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(54) **PYROTECHNIC DELAY COMPOSITION**

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(57) **ABSTRACT**

A pyrotechnic delay composition comprising at least one oxidant and at least one reducing agent. This composition comprises tungsten as the first reducing agent, a first oxidant consisting of triiron tetraoxide, and a second oxidant having an oxygen content greater than that of the first oxidant.

PYROTECHNIC DELAY COMPOSITION

[0001] The technical field of the invention is that of pyrotechnic delay compositions.

[0002] Such compositions are well known. They are implemented in the form of rigid delay columns or soft cords in a metallic sheath and allow to trigger a pyrotechnic event at the end of a specified time interval.

[0003] They are used, for example, in the munitions field to cause self-destruction of munitions that have not reached their target. They are also used in the space field in the form of delay cords between various components of a ballistic launcher.

[0004] Many pyrotechnic compositions have been developed in the past.

[0005] The most commonly known compositions combine tungsten, barium chromate and potassium perchlorate. It is also possible to incorporate ultrafine silica in these compositions, as described in patent FR 2 706 449.

[0006] These compositions have the advantage of generating little gas and may be shaped as cords of reduced diameter (sheath diameter of less than 4 mm), without the risk of the cord bursting or the combustion being stopped.

[0007] However, they use a chromium-based compound (barium chromate—$BaCrO_4$) for which the toxicity of chromium leads to its prohibition (REACH European Directives).

[0008] It is therefore necessary to define a less toxic delay composition but one that offers the same properties as those of the known composition: reduced combustion rate (less than 4 mm/s in a flexible sheath of small diameter (less than 3 mm)), absence of gas, reliability of combustion for the entire temperature range that is required for military and space applications (−40° C. to +60° C.).

[0009] It has been proposed in the patent WO2017/084916 that this composition should be replaced by a new delay composition associating one or more iron oxides with zirconium or zirconium hydride. However, the new composition is likely to generate hot spots in the reaction zone and, according to this patent, it is necessary to add one or more additives generating slag in order to mitigate the reaction.

[0010] This results in a complex pyrotechnic composition, comprising many components whose dosage is difficult.

[0011] It is the object of this invention to provide a pyrotechnic delay composition devoid of chromium compounds, thus complying with the REACH directives, wherein this delay composition has a formulation that ensures reliable operation without stopping combustion in the case of reduced diameter.

[0012] More particularly, this composition makes it possible to produce delay cords comprising a sheath based on tin and bismuth, cords whose outer diameter of the sheath is between 7.2 mm and 2.6 mm and which may, by a choice of specific formulation, ensure a burning rate of 2.64 mm/s to 4.0 mm/s.

[0013] Thus, the object of the invention is a pyrotechnic delay composition comprising at least one oxidant and at least one reducing agent, wherein the composition is characterized in that it comprises tungsten as the first reducing agent, a first oxidant constituted by triiron tetraoxide, and a second oxidant having an oxygen content higher than that of the first oxidant.

[0014] Triiron tetraoxide is a well-known iron oxide found naturally in the form of ore known as magnetite. It is a non-toxic and inexpensive material. It has the disadvantage of being a relatively weak oxidant. In fact the mass of oxygen that it can release per mass of material is of the order of 28%.

[0015] The risk with such a material is therefore the interruption of the combustion of the delay composition.

[0016] By way of comparison, the barium chromate of the known delay composition may release 63% of its oxygen mass.

[0017] The patent WO2017/084916 overcomes this disadvantage by combining the iron oxide with a strong reducing agent such as zirconium. However, the reaction then leads to the production of metal remaining incandescent, while the zirconium reacts strongly with the reduced iron resulting in an intermetallic type reaction. It then becomes necessary to mitigate the combustion with slag generating materials.

[0018] On the contrary, the invention proposes to conserve tungsten as a reducing agent. In fact, its reduction capacity (3.98 grams of reducing agent for one gram of oxygen) is good although lower than that of zirconium, while it also has a high thermal conductivity (174 $Wm^{-1}K^{1}$) which allows it to dissipate calories and reduce the burning rate of the composition by draining the heat of the reaction.

[0019] In order to avoid stopping the combustion of the delay composition, the triiron tetraoxide is associated with a second oxidant which has an oxygen content greater than that of the triiron tetraoxide.

[0020] This second oxidant makes it possible to overcome the weaknesses of the triiron tetraoxide.

[0021] For example, one of the following oxidants may be chosen: potassium perchlorate, barium peroxide, bismuth oxide, diodine pentoxide . . . .

[0022] Potassium perchlorate is preferably chosen as the second oxidant. In fact, the oxygen content of potassium perchlorate is 46.2%, which is relatively high. It is therefore sufficient to reduce the amount of this oxidant to maintain a uniform combustion front.

[0023] Advantageously, the composition according to the invention may comprise a second reducing agent constituted by aluminum.

[0024] This addition of aluminum makes it possible to correct the burning rate of the delay composition.

[0025] The delay composition will therefore comprise: from 20% to 60% by weight of tungsten, and from 30% to 70% by weight of triiron tetraoxide.

[0026] More specifically, the delay composition according to the invention will have the following composition:

[0027] 20% to 60% by weight of tungsten,

[0028] 30% to 70% by weight of triiron tetraoxide,

[0029] 1% to 30% by weight of potassium perchlorate,

[0030] 0% to 10% by weight of aluminum.

[0031] In a preferred manner, the delay composition according to the invention will have the following composition:

[0032] 30% to 40% by weight of tungsten,

[0033] 45% to 55% by weight of triiron tetraoxide,

[0034] 5% to 15% by weight of potassium perchlorate,

[0035] 0% to 10% by weight of aluminum.

