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(54) Title: THERMAL PRE-IGNITION AGENTS

(57) **Abrégé/Abstract:**

The invention relates to thermal pre-ignition agents and to their use as thermal fuses, in particular for use in gas generators of motor-vehicle safety systems.



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(54) Title: THERMAL PRE-IGNITION AGENTS

(54) Bezeichnung: THERMISCHE FRÜHZÜNDMITTEL

(57) Abstract: The invention relates to thermal pre-ignition agents and to their use as thermal fuses, in particular for use in gas
generators of motor-vehicle safety systems.(57) Zusammenfassung: Die Erfindung betrifft thermische Frühzündmittel und deren Verwendung als thermische Sicherung, ins-
besondere für den Einsatz in Gasgeneratoren für Kraftfahrzeugsicherheitssysteme.

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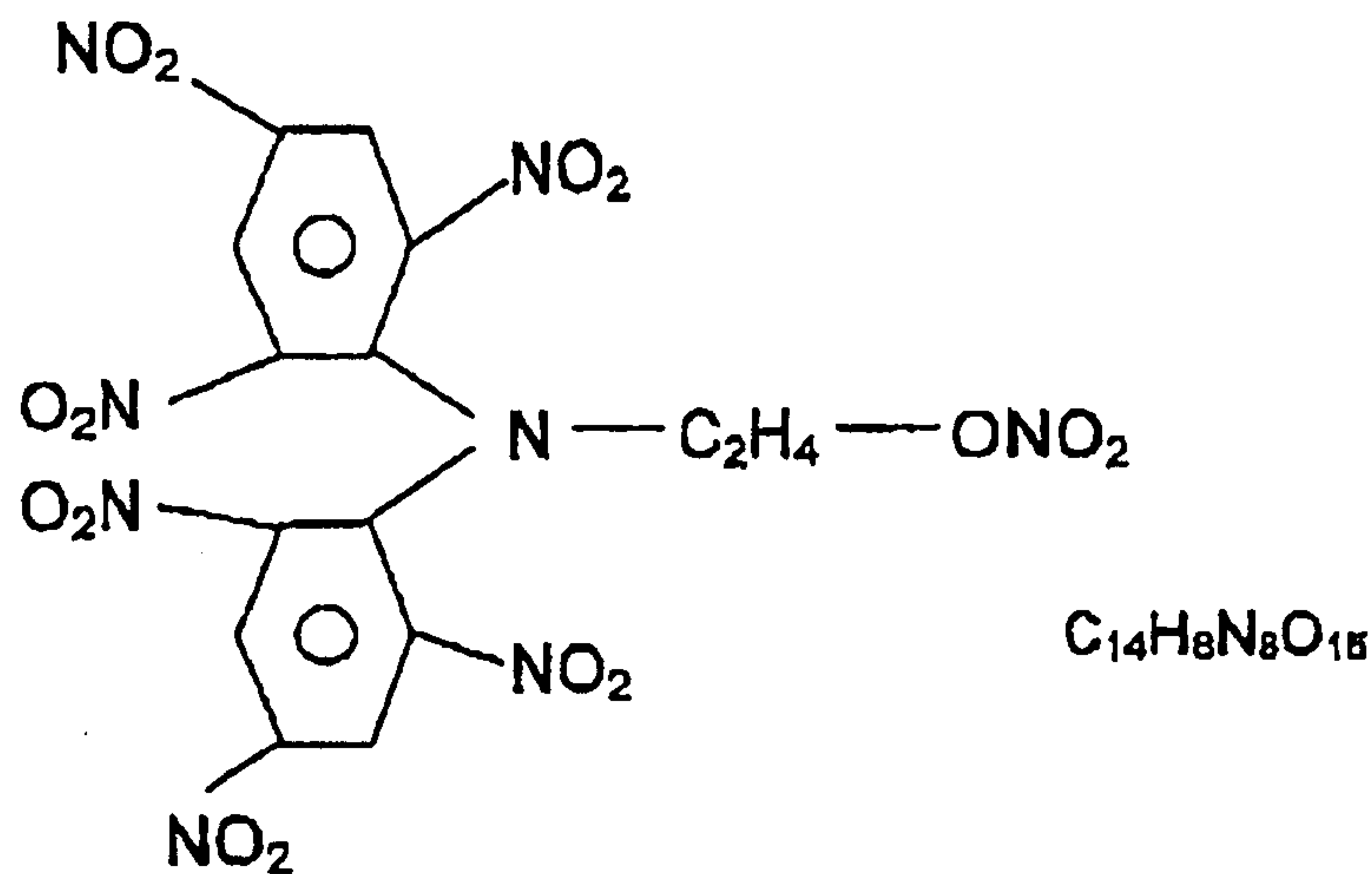
THERMAL PRE-IGNITION AGENTS

