US 20220242803A1

(19) **United States**

(12) **Patent Application Publication** (10) **Pub. No.: US 2022/0242803 A1**

KETTLE (43) **Pub. Date: Aug. 4, 2022**

(54) **EXPLOSIVES BASED ON HYDROGEN PEROXIDE WITH IMPROVED SLEEP TIME**

(71) Applicant: **CMTE DEVELOPMENT LIMITED**, Pinjarra Hills, Queensland (AU)

(72) Inventor: **Andrew KETTLE**, Pinjarra Hills, Queensland (AU)

(21) Appl. No.: **17/616,440**

(22) PCT Filed: **Jun. 5, 2020**

(86) PCT No.: **PCT/AU2020/050573**

§ 371 (c)(1),
(2) Date: **Dec. 3, 2021**

(30) **Foreign Application Priority Data**

Jun. 7, 2019 (AU) 2019901993

Publication Classification

(51) **Int. Cl.**

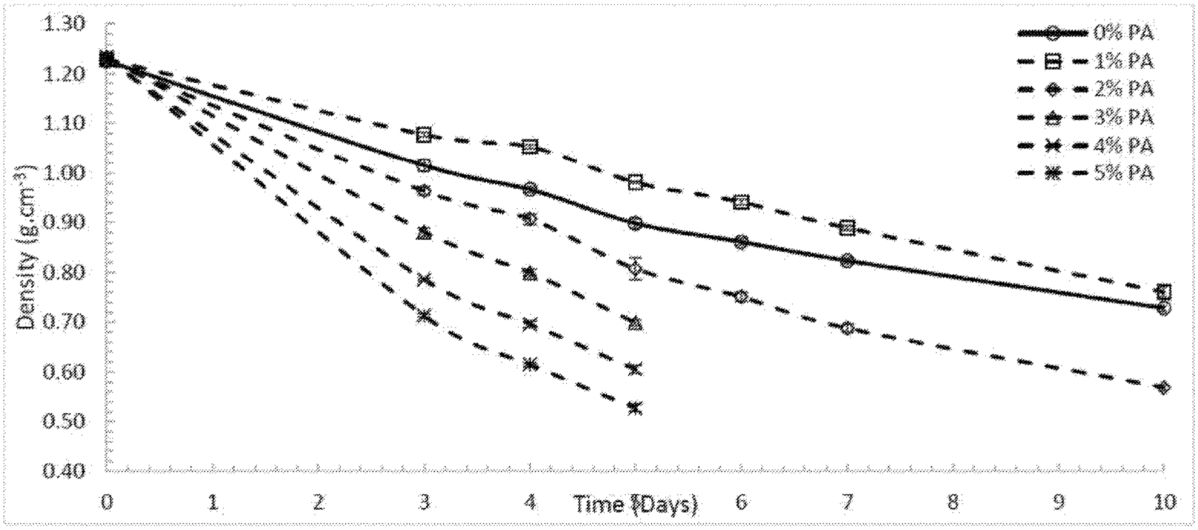
C06B 23/00	(2006.01)
C06B 43/00	(2006.01)
C06B 21/00	(2006.01)

(52) **U.S. Cl.**

CPC ***C06B 23/006*** (2013.01); ***C06B 43/00*** (2013.01); ***C06B 21/0008*** (2013.01); ***C06B 23/001*** (2013.01); ***C06B 23/004*** (2013.01)

(57) **ABSTRACT**

The present invention provides an explosive composition comprising hydrogen peroxide, fuel and one or more density stabilisers. The present invention also provides methods for preparing the compositions and method of using the compositions.