[0036] The examples of compositions which will now be described, make it possible in a nonlimiting manner to demonstrate other advantages of the composition according to the invention.

[0037] The selected tungsten has a particle size of between 0.2 mm and 0.315 mm in all the compositions produced.

[0038] The particle size of the triiron tetraoxide is between 0.2 mm and 0.315 mm.

[0039] That of potassium perchlorate is between 0.2 mm and 0.315 mm.

[0040] That of aluminum is between 0.2 mm and 0.315 mm.

[0041] A first series of tests was carried out with delay compositions in the form of cords in a tin sheath.

[0042] The materials are dry-blended and compressed into a ductile tin metal tube of 17 mm initial outside diameter, and then the loaded tube is progressively reduced in diameter by being passed through dies to obtain a 3 mm outer diameter of the delay cord.

[0043] An ignition composition is then placed at the inlet of the tube that can ignite the delay composition (for example a conventional composition combining titanium and carbon).

[0044] Several tubes having a length of 300 mm are thus produced. The burning time of each loaded tube of delay composition is then measured.

[0045] The table below lists various compositions that were prepared and whose burning rate was measured. The percentages that are given relate to the total mass of the composition.

	Tungsten W (%)	Aluminum Al (%)	Triiron tetraoxide Fe_3O_4 (%)	Potassium perchlorate $KClO_4$ (%)	Burning rate (mm/s)
Example 1	39	/	50	11	4.44
Example 2	31	8	50	11	4.35
Example 3	25	14	50	11	4.17
Example 4	25	8	56	11	3.45

[0046] Note that the relative increase in the mass of triiron tetraoxide reduces the rate of combustion (Example 4).

[0047] By containment in a sheath, aluminum decreases the burning rate of the delay composition.

[0048] Other tests have verified that, if the potassium perchlorate is omitted, ignition of the delay composition cannot be effected with the chosen ignition composition (titanium/carbon). But other ignition compositions may be considered.

[0049] Another series of tests was carried out with other compositions in which the level of aluminum was varied.

[0050] These tests were carried out in an ignition configuration of the composition on a gutter, and not with the confinement of a cord.

[0051] The results are summarized in the following table:

	Tungsten W (%)	Aluminum Al (%)	Triiron tetraoxide Fe_3O_4 (%)	Potassium perchlorate $KClO_4$ (%)	Burning rate (mm/s)
Example 5	38	1	50	11	0.87
Example 6	35	4	50	11	1.01

[0052] Note the accelerating effect of combustion provided by aluminum in this unconfined combustion configuration.

[0053] These latter compositions could also be formed into tin sheaths. The combustion rates would then be higher (of the order of 3.5 mm/s to 4.5 mm/s for a tin sheath with an external diameter 3.1 mm).

1. Pyrotechnic delay composition comprising at least one oxidant and at least one reducing agent, wherein the pyrotechnic delay composition comprises tungsten as the first reducing agent, a first oxidant consisting of triiron tetraoxide and a second oxidant having an oxygen content greater than that of the first oxidant.

2. Pyrotechnic delay composition according to claim **1**, wherein the second oxidant is selected from among the following oxidants: potassium perchlorate, barium peroxide, bismuth oxide, diiodine pentoxide.

3. Pyrotechnic delay composition according to claim **1**, wherein the pyrotechnic delay composition comprises a second reducing agent consisting of aluminum.

4. Pyrotechnic delay composition according to claim **1**, wherein the pyrotechnic delay composition comprises: from 20% to 60% by weight of tungsten, and from 30% to 70% by weight of triiron tetraoxide.

5. Pyrotechnic delay composition according to claim **4**, wherein the pyrotechnic delay composition comprises:
20% to 60% by weight of tungsten,
30% to 70% by weight of triiron tetraoxide,
1% to 30% by weight of potassium perchlorate,
0% to 14% by weight of aluminum.

6. Pyrotechnic delay composition according to claim **5**, wherein the pyrotechnic delay composition comprises:
30% to 40% by weight of tungsten,
45% to 55% by weight of triiron tetraoxide,
5% to 15% by weight of potassium perchlorate,
0% to 14% by weight of aluminum.

7. Pyrotechnic delay composition according to claim **6**, wherein the pyrotechnic delay composition comprises:
39% by weight of tungsten,
50% by mass of triiron tetraoxide,
11% by weight of potassium perchlorate.

8. Pyrotechnic delay composition according to claim **6**, wherein the pyrotechnic delay composition comprises:
31% by weight of tungsten,
8% by weight of aluminum,
50% by weight of triiron tetraoxide,
11% by weight of potassium perchlorate.

9. Pyrotechnic delay composition according to claim **5**, wherein the pyrotechnic delay composition comprises:
25% by weight of tungsten,
14% by weight of aluminum,
50% by weight of triiron tetraoxide,
11% by weight of potassium perchlorate.

10. Pyrotechnic delay composition according to claim **5**, wherein the pyrotechnic delay composition comprises:
25% by weight of tungsten,
8% by weight of aluminum,
56% by weight of triiron tetraoxide,
11% by weight of potassium perchlorate.

11. Pyrotechnic delay composition according to claim **6**, wherein the pyrotechnic delay composition comprises:
38% by weight of tungsten,
1% by weight of aluminum,
50% by weight of triiron tetraoxide,
11% by weight of potassium perchlorate.

12. Pyrotechnic delay composition according to claim **6**, wherein the pyrotechnic delay composition comprises:

35% by weight of tungsten,

4% by weight of aluminum,

50% by weight of triiron tetraoxide,

11% by weight of potassium perchlorate.

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