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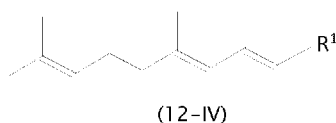
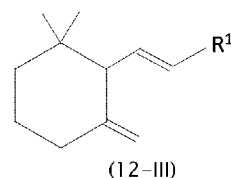
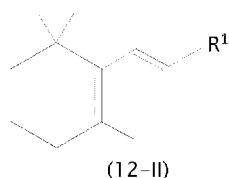
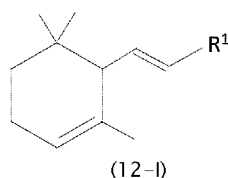
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- (54) **Title:** IONONE STABILISERS FOR NITROCELLULOSE-BASED PROPELLANTS



- (57) **Abstract:** The present invention concerns a nitrocellulose-based propellant composition comprising: (a) a nitrate ester-based propellant comprising nitrocellulose; and (b) a stabiliser comprising a non-aromatic compound (12) consisting of a general ionone formula (12-I), (12-II), (12-III) or (12-IV): Wherein R¹ represents a ketone, hydroxyl, carboxyl, aldehyde or an unsaturated alkyl group, preferably -C(O)CH₃ (corresponding to alpha, beta, gamma and pseudo ionone).

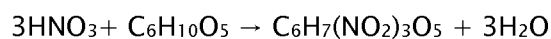
IONONE STABILISERS FOR NITROCELLULOSE-BASED PROPELLANTS

Technical Field

5 [0001] The present invention relates to stabilised nitrocellulose-based propellant compositions. In particular it concerns nitrocellulose-based propellant stabilised with a stabiliser producing little to no carcinogenic and mutagenic by-products.

Background for the invention

10 [0002] Smokeless powders have been developed since the 19th century to replace traditional black powder, which generates substantial amounts of smoke when fired. The most widely used smokeless powders are nitrocellulose-based. Nitrocellulose is obtained by using nitric acid to convert cellulose into cellulose nitrate and water according to a general reaction:



15 Nitrocellulose-based smokeless powder is then obtained by treating the thus obtained nitrocellulose by extrusion or spherical granulation, with or without solvent, two techniques which are well known to the persons skilled in the art.

[0003] Various improvements have been developed since the first discovery of nitrocellulose, by addition of further components, such as nitroglycerine and/or nitroguanidine allowing an increase of the detonation velocity. Pure nitrocellulose propellant is referred to as single-
20 base propellant, and double- and triple-base propellants refer to compositions comprising nitrocellulose and one or two additional energetic bases, respectively, typically blasting oils such as nitroglycerine, nitroguanidine, or secondary explosives.

[0004] Nitrocellulose, as most nitrate esters, is prone to self-ignition as a result of thermal degradation due to the weakness of its O-N bond. When employed as an ingredient of
25 propellants or other explosive compositions, the spontaneous ignition of nitrocellulose has caused serious accidents. It is obviously vital to inhibit or slow down this degradation for safety reasons but it is also important to retain the initial properties of the energetic

composition. Degradation usually leads to gas emissions, heat generation and reduction of molecular mass affecting negatively the material structure and ballistic properties.

[0005] The decomposition of nitrocellulose usually starts with a bond scission or hydrolysis, generating alkoxy radicals and nitrogen oxide (NO_x) species (*cf.* Figure 1). The radicals
5 further react, generating more radicals, speeding up the degradation process, and ultimately lead to chain scission accompanied by heat generation. In order to prolong the service life of the propellants, stabilisers are added to the energetic mixture in order to scavenge these radical species and slow down the degradation pattern.

[0006] All conventional stabilisers used to date for nitrocellulose-based propellants belong
10 to (a) aromatic amines (e.g., diphenylamine, 4-nitro-N-methylamine) or (b) aromatic urea derivatives (e.g., akardite, centralite) and are or produce toxic and/or potentially carcinogenic species at some point during the propellant's lifetime. For example, the most widely used stabilisers to date are diphenylamine, akardite, and centralite. These compounds,
15 however, form carcinogenic derivatives such as N-nitrosodiphenylamine (*cf.* Figure 2(a)) or N-nitrosoethylphenylamine.

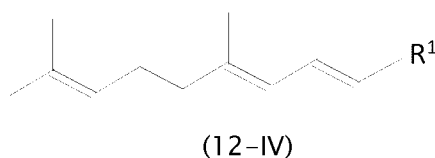
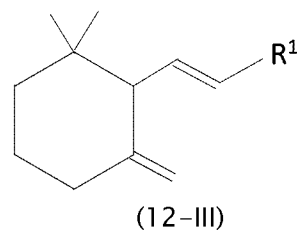
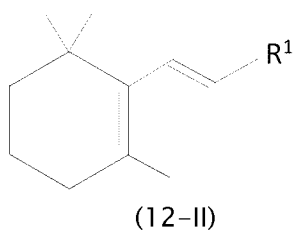
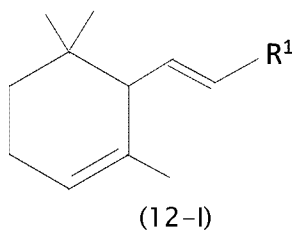
[0007] Hindered amines, such as triphenylamine, reduce the formation of N-NO groups, but fail to stabilise nitrocellulose satisfactorily. Conventional hindered phenols used in the plastics industry have been tested and at short term stabilise nitrocellulose with little to no
20 N-NO formation. The phenols are able to trap the alkoxy radicals generated during the degradation of nitrocellulose and thus form new, relatively stable alkoxy radicals, by delocalisation of an electron at the foot of electron-rich, hindered groups as illustrated in Figure 2(b). Long term stability is, however, not always guaranteed, probably due to rapid phenol depletion and relative stability of the newly formed alkoxy radicals.

[0008] There thus remains in the field of solid propellants a need for stabilisers allowing
25 long term stabilisation of nitrocellulose based propellants, fulfilling at least STANAG 4582 (Ed.1) and which do not produce carcinogenic and/or mutagenic by-products. The present invention proposes a family of stabilisers fulfilling both requirements above. These and other advantages of the present invention are presented in continuation.

Summary of the invention

[0009] The present invention is defined in the appended independent claims. Preferred embodiments are defined in the dependent claims. In particular, the present invention concerns a nitrocellulose-based propellant composition comprising:

- 5 (a) a nitrate ester-based propellant comprising nitrocellulose; and
 (b) a stabiliser consisting of a non-aromatic, ionone-type compound with a general formula (12-I), (12-II), (12-III) or (12-IV):



wherein R¹ represents a ketone, hydroxyl, carboxyl, aldehyde or (un)saturated alkyl group.

10

[0010] The nitrate ester-based propellant may be a single base propellant consisting of nitrocellulose alone or, alternatively, may be a double or higher base propellant comprising nitrocellulose in combination with at least one blasting oil and/or at least one energetic additive. As known by a person skilled in the art, a blasting oil is herein defined as an energetic compound obtained by nitration of a polyol such as glycerol, glycol, diethylene glycol, triethylene glycol, metriol. The obtained nitrate is most of the time heavy, oily and presents explosive properties. Nitroglycerine is probably the most common blasting oil employed in the industry. The term "NO_x" is used herein in its generally recognised sense, as
 15
 20 a generic term for mono-nitrogen oxides NO and NO₂ (nitric oxide and nitrogen dioxide). In a preferred embodiment, the blasting oil comprises at least a nitrated polyol, said nitrated

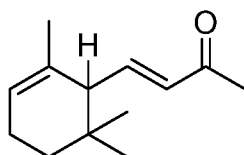
polyol is obtained by nitration of polyol selected from a group consisting of glycerol, glycol, diethylene glycol, triethylene glycol and metriol, preferably glycerol.

[0011] An energetic additive according to the present invention; like blasting oils, are used to enhance the blasting power of nitrocellulose. Energetic additives can be an energetic plasticiser or an explosive. Examples of energetic plasticisers comprise nitramines, such as butyl-NENA or dinitrodiazaalkane (DNDA). Examples of explosives suitable for use as energetic additives include RDX, HMX, FOX7, FOX12, CL20.

[0012] The preferred stabilisers of the present invention are capable of reacting with both degradation products of the nitrate ester: alkoxy radicals and NO_x. Firstly, by hydrogen abstraction of the labile proton of the stabiliser, by reaction with a radical group, thus forming a stable alcohol compound and a first by-product able to trap further alkoxy/ NO_x species. The thus formed successive by-products are capable of reacting with NO_x and alkoxy radicals from the degradation of the nitrate ester. No harmful NNO groups are formed due to the lack of nitrogen atoms in the stabiliser structure.

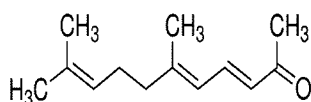
[0013] It is preferred that the blasting oil comprises at least a nitrated polyol, said nitrated polyol is obtained by nitration of polyol selected from a group consisting of glycerol, glycol, diethylene glycol, triethylene glycol and metriol, preferably glycerol.

[0014] The stabiliser of formula (12-I) is preferably alpha ionone, wherein R¹ is -C(O)CH₃:



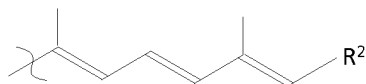
(12-Ia)

[0015] The R₁ group for the non-aromatic compound of formula 12-(IV) is preferably a methyl aldehyde, corresponding to pseudo-ionone:

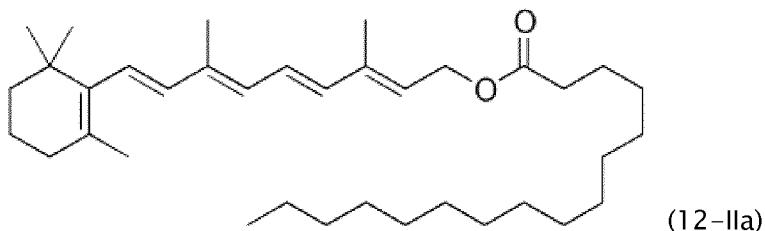


(12-IVa)

[0016] The R¹ group for stabiliser of formula (12-II) is preferably:



wherein R² represents CH₂OH, -CHO, or, -CH₂OC(=O)R³, R³ represents alkyl group substituted or not. In a preferred embodiment, the stabiliser corresponds to retinyl palmitate:



5

[0017] Unless otherwise specified, the expression “*substituted or not*” is to be construed as any -H in a molecule may be substituted by any of an alkyl, alkene, or an aromatic ring. A propellant composition is considered as being a “*nitrocellulose-based propellant composition*” if it comprises at least 40 wt.% nitrocellulose, based on the total weight of the composition.

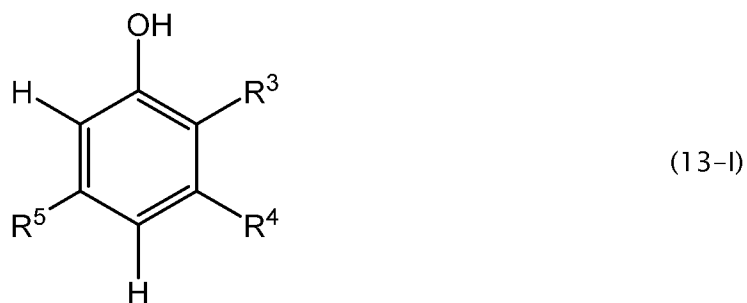
[0018] The stabiliser may be present in the composition in an amount comprised between 0.1 and 5.0 wt.%, preferably between 0.2 and 2.0 wt.%, more preferably between 0.5 and 1.5 wt.%, with respect to the total weight of the composition. The nitrate ester-based propellant may comprise nitrocellulose only, thus defining a single base propellant or, alternatively, it may comprise a blasting oil, such as nitroglycerine, to define a double base propellant. A double base propellant according to the present invention preferably comprises not more than 60 wt.% nitroglycerine, and preferably comprises between 5 and 45 wt.%, more preferably between 7 and 22 wt.% nitroglycerine, with respect of the total weight of nitrate ester based propellant.

[0019] The propellant compositions of the present invention should fulfil the stability requirements defined in STANAG 4582 (Ed.1), namely generating less than 350 μW / g of heat flow for at least 3.43 days at a temperature of 90°C. Many propellant compositions of the present invention can achieve much better than this and may remain stable for over 10 days at 90°C.