The present invention provides pre-ignition agents which can be used, for example, as thermal fuses in gas generators for motor vehicle safety systems.

Thermal pre-ignition agents are pyrotechnic substances or mixtures. They have the function, inter alia, of igniting the gas-producing mixtures of the gas generator, which generally have very high thermal stability, in a controlled manner in the event of a vehicle fire.

There are used as thermal pre-ignition agents, for example, nitrocellulose, propellant-charge powders derived therefrom, or the mixtures based on nitrotriazolone and
10 guanidine nitrate described in laid-open patent application DE 19730 873 A1. These mixtures have ignition temperatures of approximately 160°C and, in the case of nitrocellulose, have only inadequate long-term stability.

The object of the present invention is to provide pyrotechnic mixtures having ignition temperatures of about 200°C and adequate long-term stability, which mixtures can be used as thermal pre-ignition agents for gas generators in motor vehicle safety systems. The object underlying the invention is achieved by the use of 2-[bis-(2,4,6trinitrophenyl)] aminoethyl nitrate, abbreviated to dipicrylaminoethyl nitrate (DPN). This substance can be used either on its own or in mixtures with further
20 components. DPN can be prepared from 2,4-dinitrochlorobenzene and ethanolamine with subsequent nitration (lit.: R. V. Clark, Ind. Eng. Chem., 25, 1385 (1933)). The structural formula is as follows:



The deflagration point of pure DPN is at about 200°C. Surprisingly, it has been found that, in mixtures of DPN with selected components as additives, the deflagration point can be controlled in the range from 178°C to 208°C, and the deflagration temperatures of the mixtures may be lower than those of the individual components. For pre-ignition agents, deflagration temperatures below 200°C are of particular interest. The mixtures according to the invention meet this demand, while having excellent long-term stability.

10 More specifically, the invention as claimed is directed to a thermal pre-ignition agent containing from 10 to 90 wt.%, preferably from 25 to 75 wt.%, and particularly preferably from 40 to 60 wt.%, of dipicrylaminoethyl nitrate and from 10 to 90 wt.%, preferably from 25 to 75 wt.%, and particularly preferably from 40 to 60 wt.%, of an oxidising agent.

Examples of oxidising agents and other additives that could also be used, are as follows:

1. **Nitrogen-containing compounds** (on their own or in mixtures)

nitroguanidine, nitroaminoguanidine, nitrotriazolone, derivatives of tetrazole, such as 5-aminotetrazole, ditetrazolylamine, ditetrazole and salts thereof, nitraminotetrazole and its salts, such as ammonium nitraminotetrazole and aminoguanidinium nitramino-tetrazole, aminoguanidine nitrate,

diaminoguanidine nitrate, triaminoguanidine nitrate, guanidine nitrate, dicyandiamidine nitrate, diaminoguanidine azotetrazolate.

2. **Oxidising agents** (on their own or in mixtures)

nitrates of the alkali or alkaline earth metals or of ammonium such as sodium nitrate or potassium nitrate, perchlorates of the alkali or alkaline earth metals or of ammonium, peroxides of the alkaline earth metals or of zinc.

