions. Please use the above to prepare and file a suitable response today.

Yours sincerely,

John A. Bags

Boom Technology PLC



Proposed set of claims

1. Airbag composition comprising,
 - (i) 20 to 50 wt.% of a fuel being selected from the group of tetrazole, aminotetrazole, nitrotetrazole, nitroaminotetrazole and triazole;
 - (ii) 30 to 70 wt.% of an oxidant being selected from alkali metal or alkaline earth metal nitrate, chlorate or perchlorate;
 - (iii) 10 to 20 wt.% of a slag forming agent comprising a carbide or nitride of boron, aluminium or silicon and hydrotalcite as a secondary slag former, the hydrotalcite being present in a weight ratio of 1:5 to 5:1 with respect to nitride and carbide.
2. Airbag composition according to claim 1 in which the slag forming agent comprises a secondary slag forming agent selected from oxides or hydroxides of titanium or aluminium.
- ~~3. Airbag composition according to claim 1 in which the slag forming agent comprises a secondary slag forming agent of hydrotalcite but only in the case of carbides as slag forming agent.~~
- ~~4. Airbag composition according to either claim 2 or 3 in which the secondary slag forming agent is added in a weight ratio of 1:5 to 5:1 with respect to the nitride or carbide.~~
- ~~5-3.~~ 3. Process for making the airbag composition according to any of claims 1 or 2 ~~to 4~~ comprising the steps:
 - (i) mixing the ingredients carbide or nitride slag forming agent with the hydrotalcite
 - (ii) mixing the mixture of step (i) with the remaining ingredients
 - ~~(iii)~~ (iii) pressing, for at least 5 minutes, the mixture into pellets
 - ~~(iii)~~ (iv) heat treating the pellets at a temperature between 80 and 120°C for at least 10 hours.
- ~~6-4.~~ 4. Airbag comprising the airbag composition according to any one of claims 1 or 2 ~~to 4~~.