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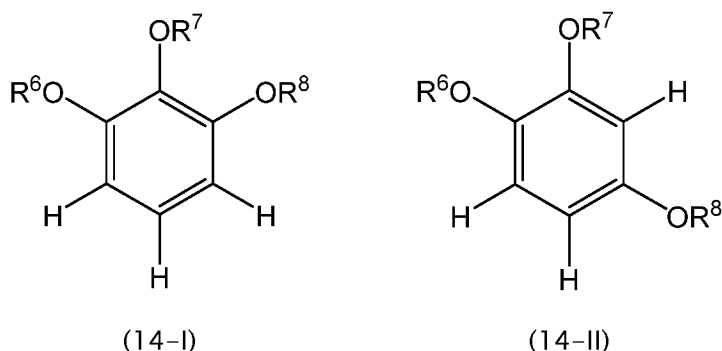
[0020] The composition of the present invention may further comprise an aromatic compound as complementary stabiliser. In particular, said complementary stabiliser may comprise one of the following compounds:

(a) a substituted phenol compound (13) having the general formula (13-I):



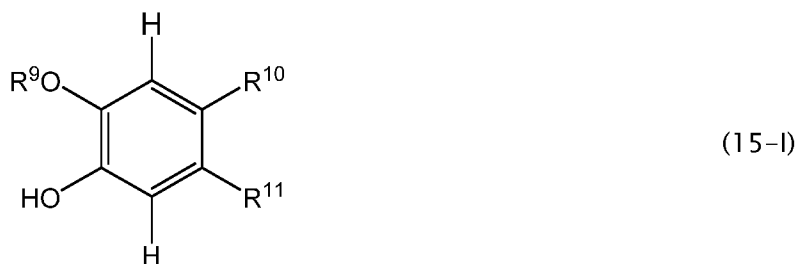
5 wherein: R³ represents: (i) H, (ii) alkyl substituted or not, or (iii) an alkoxy group; and R⁴ and R⁵ are same or different, and represent (i) alkyl substituted or not, or (ii) alkoxy group;

(b) a trialkoxy benzene (14) having the general formulae (14-I) or (14-II):

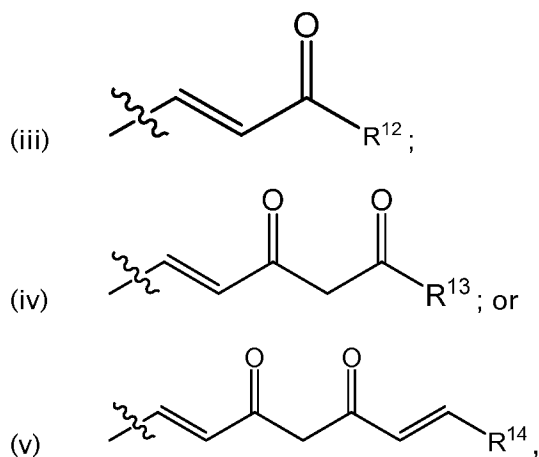


wherein R⁶, R⁷ and R⁸ are same or different and represent C₁₋₅ alkyl unsubstituted or substituted with an alkoxy group; or

10 (c) an aromatic compound (15) having a general formula (15-I):



Wherein: R⁹ represents, alkyl substituted or not; R¹⁰ represent (i) H, (ii) unsaturated alkyl group,



R¹¹ represents, H, alkyl substituted or not, or OR¹⁵;

5 R¹² represents, alkyl substituted or not, aromatic ring substituted or not, or OR¹⁵;

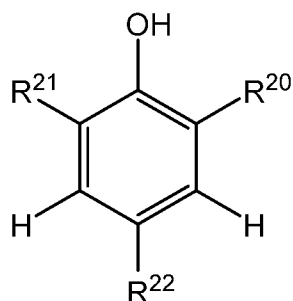
R¹³ represents, alkyl substituted or not, aromatic ring substituted or not, or OR¹⁶;

R¹⁴ represents, aromatic ring substituted or not;

R¹⁵ represents, alkyl substituted or not, or aromatic ring substituted;

R¹⁶ represents, alkyl substituted or not, or aromatic ring substituted

10 (d) a substituted phenol compound (16) having the general formula (16-I):

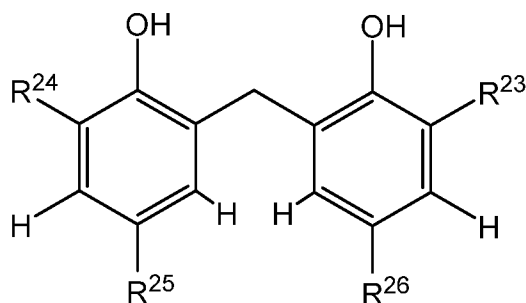


(16-I)

wherein: R²⁰, R²¹ and R²² are the same or different and represent: (i) alkyl-substituted or not,

(ii) alkoxy group.

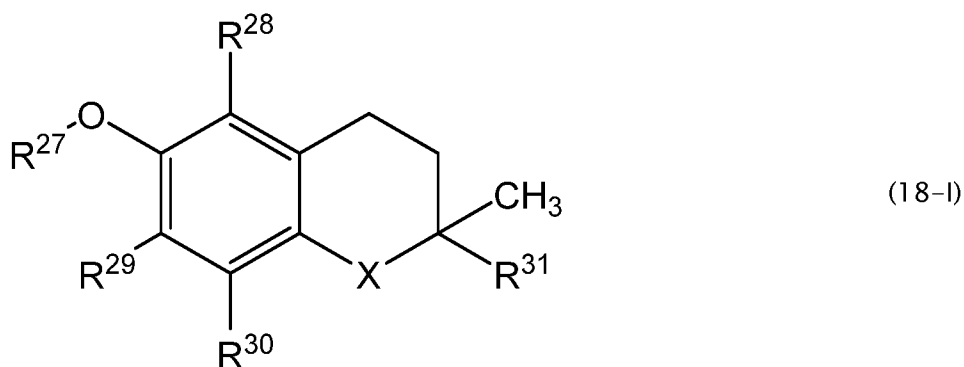
(e) a substituted phenol compound (17) having the general formula (17-I):



(17-I)

wherein: R²³, R²⁴, R²⁵ and R²⁶ are the same or different and represent: (i) alkyl-substituted or not, (ii) alkoxy group.

(f) A tocopherol-class compound (18) with the general formula (18-I):



5

wherein:

X is oxygen or nitrogen;

R²⁷ is selected from the group consisting of hydrogen, alkyl, alkenyl, alkynyl, aryl, heteroaryl, carboxylic acid, carboxylate, ester, saccharide, alkoxy-linked saccharide, alcohol, and ether;

10 R²⁸ is selected from the group consisting of hydrogen methyl, benzyl carboxylic acid, benzyl carboxylate, benzylester, and saccharide;

R²⁹ is selected from the group consisting of hydrogen, methyl, benzyl carboxylic acid, benzyl carboxylate, benzylester and , saccharide;

15 R³⁰ is selected from the group consisting of methyl, benzyl carboxylic acid, benzyl carboxylate, benzylester, and saccharide;

R³¹ is selected from the group consisting of alkyl and alkenyl;

Wherein when X is nitrogen, said nitrogen is substituted with R³², wherein R³² is selected from the group consisting of hydrogen and methyl.

[0021] Beside a nitrate ester based propellant and a stabiliser, the propellant compositions
20 of the present invention may comprise additives. In particular, they may comprise one or more of the following additives:

(a) a potassium salt, such as potassium nitrate (KNO₃) or sulphate (K₂SO₄), preferably in an amount comprised between 0.01 and 1.5 wt. %;

- (b) combustion moderators such as phthalates, Cl and citrate derivatives, preferably in an amount comprised between 1.0 and 10.0 wt. %;
- (c) an anti-static agent such as graphite, preferably in an amount comprised between 0.01 and 0.5 wt. %; and
- 5 (d) calcium carbonate, preferably in an amount comprised between 0.01 and 0.7 wt.%,

Wherein the wt.% are expressed in terms of the total weight of the propellant composition.

[0022] The present invention also concerns the use of a stabiliser of formula (12-I) to (12-IV) as defined above, for stabilising a nitrocellulose based propellant composition. The
10 stabiliser is preferably of a formula (12-Ia) or (12-IVa) as defined supra.

The present invention also concerns an environmentally-friendly stabiliser, which produces no mutagenic or carcinogenic by-products for stabilising a nitrate ester-based propellant comprising nitrocellulose. The said carcinogenic-free stabiliser being in the form of a mixture comprising: (a) a non-aromatic compound of formula (12) as defined supra and (b)
15 an aromatic compound as complementary stabiliser. Any of the aromatic compounds (13) to (18) defined above can be used as complementary stabiliser.

Brief description of the Figures

[0023] For a fuller understanding of the nature of the present invention, reference is made
20 to the following detailed description taken in conjunction with the accompanying drawings in which:

Figure 1 shows a reaction of spontaneous decomposition of nitrocellulose with formation of free radicals and NO_x.

Figure 2 shows assumed stabilisation mechanisms of akardite (AkII) and diphenylamine
25 (DPA) (prior art).

Figures 3(a) to 3(c) show the normalised heat flow expressed in $\mu\text{W} / \text{g}$ generated by propellant compositions stabilised with diphenylamine (DPA) as conventional stabiliser or a stabiliser comprising a non-aromatic compound consisting of formulae (12-Ia) and (12-IVa) for (a) single base nitrocellulose propellants; (b) double base nitrocellulose / nitroglycerine

(80 / 20 wt.%) propellants and (c) double base nitrocellulose / nitroglycerine (60 / 40 wt.%) propellants.

Figure 4 shows the normalised total heat flows expressed in $\mu\text{W} / \text{g}$ generated by propellant compositions stabilised with a stabiliser comprising the non-aromatic compound of formula (12-1a) for double base nitrocellulose / nitroglycerine (90 / 20 wt.%) propellants, double base nitrocellulose / nitroglycerine (80 / 20 wt.%) propellants and double base nitrocellulose / nitroglycerine (60 / 40 wt.%) propellants according to the present invention. This figure shows the stabilisation effect of alpha ionone (12-1a). on double-base nitrocellulose-based propellant compositions as a function of the amount of nitroglycerine in the compositions.

Figure 5 shows the normalised heat flows expressed in $\mu\text{W} / \text{g}$ generated by propellant compositions stabilised with 1 wt.% of the non-aromatic compound (alpha ionone 12-1a) alone (mixed line), 1 wt.% of the aromatic compound (eugenol 15-III) alone (dashed line), the combination of 0.5 wt.% of 12-1a with 0.5 wt.% of a complementary stabiliser 15-III as actual value (double dotted mixed line), and the combination of 0.5 wt.% of 12-1a with 0.5 wt.% of complementary stabiliser 15-III as theoretical value for a zero synergy effect (solid line).

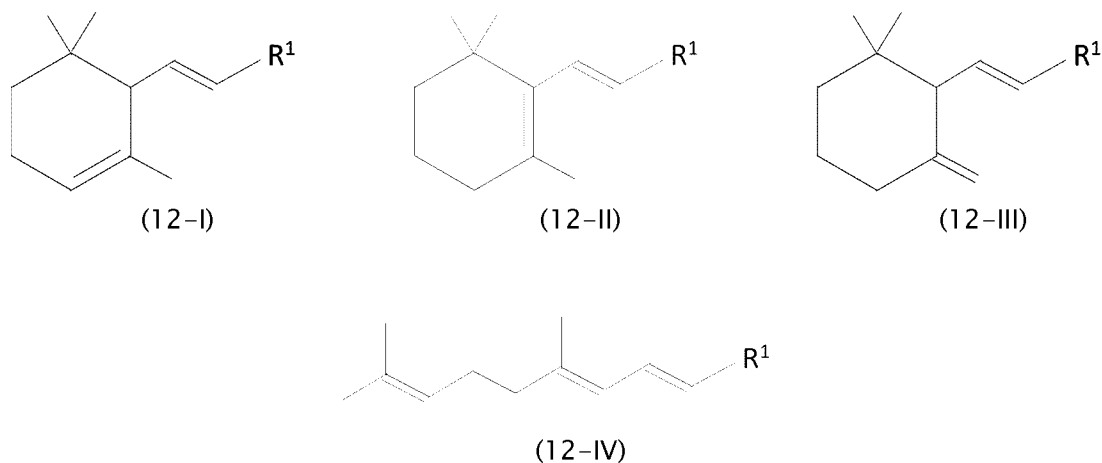
Figure 6 shows the normalised heat flows expressed in $\mu\text{W} / \text{g}$ generated by propellant compositions stabilised with 1 wt.% of the non-aromatic compound (alpha ionone 12-1a) alone (mixed line), 1 wt.% of the aromatic compound (2,3,5-trimethylphenol, 13-1a) alone (dashed line), the combination of 0.5 wt.% of 12-1a with 0.5 wt.% of a complementary stabiliser 13-1a as actual value (double dotted mixed line), and the combination of 0.5 wt.% of 12-1a with 0.5 wt.% of complementary stabiliser 13-1a as theoretical value for a zero synergy effect (solid line).