3. **Reducing agents** (on their own or in mixtures)

aluminium, titanium, titanium hydride, boron, boron hydride, zirconium, zirconium hydride, silicon, graphite, activated carbon, carbon black.

10 4. **Binders** (on their own or in mixtures)

cellulose and derivatives thereof, polyvinylbutyrals, polynitropolyphenylene, polynitrophenyl ether, Plexigum*, polyvinyl acetate and copolymers.

5. **High-energy additives** (on their own or in mixtures)

hexogen, octogen and nitrocellulose.

6. **Combustion moderators and processing aids** (on their own or in mixtures)

ferrocene and derivatives, acetonylacetates, salicylates, silicates, silica gels, boron nitride.

20 Production and processing are carried out according to known and conventional processes. These include, for example, kneading, extrusion, extrusion moulding, pelleting or granulation.

The Examples which follow are intended to illustrate the invention in greater detail without limiting it.

Table 1 shows the compositions of twelve different mixtures. The components were weighed in the indicated weight ratios (amounts are in percent by weight (wt.%) into plastics beakers and homogenised for 30 minutes in a tumbler mixer.

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Table 1: Examples

Mixture	DPN in wt. %	Nitroguanidine in wt. %	5-Amino- tetrazole in wt. %	Guanidine nitrate in wt. %	Potassium nitrate in wt. %	Sodium nitrate in wt. %	Potassium perchlorate in wt. %
1	50				50		
2	50					50	
3	50						50
4	20	30			50		
5	20	30				50	
6	20	30					50
7	20		30		50		
8	20		30			50	
9	20		30				50
10	20			30	50		
11	20			30		50	
12	20			30			50

Table 2 shows the heat of explosion of the mixtures and their friction and impact sensitivity. The friction and impact sensitivity was measured according to methods of the Bundesanstalt für Materialforschung [Federal Institute of Materials Research] (BAM), while the heat of explosion was measured using a calorimeter from EKA.

Table 2: Overview of the heat of explosion and friction and impact sensitivity

Mixture	Heat of explosion in J/g	Friction sensitivity in N	Impact sensitivity in J
1	4859	240	6
2	3280	240	7.5
3	5915	120	5
4	5157	360	7.5
5	3125	120	>30
6	5523	80	10
7	4014	240	6
8	3187	360	15
9	5056	80	6
10	4509	360	7.5
11	3484	360	10
12	5115	160	10

Table 3 summarises the deflagration points before and after exposure to heat (400 h, 110°C) and the weight losses after exposure to heat for 72 hours and 400 hours at 110°C. The deflagration points were determined by thermogravimetric analysis (Mettler) at a rate of heating of 10°C per minute. The weight loss was measured analogously to the Holland test.

After 400 hours, only slight weight losses of from 0.2 to 0.5 wt.% are found, and there is no significant change in the deflagration temperature after exposure to heat.

Table 3: Overview of weight losses and deflagration temperatures

Mixture	Weight loss 72 h 110°C in wt. %	Weight loss 400 h 110°C in wt. %	Deflagration temperature in °C	Deflagration temperature after 400 h, 110°C in °C
1	0.11	0.27	203	202
2	0.15	0.35	203	203
3	0.12	0.29	201	201
4	0.11	0.49	207	206
5	0.16	0.53	196	194
6	0.11	0.49	201	202
7	0.10	0.44	196	200
8	0.11	0.42	178	184
9	0.11	0.42	196	198
10	0.09	0.18	205	205
11	0.12	0.26	206	208
12	0.11	0.31	205	205

The Examples show that the mixtures defined according to the invention have deflagration temperatures in the range from 178 to 208°C and are to be regarded as stable according to the requirements of the automotive industry.

The present invention specifically provides:

Thermal pre-ignition agents which contain as a component dipicrylaminoethyl nitrate (DPN) in amounts by weight of from 10 to 100 %.