Detailed description of the invention

[0024] As illustrated in Figure 1, degradation of nitrocellulose forms free oxide radicals (R-O) and NO_x . These degradation products are capable of reacting further and with nitrocellulose 1, which can rapidly lead to an explosion of the nitrate ester-based propellant due to excess heat generation. The most commonly used stabilisers are certainly akardite (AkII) 4 and diphenyl amine (DPA) 5 as illustrated in Figure 2(a). Akardite (AkII) 4 when

exposed to NO_x, forms carcinogenic N–NO compounds **6** as illustrated in reaction (A) of Figure 2(a). Simultaneously or sequentially, it dissociates upon exposure to heat to form diphenyl amine (DPA) **5** following reaction (B) of Figure 2(a). Whether used directly as a stabiliser, or present in the composition following heat dissociation (B) of akardite **4**, diphenyl amine (DPA) **5** stabilises a propellant composition by the following mechanism. A free radical alkoxy group generated by the propellant abstracts the hydrogen of the amine group of DPA **5** to form a stable compound (ROH, **9**) (cf. reaction (C) of Figure 2(a)). The radical formed on the amine **8** can react with a NO_x to form stable N–nitrosodiphenylamine **10** (cf. reaction (D) of Figure 2(a)). The NNO group of N–nitrosodiphenylamine **10** is, however, carcinogenic and should be avoided for safety reasons. Triphenylamine has been tested in the past in order to prevent formation of NNO groups, but with little success in stabilisation properties. Hindered phenols as illustrated in Figure 2(b) effectively react with free oxide radicals (R–O[•]) but forming stable components which are unlikely to further react with NO_x (cf. reaction ① of Figure 2(b)). The efficiency of such stabilisers is limited to short periods of time only because of rapid phenols depletion.

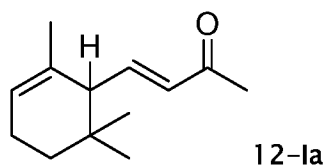
[0025] A non–aromatic compound **12** comprised in a stabiliser as used in the present invention has a general formula (12–I), (12–II), (12–III) or (12–IV):



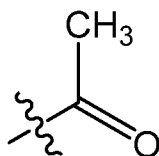
wherein R¹ represents a ketone, hydroxyl, carboxyl, aldehyde or (un)saturated alkyl group.

20

[0026] The non–aromatic compound of formula (12–I) is preferably alpha ionone **12–Ia**, wherein R¹ is –C(O)CH₃:



[0027] The R¹ group of the non-aromatic compound of formula (12-IV) is preferably:



In a preferred embodiment, the stabiliser corresponds to pseudo ionone.

- 5 [0028] Not wishing to be bound by any theory, it is believed that a stabiliser 12, as defined in the present invention contains a very labile proton which can react with radical alkoxy groups 2 and NO_x species (**Figure 1**) formed by degradation of the nitrate ester 1. Successive by-products are likely formed, and are also capable of reacting with NO_x and alkoxy radicals from the degradation of the nitrate ester 1, increasing the efficiency of stabiliser function.
- 10 Since no harmful NNO groups are formed due to the lack of nitrogen atoms in the non-aromatic compound 12 structure, the stabiliser according to the present invention produces little to no carcinogenic and mutagenic by-products.

[0029] It has been observed that even better stabilisation was obtained when combining a non-aromatic compound of formula (12) with an aromatic compound as complementary stabiliser yielding a synergistic effect on stabilisation as illustrated in Figures 5 and 6 by comparing the actual values (double dotted mixed lines) measured on a nitrocellulose composition stabilised with such combination with the theoretical values (solid lines) of the heat flows calculated by averaging the effects of each compound individually.

[0030] For example, a substituted phenol compound (13) can be used as a complementary stabiliser producing little to no carcinogenic and mutagenic by-products in the present invention together with the non-aromatic compound (12). Said complementary stabiliser can also be used instead of, rather than together with the non-aromatic compound (12), but the combination of a non-aromatic component (12) with a substituted phenol compound (13)

yielded enhanced stabilisation. Said phenol compound has the following general formula (13-I):



Wherein R³ represents: (i) H, (ii) alkyl substituted or not, or (iii) an alkoxy group, preferably not an aromatic group bound to the phenol through a ketone; and R⁴ and R⁵ are same or different, and represent (i) alkyl substituted or not, or (ii) alkoxy group. In a preferred embodiment, R³ represents CH₃. Again, R⁴ and R⁵ can be same, and preferably represent CH₃, yielding a complementary stabiliser of formula (13-Ia):

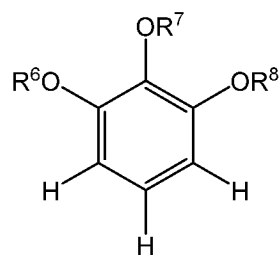


In another embodiment, R³ represents H. R⁴ and R⁵ are then preferably same. R⁴ and R⁵ can be alkyls, in particular *tert*-C₄H₉. Alternatively, R⁴ and R⁵ can be an alkoxy group, advantageously, methoxy, yielding a complementary stabiliser of formula (13-Ib):

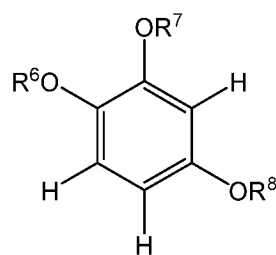


Alternatively, R⁴ and R⁵ may represent *tert*-C₄H₉.

[0031] In an alternative embodiment, a trialkoxy benzene (14) can also be used as complementary stabiliser producing little to no carcinogenic and mutagenic by-product in the present invention. Said trialkoxy benzene 14 has the following general formulae (14-I) or (14-II):



(14-I)



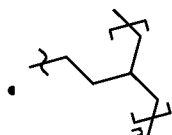
(14-II)

Wherein R^6 , R^7 and R^8 are same or different and represent C_{1-5} alkyl unsubstituted or substituted with an alkoxy group.

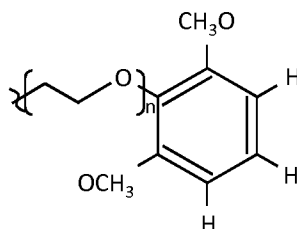
R^6 and R^8 in formulae (14-I) or (14-II) preferably represent CH_3 . More preferably, R^7

5 represents one of:

- CH_3

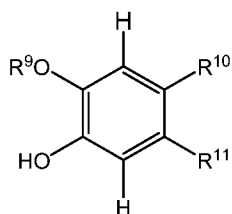


- a polymeric alkoxy chain, preferably endcapped with a benzene of formula (14-I) of the type,



wherein n is comprised between 1 and 20, preferably between 3 and 10.

[0032] In an alternative embodiment, an aromatic compound (15) having a general formula (15-I) can be also used as a complementary stabiliser together with a non-aromatic compound (12) in the present invention or, alternatively, on its own,



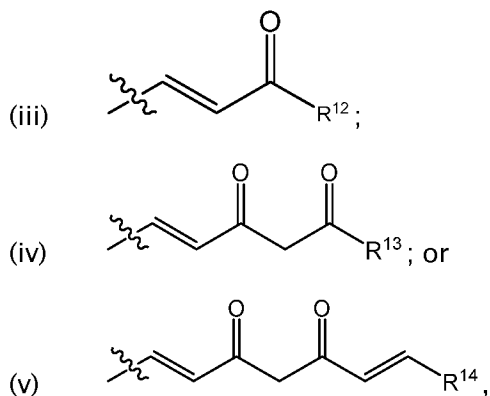
(15-I)

Wherein:

R⁹ represents, alkyl substituted or not;

R¹⁰ represents

- (i) H;
- 5 (ii) unsaturated alkyl group;



10 R¹¹ represents, H, alkyl substituted or not, or OR¹⁵;

R¹² represents, alkyl substituted or not, aromatic ring substituted or not, or OR¹⁵;

R¹³ represents, alkyl substituted or not, aromatic ring substituted or not, or OR¹⁶;

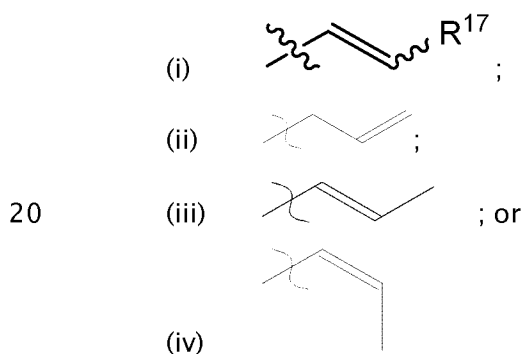
R¹⁴ represents, aromatic ring substituted or not;

R¹⁵ represents, alkyl substituted or not, or aromatic ring substituted;

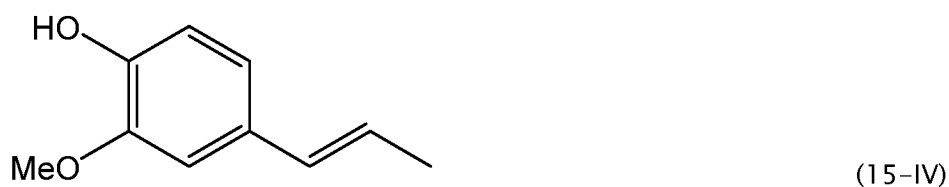
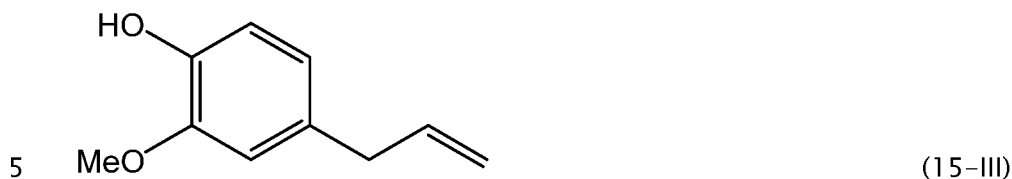
15 R¹⁶ represents, alkyl substituted or not, or aromatic ring substituted

In a preferred embodiment, R⁹ represents C₁₋₅ alkyl substituted or not, preferably CH₃;

Further, it is preferred that R¹⁷ represents:

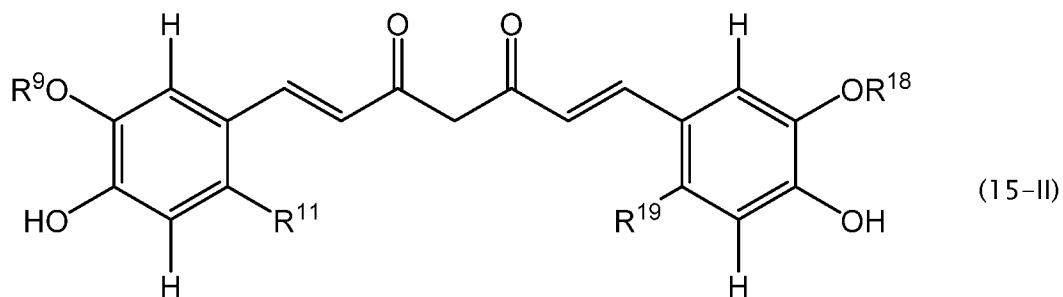


wherein R¹⁷ represents H, alkyl substituted or not, or aromatic ring substituted or not. For example, eugenol (15-III) or isoeugenol (15-IV) are suitable complementary stabilisers according to the present invention.



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A more preferred embodiment of composition according to the present invention comprises a curcumin derivative of formula (15-II) as stabiliser,

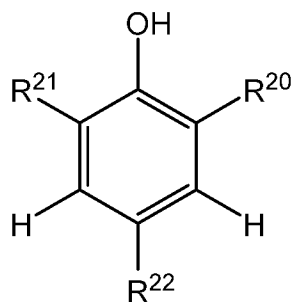


Wherein

R⁹ and R¹⁸ are same or different and represent alkyl substituted or not, preferably C₁₋₅, more preferably CH₃; R¹¹ and R¹⁹ are same or different and represent H or alkyl substituted or not (e.g., C₁₋₅ alkyl), wherein each of R⁹ and R¹⁸, and R¹¹ and R¹⁹, are preferably same, and more preferably both are H.

15

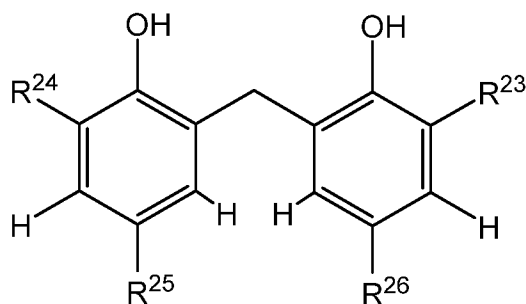
[0033] In another alternative embodiment, a substituted phenol compound (16) having the general formula (16-I) can also be used as a complementary stabiliser:



(16-I)

wherein: R²⁰, R²¹ and R²² are the same or different and represent: (i) alkyl-substituted or not, (ii) alkoxy group.

[0034] In another alternative embodiment, a substituted phenol compound (17) having the general formula (17-I) can also be used as a complementary stabiliser:

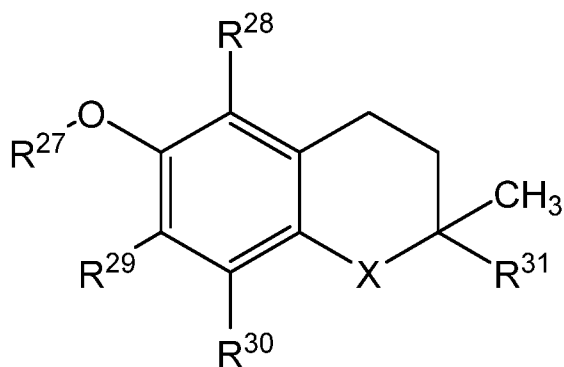


(17-I)

wherein: R²³, R²⁴, R²⁵ and R²⁶ are the same or different and represent: (i) alkyl-substituted or not, (ii) alkoxy group.

[0035] In another alternative embodiment, a tocopherol-class compound (18) with the general formula (18-I) can also be used as a complementary stabiliser:

10



(18-I)

wherein:

X is oxygen or nitrogen;

R²⁷ is selected from the group consisting of hydrogen, alkyl, alkenyl, alkynyl, aryl, heteroaryl, carboxylic acid, carboxylate, ester, saccharide, alkoxy-linked saccharide, alcohol, and ether;

R²⁸ is selected from the group consisting of hydrogen methyl, benzyl carboxylic acid, benzyl carboxylate, benzylester, and saccharide;

5 R²⁹ is selected from the group consisting of hydrogen, methyl, benzyl carboxylic acid, benzyl carboxylate, benzylester and , saccharide;

R³⁰ is selected from the group consisting of methyl, benzyl carboxylic acid, benzyl carboxylate, benzylester, and saccharide;

R³¹ is selected from the group consisting of alkyl and alkenyl;

10 Wherein when X is nitrogen, said nitrogen is substituted with R³², wherein R³² is selected from the group consisting of hydrogen and methyl.

[0036] Surprisingly a stabiliser comprising the non-aromatic compound 12 and a complementary stabiliser comprising an aromatic selected from one or more of a substituted phenol compound (13, 16 or 17), a trialkoxy benzene (14), an aromatic compound (15) or a
15 tocopherol species (18) provides a synergic stabilising effect. For example, Figure 5 shows the positive synergic effect when stabiliser 12-Ia is used with compound 15-III. The total heat release is less for the combination of the two molecules (cf. double dotted mixed line), than for the averaged sum of the individual heat releases for each stabiliser (cf. solid line).
Figure 6 is another example of a positive synergic effect for the combination of molecules
20 12-Ia and 13-Ia (compare actual (double dotted mixed line) and theoretical (solid line) values of heat flow, showing a significantly lower heat flow after two days testing.

[0037] The propellant composition of the present invention may be a single base propellant, wherein the nitrate ester propellant consists of nitrocellulose only or a double base propellant, wherein nitrocellulose is combined with a blasting oil and/or at least one
25 energetic additive. The most common blasting oil is nitroglycerine. Figures 3(a) compares the stability of a single base propellant composition stabilised with 1 wt.% of DPA 5 as conventional stabiliser of the prior art with a stabiliser comprising 1 wt.% of a non-aromatic compound 12 consisting of formula 12-Ia and 12-IVa-according to the present invention. Figure 3(b) illustrates the same for a double base propellant composition wherein the nitrate
30 ester propellant comprises 80 wt.% nitrocellulose and 20 wt.% nitroglycerine. Figure 3(c)

compares the stability of a 60 wt.% nitrocellulose and 40 wt.% nitroglycerine double base propellant composition stabilised with 1 wt.% of DPA 5 as conventional stabiliser of the prior art, 1% of the non-aromatic compound 12-1a and 1% of 12-IVa. Nitroglycerine is a commonly used blasting oil. Energetic additives, on the other hand, can be an energetic plasticiser selected from the group of nitramines such as butyl-NENA, dinitrodiazaalkane (DNDA), or an explosive such as RDX, HMX, FOX7, FOX12, CL20. A double base propellant composition according to the present invention preferably comprises a nitrate ester-based propellant comprising not more than 60 wt.% blasting oil (such as nitroglycerine) or energetic additive with respect to the total weight of nitrate ester based propellant. More preferably, it comprises between 5 and 45 wt.%, most preferably between 7 and 22 wt.% blasting oil or energy additive, with respect of the total weight of nitrate ester-based propellant. A most preferred blasting oil is nitroglycerine.

[0038] A propellant composition according to the present invention comprises a stabiliser comprising a non-aromatic compound (12), for example consisting of formula (12-I), preferably in an amount comprised between 0.1 and 5.0 wt.%, more preferably between 0.2 and 2.0 wt.%, most preferably between 0.5 and 1.5 wt.%, with respect to the total weight of the composition.

[0039] Unless otherwise specified, the expression "*substituted or not*" is to be construed as any -H in a molecule may be substituted by any of an alkyl, alkene, or an aromatic ring. A propellant composition is considered as being a "*nitrocellulose-based propellant composition*" if it comprises at least 40 wt. % nitrocellulose, based on the total weight of the composition.

[0040] Beside a nitrate ester based propellant and a stabiliser, a propellant composition according to the present invention may comprise additives. In particular, it may comprise one or more of the following additives:

- (a) a potassium salt, such as potassium nitrate (KNO_3) or sulphate (K_2SO_4), preferably in an amount comprised between 0.01 and 1.5 wt. %;

- (b) combustion moderators such as phthalates, centralite or citrate derivatives, preferably in an amount comprised between 0.5 and 10.0 wt. %;
- (c) an anti-static agent such as graphite, preferably in an amount comprised between 0.01 and 0.5 wt. %; and

5 (d) calcium carbonate, preferably in an amount comprised between 0.01 and 0.7 wt. %,

Wherein the wt.% are expressed in terms of the total weight of the propellant composition.

[0041] An example of propellant composition according to the present invention is listed in Table 1.

Table 1: typical propellant compositions according to the present invention

component	single base wt.%	double base wt.%
nitrocellulose	89.0-96.0	82.0-86.0
nitroglycerine	0.0	7.0-11.0
KNO ₃	0.5-1.0	0.5-1.0
dibutylphthalate	3.0-7.0	3.0-7.0
graphite	0.2-0.4	0.2-0.4
calcium carbonate	<0.7	<0.7
stabiliser of formula (12)	0.15-2.0	0.15-2.0

10

EXPERIMENTAL TESTS

[0042] STANAG 4582 (Ed. 1) of March 9, 2007 entitled *“Explosives, nitrocellulose based propellants, stability test procedure and requirements using heat flow calorimetry”*, defines an accelerated stability test procedure for single-, double-, and triple base propellants using heat flow calorimetry (HFC). The test is based on the measurement of the heat generated by a propellant composition at a high temperature. Fulfilment of the STANAG 4582 (Ed.1) test qualifies a propellant composition for a 10 year stability at 25°C.

15

[0043] A sample of propellant composition is enclosed in a hermetically sealed vial and positioned in a heat flow calorimeter having a measuring range corresponding to 10 to 500 µW/g. The sample is heated and maintained at a constant temperature of 90°C for the whole duration of the test and the heat flow is measured and recorded. A heat flow not exceeding 350 µW / g for a period of 3.43 days at 90°C is considered to be equivalent to at least 10 years of safe storage at 25°C. The graphs of Figures 3 to 6 show the stability of a

20

composition as a function of time measured as defined above. The full scale of the ordinate (normalised heat flow) corresponds to a value of $350 \mu\text{W} / \text{g}$ not to be exceeded according to STANAG 4582 (Ed.1), and the vertical straight line indicates 3.43 days. The initial heat flow peak of the graphs of Figures 3 to 6 is ignored as it is not representative of any specific reaction or phase transformation of the propellant composition, provided it does not exceed an exotherm of 5 J.

[0044] Figures 3(a), (b) and (c) show the results of the stability tests carried out on a single- and double-base nitrocellulose based propellants, the latter comprising 40 wt.% nitroglycerine, for DPA 5 as prior art stabiliser and stabilisers comprising a non-aromatic compound (12-1a) or (12-IVa), in amounts of 1 wt.%, with respect to total weight of the propellant composition. The results for the stabilisers comprising component (12-1a) and (12-IVa) according to the present invention are shown by a solid line and a long dashed line, respectively, and those for diphenyl amine (DPA) of the prior art are shown by a dotted line. The heat flow never exceeds $100 \mu\text{W} / \text{g}$ for 3.43 days with non-aromatic compounds (12-1a and 12-IVa), when STANAG 4582 (Ed.1) requires to maintain the heat flow below $350 \mu\text{W} / \text{g}$ (full scale of the ordinate) as shown in Figure 3(c). The tests on single base propellants were carried out for a longer period, showing a prolonged stability of the compositions with a heat flow continuously lower than $250 \mu\text{W} / \text{g}$ for up to 8 days (which corresponds to a stability of more than 25 years at normal storage conditions. It can be seen that both stabilisers according to the present invention as well as DPA according to prior art fulfil the requirements of STANAG 4582 (Ed.1).

[0045] Stabilisers comprising a non-aromatic component such as 12-1a and 12-IVa according to the present invention are advantageous over conventional stabilisers (i.e. DPA 5 and AKII 4) because,

- (a) Contrary to DPA and Akardite, stabilisers according to the present invention do not generate any N-NO carcinogenic by-product upon their stabilisation activity.

(b) DPA curve (dotted line) for double based propellant in Figures 3(b) and 3(c) shows a sharp peak stabilising in a plateau at higher heat flow values, suggesting that all DPA was spent after only about two days (cf. reactions (C) and (D) in Figure 2(a)) whence stabilisation probably proceeds by reactions with by-products. By contrast, no discontinuity in the heat flow can be identified with stabilisers comprising 12-**Ia** or 12-**IVa** over 3.5 days and even for over 7 days, as revealed in Figures 3(b) and 3(c).