Thermal pre-ignition agents which, in addition to DPN, contain nitrogen-containing compounds, on their own or in mixtures, in amounts by weight of from 0 to 90 %, such as, for example, nitroguanidine, nitroaminoguanidine, nitrotriazolone, derivatives of tetrazole, such as 5-aminotetrazole, ditetrazolylamine, ditetrazole and salts thereof, nitraminotetrazole and its salts, such as ammonium nitraminotetrazole and aminoguanidinium nitraminotetrazole, aminoguanidine nitrate, diaminoguanidine nitrate, triaminoguanidine nitrate, guanidine nitrate, dicyandiamidine nitrate, diaminoguanidine azotetrazolate.

Thermal pre-ignition agents which, in addition to DPN and the above-mentioned nitrogen-containing compounds, on their own or in mixtures, contain oxidising agents, on their own or in mixtures, in amounts by weight of from 10 to 90 %, such as, for example, nitrates of the alkali or alkaline earth metals or of ammonium, such as sodium nitrate or potassium nitrate, perchlorates of the alkali or alkaline earth metals or of ammonium, peroxides of the alkaline earth metals or of zinc.

Thermal pre-ignition agents which, in addition to DPN, the above-mentioned nitrogen-containing compounds, on their own or in mixtures, and/or the above-mentioned oxidising agents, on their own or in mixtures, contain reducing agents, on their own or in mixtures, in amounts by weight of from 1 to 80 %, such as, for example, aluminium, titanium, titanium hydride, boron, boron hydride, zirconium, zirconium hydride, silicon, graphite, activated carbon, carbon black.

Thermal pre-ignition agents which, in addition to DPN, the above-mentioned nitrogen-containing compounds, on their own or in mixtures, the above-mentioned oxidising agents, on their own or in mixtures, and/or the above-mentioned reducing agents, on their own or in mixtures, contain binders, on their own or in mixtures, in amounts by weight of from 1 to 80 %, such as, for example,

cellulose and derivatives thereof, polyvinylbutyrals, polynitropolyphenylene, polynitrophenyl ether, Plexigum, polyvinyl acetate and copolymers.

5 Thermal pre-ignition agents which, in addition to DPN, the above-mentioned nitrogen-containing compounds, on their own or in mixtures, the above-mentioned oxidising agents, on their own or in mixtures, the above-mentioned reducing agents, on their own or in mixtures, and/or the above-mentioned binders, on their own or in mixtures,
10 contain high-energy additives, on their own or in mixtures, in amounts by weight of from 10 to 80 %, such as, for example, hexogen, octogen and nitrocellulose.

Thermal pre-ignition agents which, in addition to DPN, the above-mentioned nitrogen-containing compounds, on
15 their own or in mixtures, the above-mentioned oxidising agents, on their own or in mixtures, the above-mentioned reducing agents, on their own or in mixtures, the above-mentioned binders, on their own or in mixtures, and/or the above-mentioned high-energy additives, on their own
20 or in mixtures, contain combustion moderators and processing aids, on their own or in mixtures, in amounts by weight of from 0.1 to 20 %, such as, for example, ferrocene and derivatives, acetylacetates, salicylates, silicates, silica gels, boron nitride.

WHAT IS CLAIMED IS:

1. A thermal pre-ignition agent containing from 10 to 90 wt.% of dipicrylaminoethyl nitrate and from 10 to 90 wt.% of an oxidising agent.
2. The thermal pre-ignition agent according to claim 1, characterised in that the oxidising agent is selected from the group consisting of nitrates of alkali metals, alkaline earth metals and ammonium; perchlorates of alkali metals, alkaline earth metals and ammonium; peroxides of alkaline earth metals and zinc; and mixtures thereof.
3. The thermal pre-ignition agent according to claim 1 or 2, characterized in that
10 it contains 25 to 75 wt.% of said dipicrylaminoethyl nitrate and from 25 to 75 wt.% of said oxidising agent.
4. The thermal pre-ignition agent according to claim 1 or 2, characterized in that it contains 40 to 60 wt.% of said dipicrylaminoethyl nitrate and from 40 to 60 wt.% of said oxidising agent.
5. The thermal pre-ignition agent according to claim 1 or 2, characterized in that it also contains 10 to 90 wt.% of a nitrogen-containing compound.
6. The thermal pre-ignition agent according to claim 5, characterised in that the
20 nitrogen-containing compound is selected from the group consisting of nitroguanidine, nitroaminoguanidine, nitrotriazolone, derivatives of tetrazole and salts thereof; nitraminotetrazole and its salts; aminoguanidine nitrate, diaminoguanidine nitrate, triaminoguanidine nitrate, guanidine nitrate, dicyandiamidine nitrate, diaminoguanidine azotetrazolate, and mixtures thereof.