(c) As revealed in Figure 3(a) discussed supra with respect to single base nitrocellulose propellants, the stabilisers of the present invention allow the maintenance of a heat flow substantially lower than 350 $\mu\text{W} / \text{g}$ at a temperature of 90°C for periods up to 8 days. Longer term tests with DPA, however, are not easily performed because vials containing a composition stabilised with DPA leaked (Figure 3c), as shown by the sudden drop in the curve appearing earlier than the ones stabilised according to the present invention. It is assumed that gas generation by the reactions with DPA raises the pressure inside the vials above their limit of resistance, leading to the bursting open of the vials after a few days testing. Uncontrolled pressure rises must be avoided during transportation or storage of propellant compositions for obvious reasons.

[0046] Figure 4 shows the results of the stability tests carried out on a double-base nitrocellulose based propellants, comprising 10, 20 and 40 wt.% nitroglycerine, each composition comprising the non-aromatic compound 12-**Ia** in an amount of 1 wt.%, with respect to the total weight of the propellant composition.

[0047] Figure 5 shows the normalised heat flows expressed in $\mu\text{W} / \text{g}$ generated by propellant compositions stabilised with:

- 1 wt.% of the non-aromatic compound (alpha ionone 12-**Ia**) alone (mixed line) according to the present invention,
- 1 wt.% of the aromatic compound (eugenol 15-**III**) alone (dashed line), not according to the present invention,

- the combination of 0.5 wt.% of stabiliser 12-1a with 0.5 wt.% of complementary stabiliser 15-III (double dotted mixed line), according to the present invention as actually measured on a sample, and
- the theoretical combination of 0.5 wt.% of stabiliser 12-1a with 0.5 wt.% of complementary stabiliser 15-III (solid line), calculated by averaging the individual contribution of each component thus ignoring any synergy effect.

It can be seen that the two best stabiliser compositions are the ones according to the present invention, namely, a non-aromatic compound of formula 12-1a used alone or in combination with a complementary stabiliser of formula 15-III.

10 **Figure 6** shows the normalised heat flows expressed in $\mu\text{W} / \text{g}$ generated by propellant compositions stabilised with:

- 1 wt.% of the non-aromatic compound (alpha ionone 12-1a) alone (mixed line) according to the present invention,
- 1 wt.% of the aromatic compound (2,3,5-trimethylphenol, 13-1a) alone (dashed line),
15 not according to the present invention,
- the combination of 0.5 wt.% of 12-1a with 0.5 wt.% of a complementary stabiliser 13-1a as actual value (double dotted mixed line), according to the present invention as actually measured on a sample, and
- the theoretical combination of 0.5 wt.% of stabiliser 12-1a with 0.5 wt.% of
20 complementary stabiliser 13-1a (solid line), calculated by averaging the individual contribution of each component thus ignoring any synergy effect.

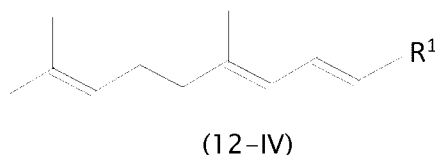
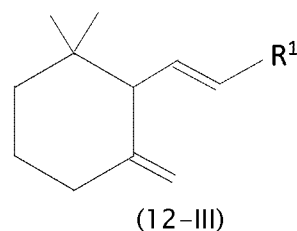
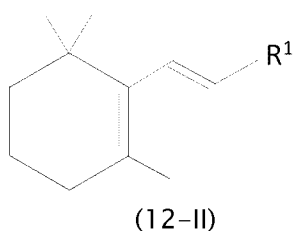
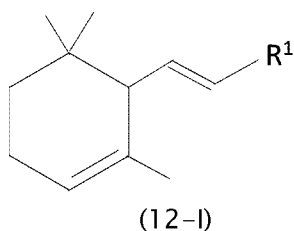
[0048] The propellant compositions of the present invention mark the beginning of the use of a new generation of stabilisers which can be referred to as “green or environmentally-friendly stabilisers,” which combine efficient, long term stability of nitrocellulose-based
25 propellants without formation of any detectable amounts of carcinogenic or mutagenic by-products.

CLAIMS

1. Nitrocellulose-based propellant composition comprising:

- (a) a nitrate ester-based propellant comprising nitrocellulose; and
- (b) a stabiliser comprising a non-aromatic compound (12) consisting of a general

5 ionone formula (12-I), (12-II), (12-III) or (12-IV):



Wherein R¹ represents a ketone, hydroxyl, carboxyl, aldehyde or an (un)saturated alkyl group, preferably -C(O)CH₃ (corresponding to alpha, beta, gamma and pseudo ionone).

10 2. Propellant composition according to claim 1, wherein the nitrate ester-based propellant consists of nitrocellulose alone (single base) or of a mixture comprising nitrocellulose in combination with at least a blasting oil and/or at least one energetic additive (double or higher base).

15 3. Propellant composition according to claim 1 or 2, wherein the non-aromatic compound (12) is a substance capable of reacting by H-abstraction with radical groups formed by degradation of the nitrate ester to form a first by-product capable of further reacting with NO_x and/or alkoxy groups formed by degradation of the nitrate ester to form a second by-product comprising no NNO groups.

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4. Propellant composition according to claim 3, wherein the second by-product is capable of reaction with radical groups formed by degradation of the nitrate ester, preferably

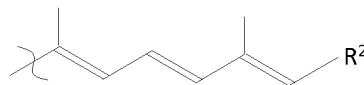
forming third and subsequent by-products capable of reacting with such radical alkoxy groups or with NO_x.

5. Propellant composition according to any of claims 2 to 4, wherein the blasting oil comprises at least a nitrated polyol, said nitrated polyol is obtained by nitration of polyol selected from a group consisting of glycerol, glycol, diethylene glycol, triethylene glycol and metriol, preferably glycerol, and wherein the at least one energetic additive is an energetic plasticizer selected from the group of nitramines, including butyl-NENA, dinitrodiazaalkane (DNDA), or is an explosive such as RDX, HMX, FOX-7, FOX-12, CL20.

10

6. Propellant composition according to any one of the preceding claims, wherein R¹ represents one of:

- acetyl ketone -C(O)CH₃; or
- a component of formula



15

wherein R² represents CH₂OH, -CHO, or, -CH₂OC(=O)R³, R³ represents alkyl group substituted or not, and

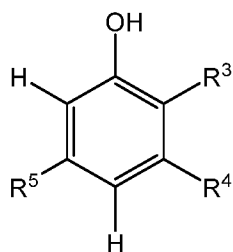
wherein said non-aromatic compound (12) is preferably retinyl palmitate.

7. Propellant composition according to any one of the preceding claims, wherein the non-aromatic compound (12) is present in the composition in an amount comprised between 0.1 and 5.0 wt. %, preferably between 0.2 and 2.0 wt. %, more preferably between 0.5 and 1.0 wt. %, with respect to the total weight of the composition.

8. Propellant composition according to any one of preceding claims, further comprising an aromatic compound as complementary stabiliser.

9. Propellant composition according to the preceding claim, wherein the complementary stabiliser comprises one or more of the following compounds:

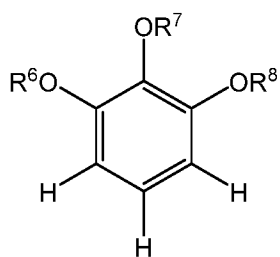
- (a) a substituted phenol compound (13) having the general formula (13-I):



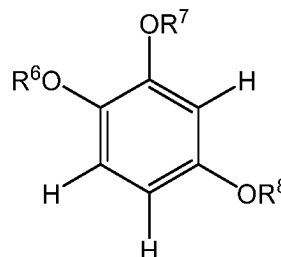
(13-I)

wherein: R³ represents: (i) H, (ii) alkyl substituted or not, or (iii) an alkoxy group; and R⁴ and R⁵ are same or different, and represent (i) alkyl substituted or not, or (ii) alkoxy group;

(b) a trialkoxy benzene (14) having the general formulae (14-I) or (14-II):



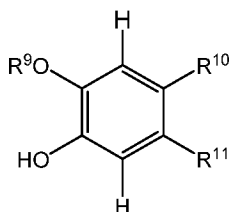
(14-I)



(14-II)

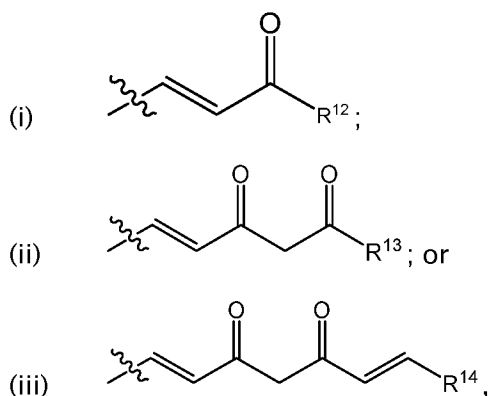
wherein R⁶, R⁷ and R⁸ are same or different and represent C₁₋₅ alkyl unsubstituted or substituted with an alkoxy group; and

(c) an aromatic compound (15) having a general formula (15-I):



(15-I)

Wherein: R⁹ represents, alkyl substituted or not; R¹⁰ represent (i) H, (ii) unsaturated alkyl group,



10

R¹¹ represents, H, alkyl substituted or not, or OR¹⁵;

R¹² represents, alkyl substituted or not, aromatic ring substituted or not, or OR¹⁵;

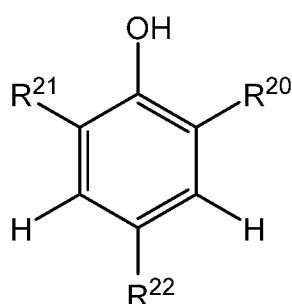
R¹³ represents, alkyl substituted or not, aromatic ring substituted or not, or OR¹⁶;

R¹⁴ represents, aromatic ring substituted or not;

5 R¹⁵ represents, alkyl substituted or not, or aromatic ring substituted;

R¹⁶ represents, alkyl substituted or not, or aromatic ring substituted.

(d) a substituted phenol compound (16) having the general formula (16-I):

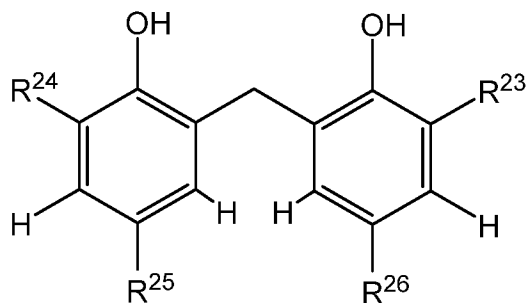


(16-I)

wherein: R²⁰, R²¹ and R²² are the same or different and represent: (i) alkyl-substituted or not,

10 (ii) alkoxy group.

(e) a substituted phenol compound (17) having the general formula (17-I):

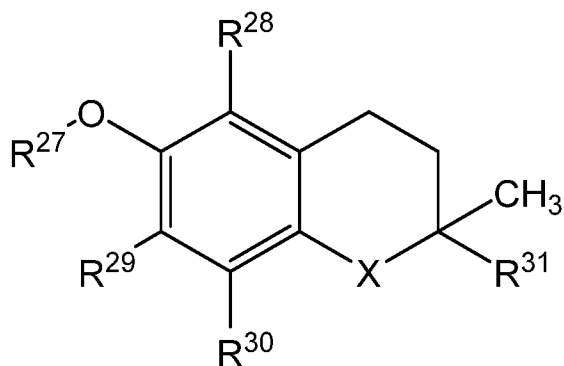


(17-I)

wherein: R²³, R²⁴, R²⁵ and R²⁶ are the same or different and represent: (i) alkyl-substituted or not, (ii) alkoxy group.

(g) A tocopherol-class compound (18) with the general formula (18-I):

15



(18-I)

wherein:

X is oxygen or nitrogen;

R²⁷ is selected from the group consisting of hydrogen, alkyl, alkenyl, alkynyl, aryl, heteroaryl,
5 carboxylic acid, carboxylate, ester, saccharide, alkoxy-linked saccharide, alcohol, and ether;

R²⁸ is selected from the group consisting of hydrogen methyl, benzyl carboxylic acid, benzyl
carboxylate, benzylester, and saccharide;

R²⁹ is selected from the group consisting of hydrogen, methyl, benzyl carboxylic acid, benzyl
carboxylate, benzylester and saccharide;

10 R³⁰ is selected from the group consisting of methyl, benzyl carboxylic acid, benzyl
carboxylate, benzylester, and saccharide;

R³¹ is selected from the group consisting of alkyl and alkenyl;

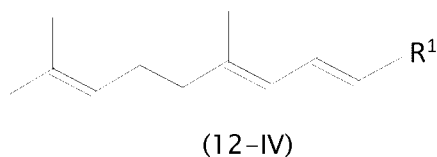
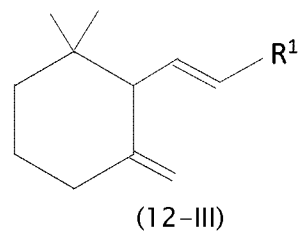
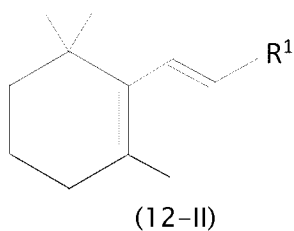
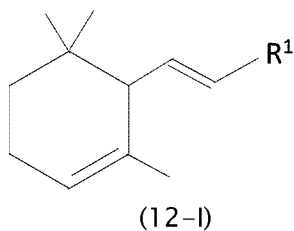
Wherein when X is nitrogen, said nitrogen is substituted with R³², wherein R³² is selected
from the group consisting of hydrogen and methyl.

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10. Propellant composition according to any one of preceding claims, wherein the nitrate
ester based propellant comprises not more than 60 wt.% nitroglycerine, and preferably
comprises between 5 and 45 wt.%, more preferably between 7 and 22 wt.% nitroglycerine,
with respect of the total weight of nitrate ester based propellant.

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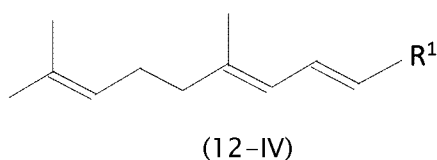
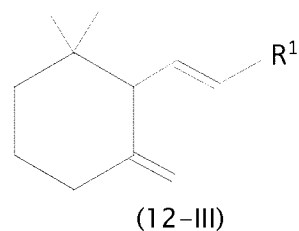
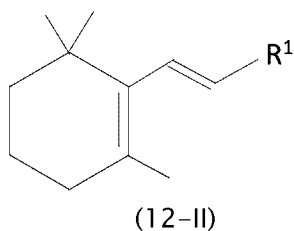
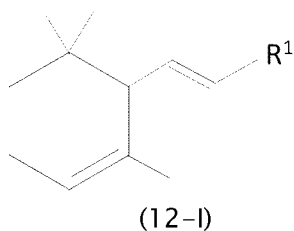
11. Use of a non-aromatic component (12) of a general formula (12-I), (12-II), (12-III) or
(12-IV):



for stabilising a nitrate ester based propellant comprising nitrocellulose, wherein:
R¹ represents ketone, hydroxyl, aldehyde, carboxyl or unsaturated alkyl group.

12. An environmentally-friendly stabiliser, which produces no mutagenic or carcinogenic by-products for stabilising a nitrate ester-based propellant comprising nitrocellulose. The said carcinogenic-free stabiliser being in the form of a mixture comprising:

(a) a non-aromatic compound (12) of general formula (12-I), (12-II), (12-III) or (12-IV):

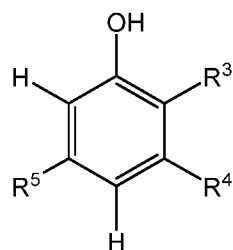


Wherein R¹ represents a ketone, hydroxyl, carboxyl, aldehyde or an unsaturated alkyl group;
and

(b) one or more aromatic compounds as complementary stabilisers.

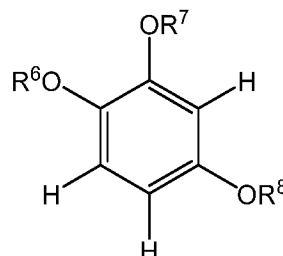
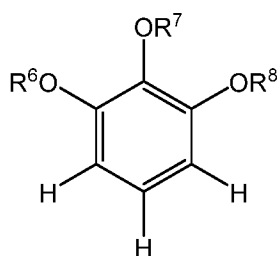
13. A carcinogenic-free stabiliser according to the preceding claim, wherein the complementary stabiliser is selected from one or more of the following compounds:

(a) a substituted phenol compound (13) having the general formula (13-I):



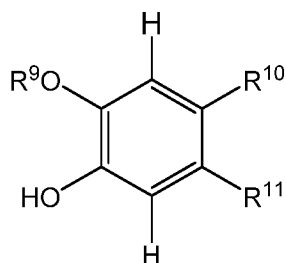
wherein: R³ represents: (i) H, (ii) alkyl substituted or not, or (iii) an alkoxy group; and R⁴ and R⁵ are the same or different, and represent (i) alkyl substituted or not, or (ii) alkoxy group; or

(b) a trialkoxy benzene (14) having the general formulae (14-I) or (14-II):

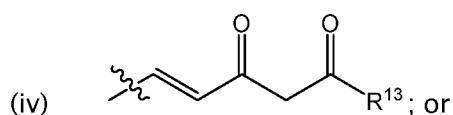
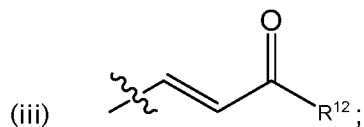


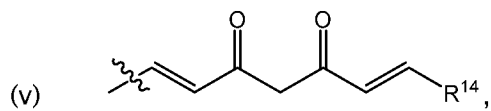
wherein R⁶, R⁷ and R⁸ are same or different and represent C₁₋₅ alkyl unsubstituted or substituted with an alkoxy group. or

(c) an aromatic compound (15) having a general formula (15-I):



Wherein: R⁹ represents, alkyl substituted or not; R¹⁰ represent (i) H, (ii) unsaturated alkyl group,





R¹¹ represents, H, alkyl substituted or not, or OR¹⁵;

R¹² represents, alkyl substituted or not, aromatic ring substituted or not, or OR¹⁵;

R¹³ represents, alkyl substituted or not, aromatic ring substituted or not, or OR¹⁶;

5 R¹⁴ represents, aromatic ring substituted or not;

R¹⁵ represents, alkyl substituted or not, or aromatic ring substituted;

R¹⁶ represents, alkyl substituted or not, or aromatic ring substituted.

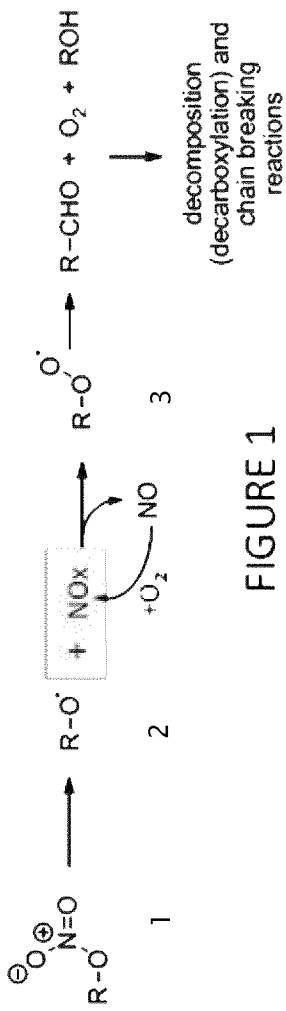


FIGURE 1

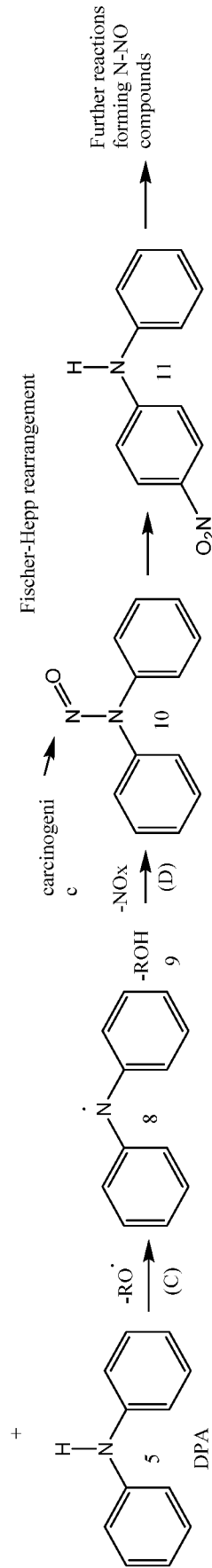
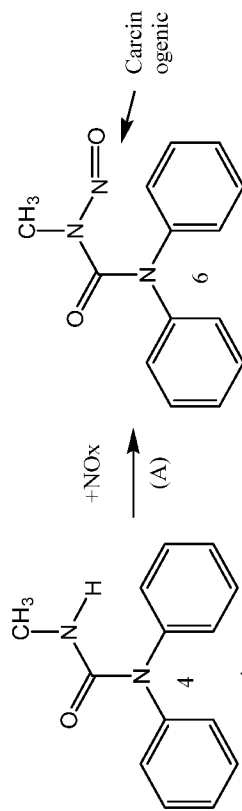


FIGURE 2(a)

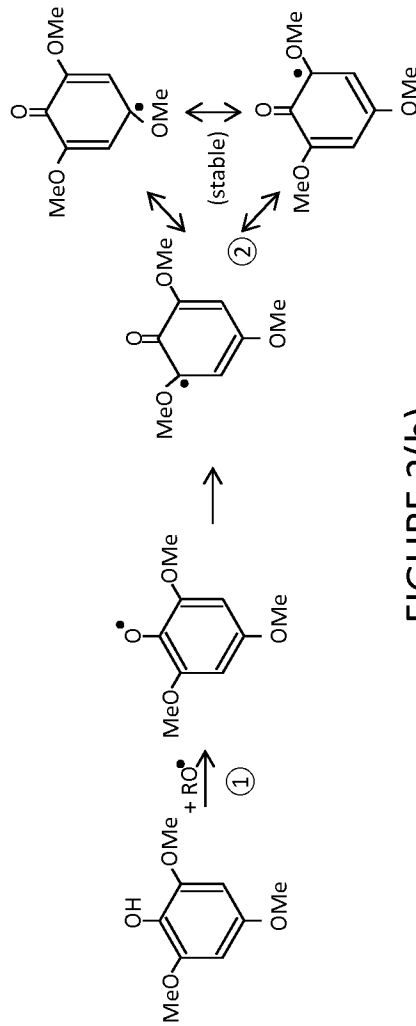


FIGURE 2(b)