7. The thermal pre-ignition agent according to claim 5 or 6, characterized in that it contains from 10 to 50 wt.% of said dipicrylaminoethyl; from 10 to 60 wt.% of said nitrogen-containing compound; and from 25 to 75 wt.% of said oxidising agent.

8. The thermal pre-ignition agent according to claim 7, characterized in that it contains from 10 to 30 wt.% of said dipicrylaminoethyl; from 20 to 40 wt.% of said nitrogen-containing compound; and from 40 to 60 wt.% of said oxidising agent.

9. The thermal pre-ignition agent according to any one of claims 1 to 8, characterised in that it also contains from 1 to 80 wt.% of a reducing agent.

10. The thermal pre-ignition agent according to claim 9, characterised in that the reducing agent is selected from the group consisting of aluminium, titanium, titanium hydride, boron, boron hydride, zirconium, zirconium hydride, silicon, graphite, activated carbon, carbon black and mixture thereof.

11. The thermal pre-ignition agent according to claim 9 or 10, characterised in that it contains 1 to 40 wt.% of said reducing agent.

12. The thermal pre-ignition agent according to claim 11, characterised in that it contains 1 to 15 wt.% of said reducing agent.

13. The thermal pre-ignition agent according to any one of claims 1 to 12, characterised in that its also contains from 1 to 80 wt.% of a binder.

20 14. The thermal pre-ignition agent according to claim 13, characterised in that the binder is selected from the group consisting of cellulose and derivatives thereof, polyvinylbutyrals, polynitropolyphenylene, polynitrophenyl ether, Plexigum*, polyvinyl acetate, copolymers and mixtures thereof.

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15. The thermal pre-ignition agent according to claim 13 or 14, characterised in that it contains from 1 to 40 wt.% of said binder.

16. The thermal pre-ignition agent according to claim 15, characterised in that it contains from 1 to 20 wt.% of said binder.

17. The thermal pre-ignition agent according to any one of claims 1 to 16, characterised in that it also contains from 10 to 80 wt.% of high-energy additives.

18. The thermal pre-ignition agent according to claim 17, characterised in that the high-energy additives are selected from the group consisting of hexogen, octogen, nitrocellulose and mixtures thereof.

10 19. The thermal pre-ignition agent according to claim 17 or 18, characterised in that it contains from 10 to 50 wt.% of said high-energy additives.

20. The thermal pre-ignition agent according to claim 19, characterised in that it contains from 10 to 30 wt.% of said high-energy additives.

21. The thermal pre-ignition agent according to any one of claims 1 to 20, characterised in that its contain from 0.1 to 20 wt.% of combustion moderators and processing aids.

20 22. The thermal pre-ignition agent according to claim 17, characterised in that said combustion moderators and processing aids are selected from the group consisting of ferrocene and derivatives thereof, acetonylacetates, salicylates, silicates, silica gels, boron nitride and mixtures thereof.

23. The thermal pre-ignition agent according to any one of claims 21 to 22, characterised in that its contain from 0.1 to 10 wt.% of said combustion moderators and processing aids.

24. Use of a thermal pre-ignition agent according to any one of claims 1 to 23 as a thermal fuse in a gas generator for a motor vehicle safety system.