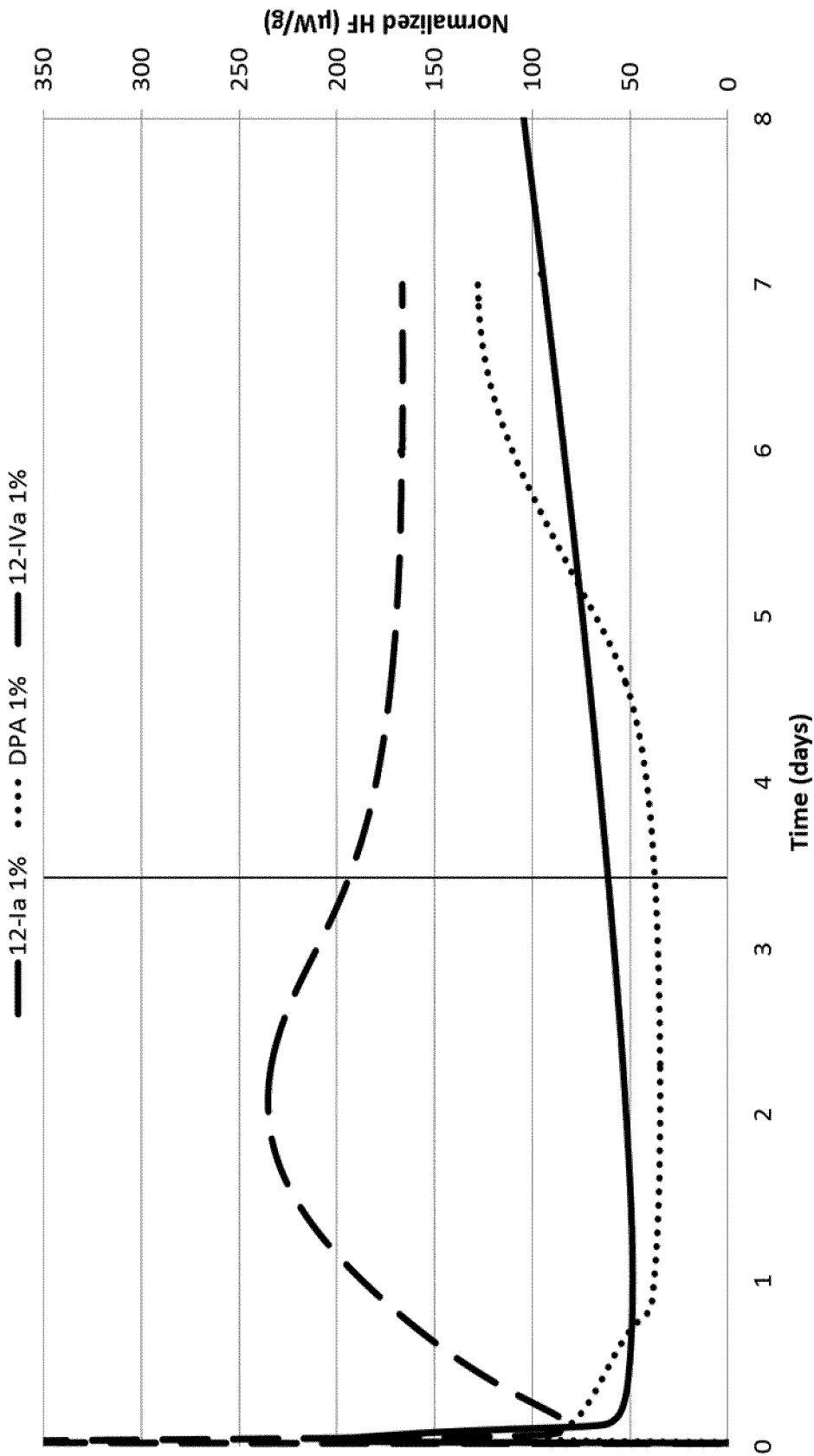


FIGURE 3a

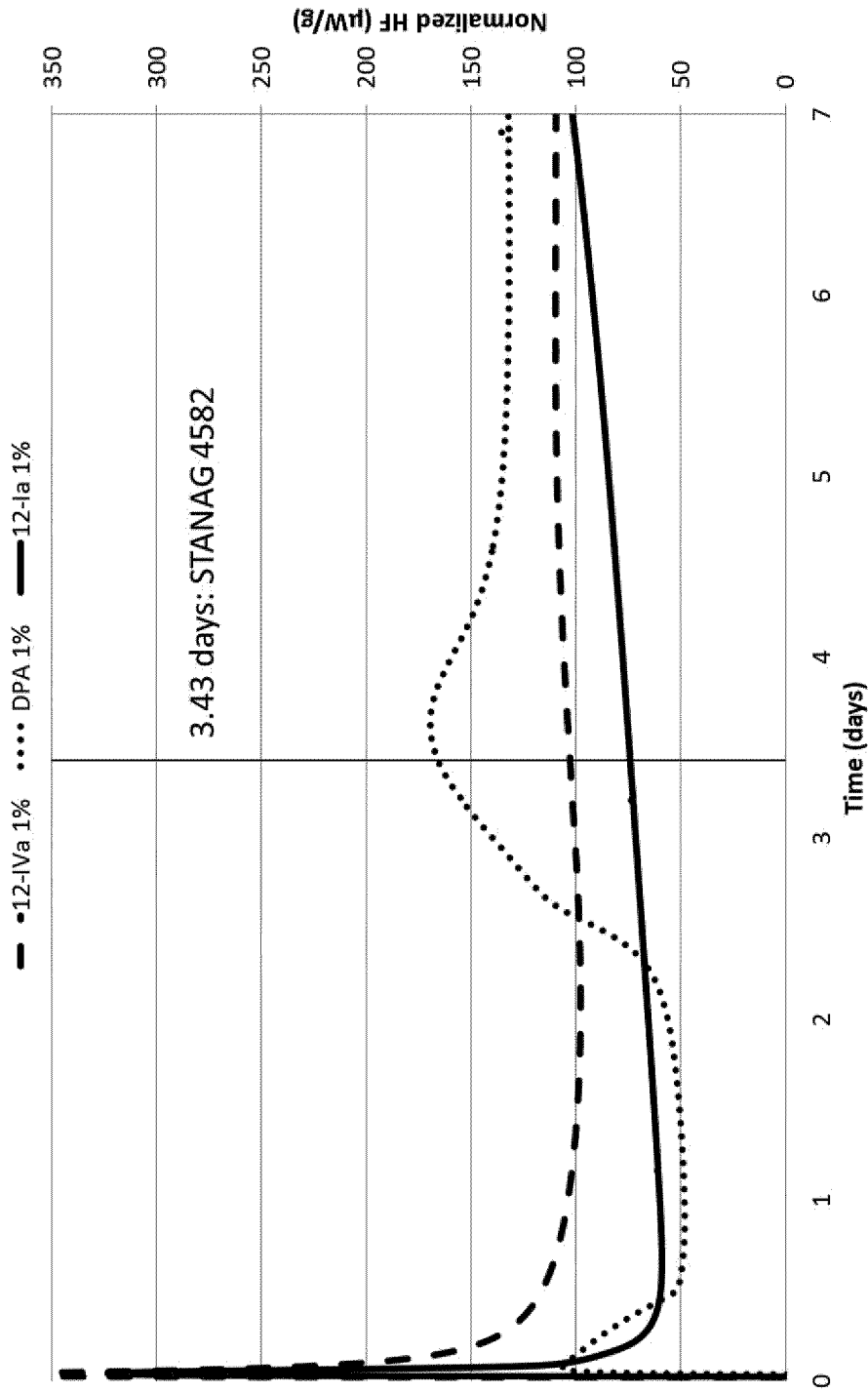


FIGURE 3b

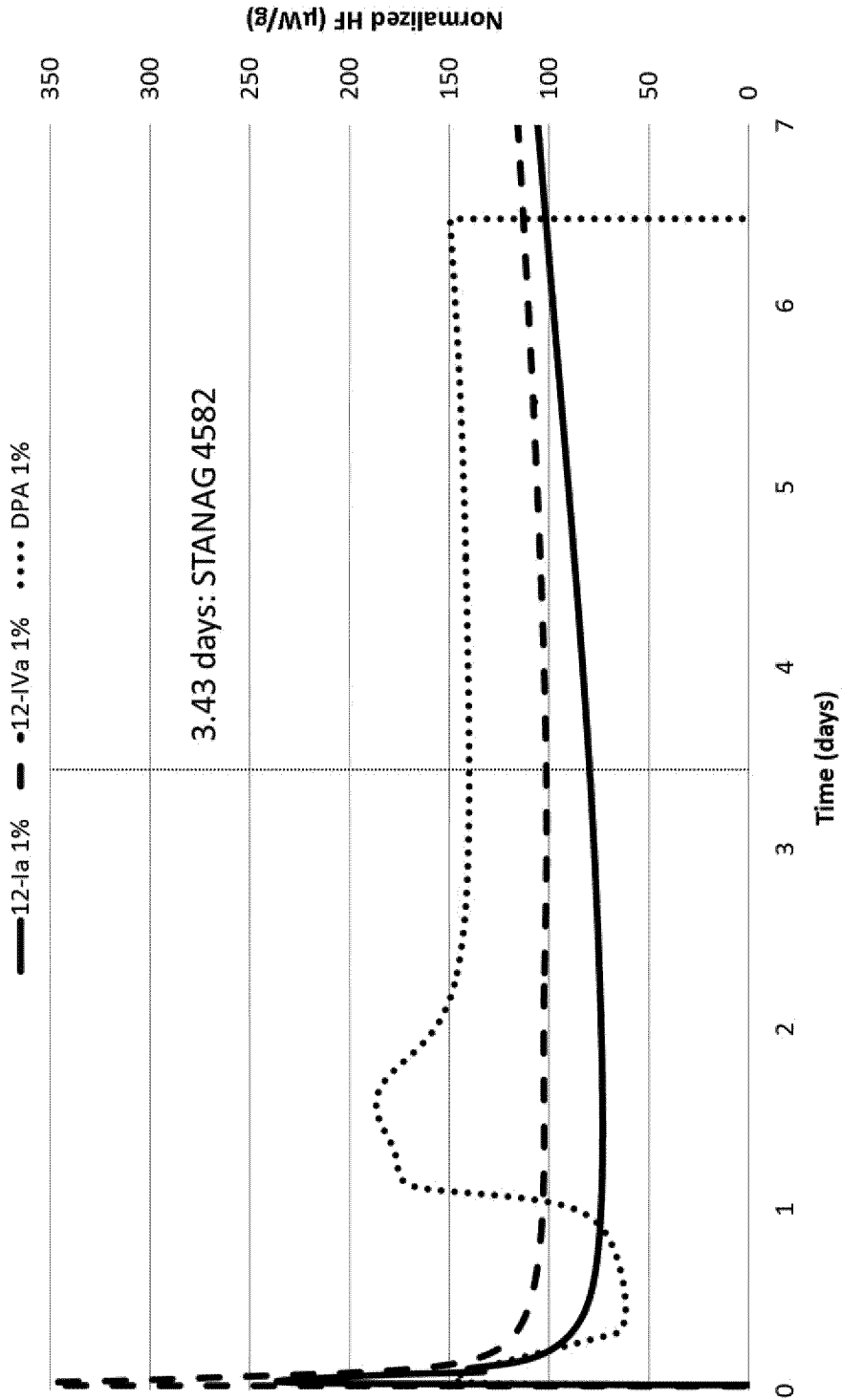


FIGURE 3C

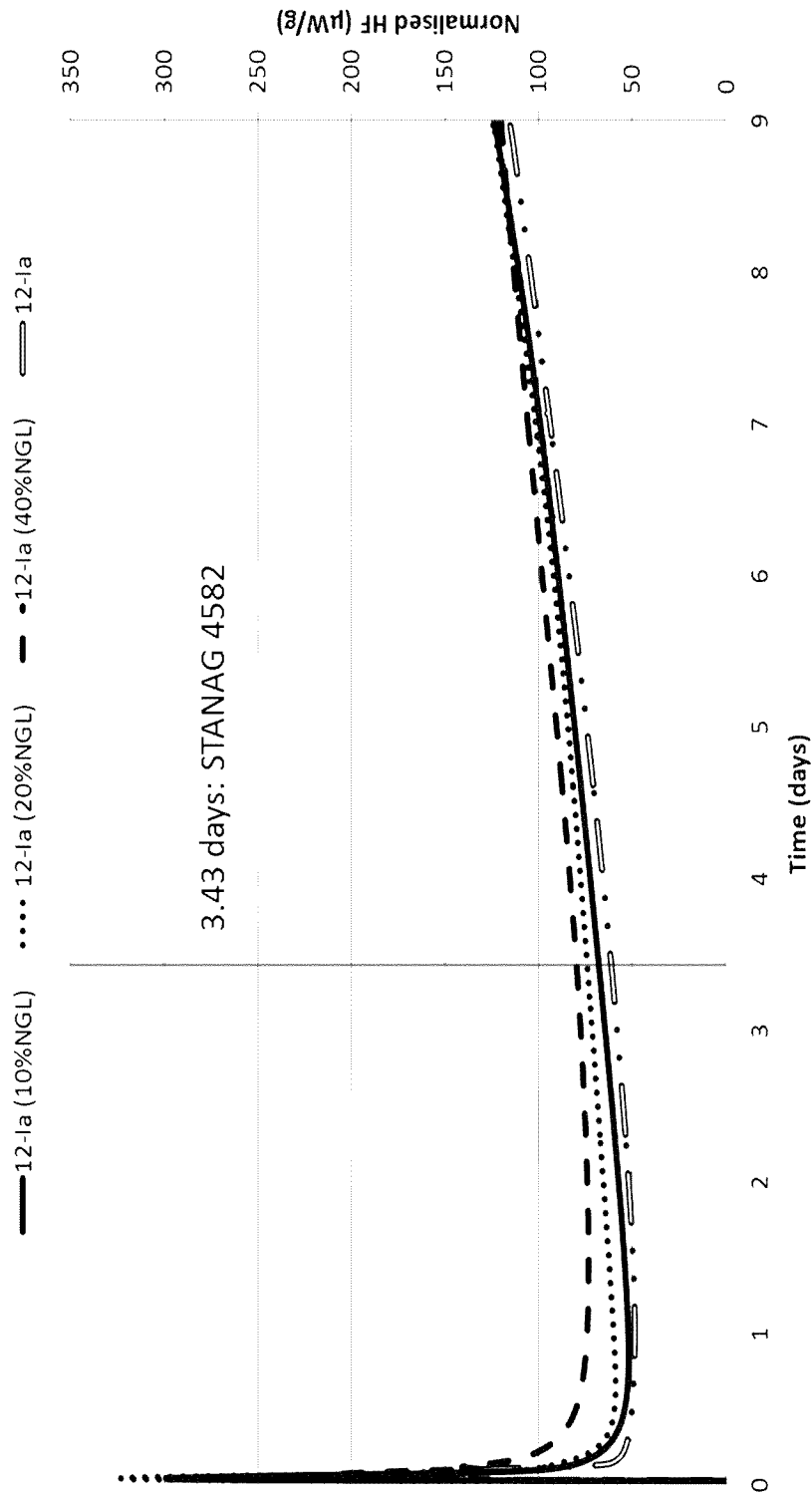


FIGURE 4

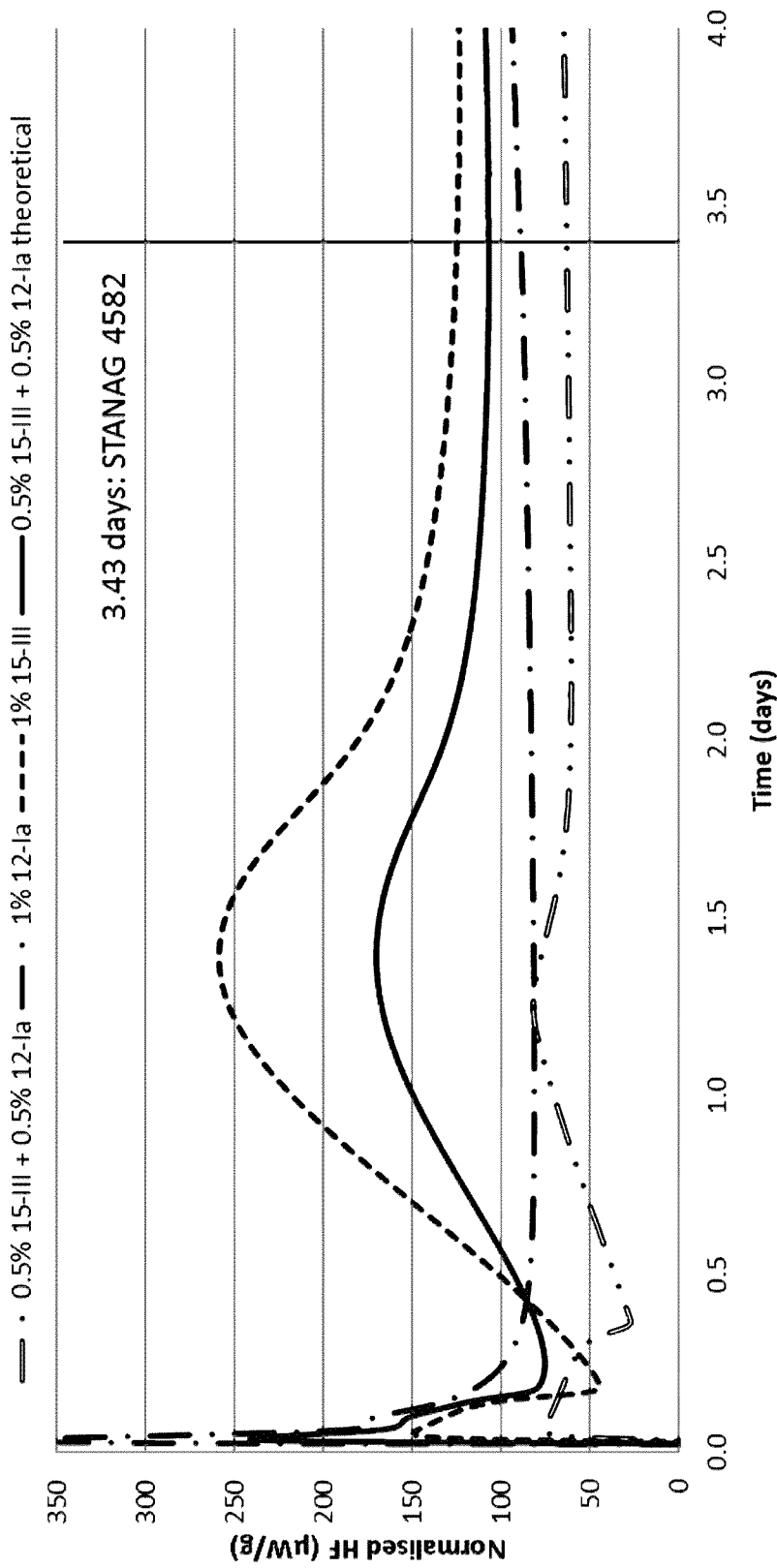


FIGURE 5

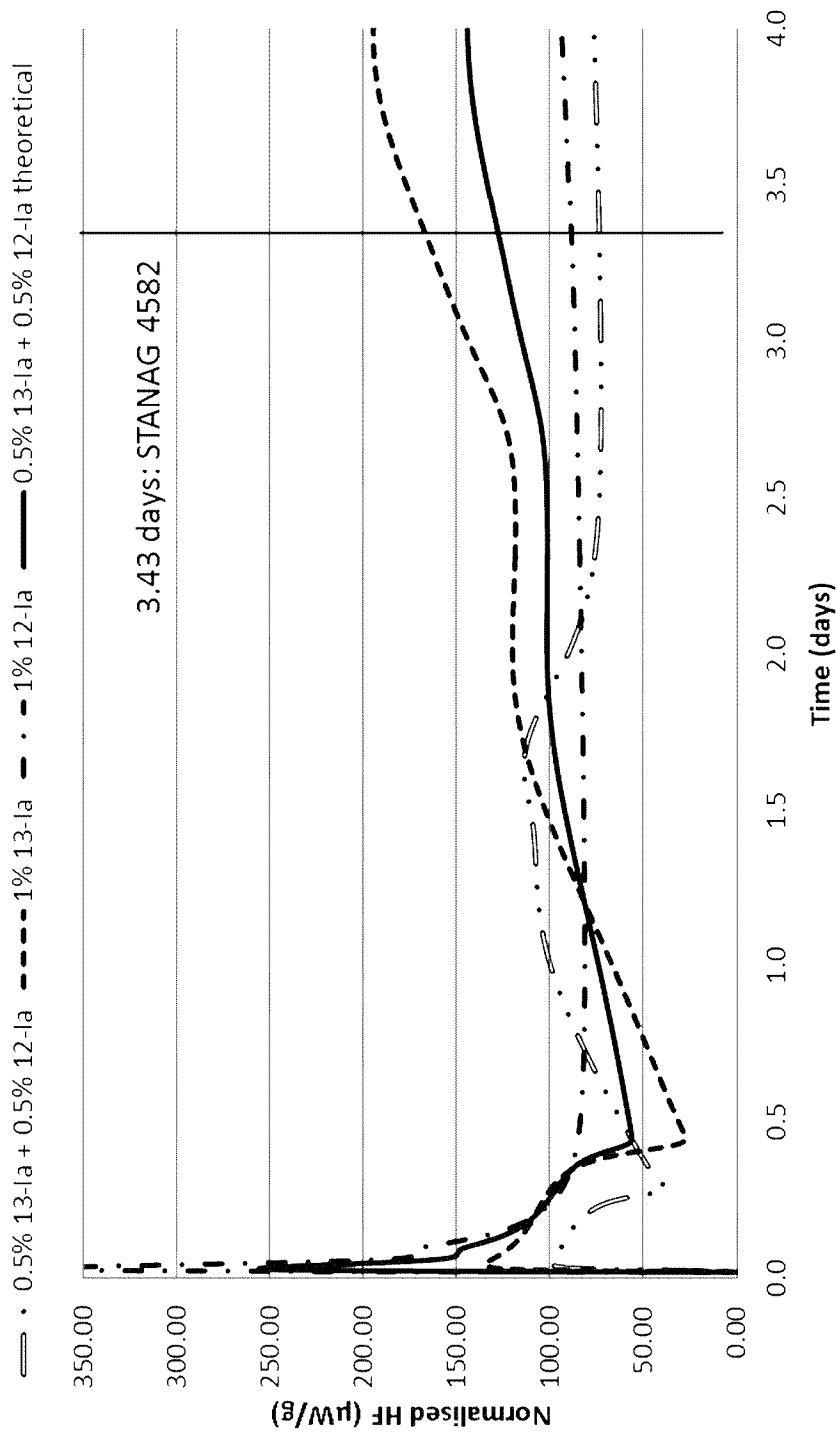


FIGURE 6

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/053946A. CLASSIFICATION OF SUBJECT MATTER
INV. C06B23/00 C06B25/20
ADD.

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)
C06B

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

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

EPO-Internal, COMPENDEX, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	HARRISON J C ET AL: "[beta]-ionone reactions with the nitrate radical: Rate constant and gas-phase products", INTERNATIONAL JOURNAL OF CHEMICAL KINETICS OCTOBER 2009 JOHN WILEY AND SONS INC. USA, vol. 41, no. 10, October 2009 (2009-10), pages 629-641, XP002743755, DOI: 10.1002/KIN.20438 page 639 ----- -/--	1-13



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

"&" document member of the same patent family

Date of the actual completion of the international search

22 March 2016

Date of mailing of the international search report

04/04/2016

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
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Authorized officer

Schut, Robert

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/053946

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>FORESTER ET AL: "beta-Ionone reactions with ozone and OH radical: Rate constants and gas-phase products", ATMOSPHERIC ENVIRONMENT, PERGAMON, GB, vol. 41, no. 38, 26 November 2007 (2007-11-26), pages 8758-8771, XP022362095, ISSN: 1352-2310, DOI: 10.1016/J.ATMOENV.2007.07.047 paragraph [0004]</p>	1-13
A	<p>-----</p> <p>ANTON CHIN ET AL: "Investigation of the decomposition mechanism and thermal stability of nitrocellulose/nitroglycerine based propellants by electron spin resonance", PROPELLANTS, EXPLOSIVES, PYROTECHNICS, WILEY - V C H VERLAG GMBH & CO., WEINHEIM, DE, vol. 32, no. 2, 1 April 2007 (2007-04-01), pages 117-126, XP002734046, ISSN: 0721-3115, DOI: 10.1002/PREP.200700013 [retrieved on 2007-04-11] the whole document</p>	1-13
A	<p>-----</p> <p>ANDRE VENTER ET AL: "A desorption electrospray ionization mass spectrometry study of aging products of diphenylamine stabilizer in double-base propellants", PROPELLANTS, EXPLOSIVES, PYROTECHNICS, WILEY - V C H VERLAG GMBH & CO., WEINHEIM, DE, vol. 31, no. 6, 1 December 2006 (2006-12-01), pages 472-476, XP002734045, ISSN: 0721-3115, DOI: 10.1002/PREP.200600064 [retrieved on 2006-12-27] the whole document</p>	1-13
A	<p>-----</p> <p>DATABASE CA, [Online]</p> <p>1 January 2006 (2006-01-01), WILKER STEPHAN ET AL: "Stability analysis of propellants containing new stabilizers - part IV: are phenols a possible alternative to aromatic amines?", XP002737946, retrieved from CA; STN Database accession no. 146-382822 abstract</p> <p>-----</p>	1-13