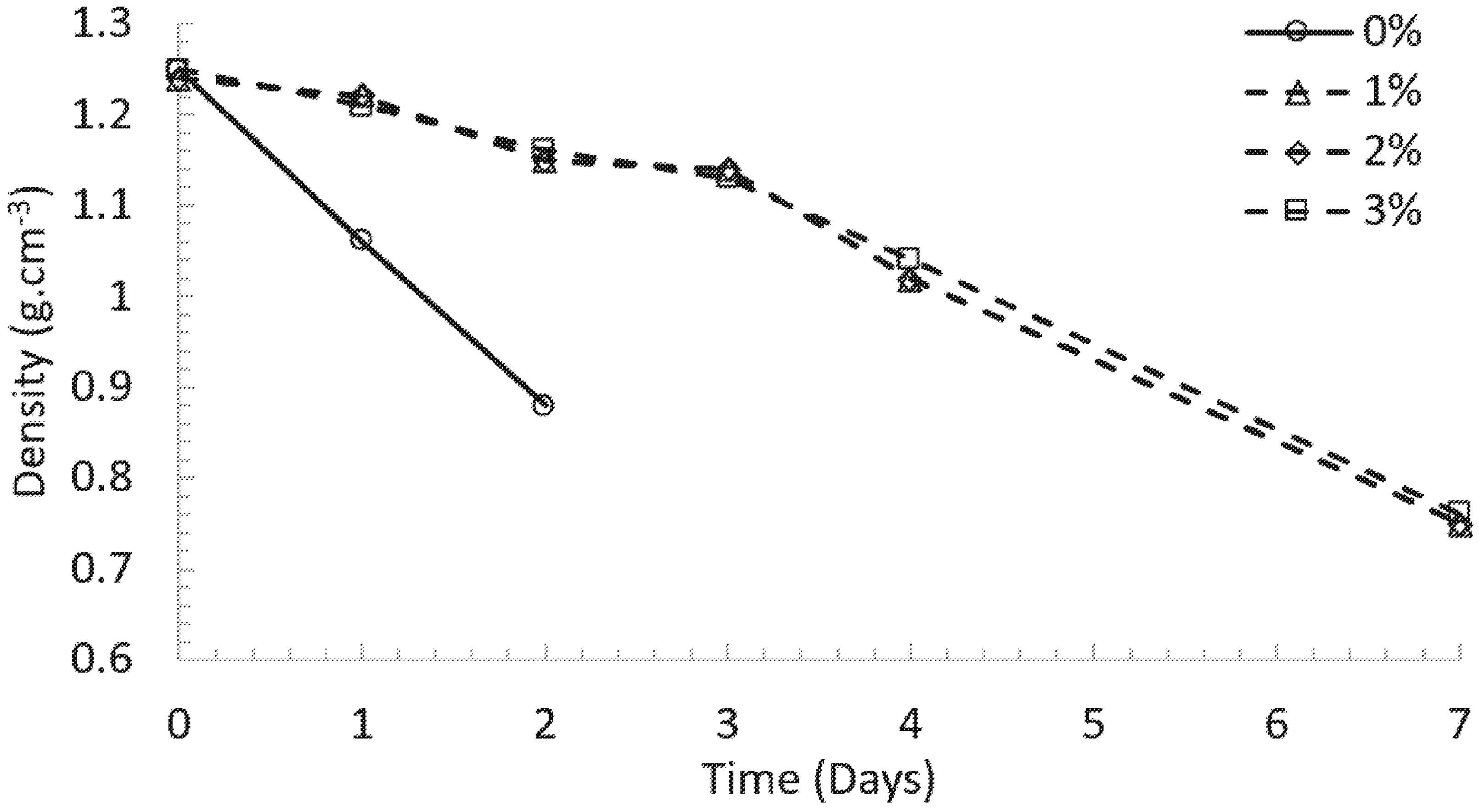


Fig. 1

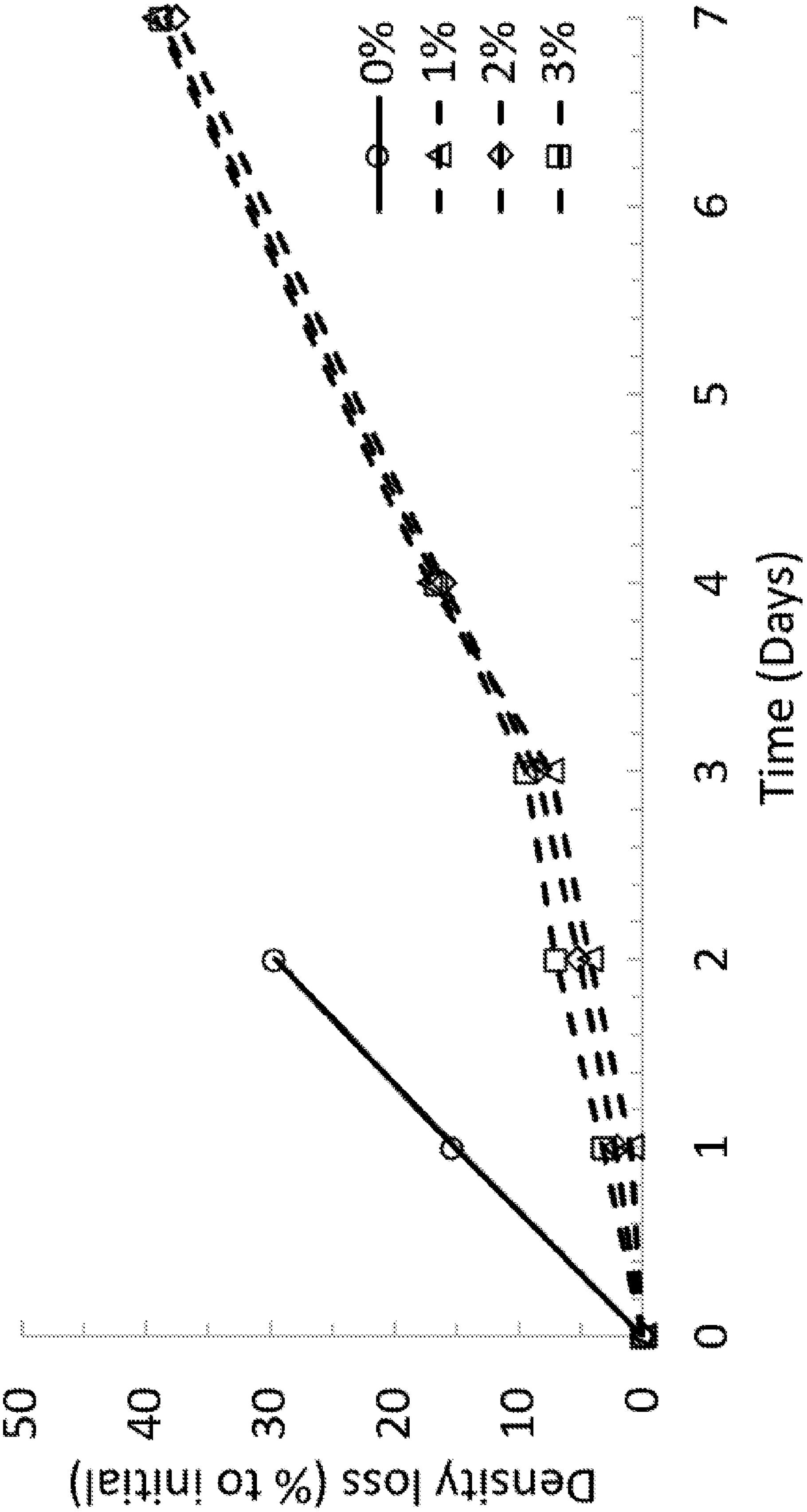

Density loss (% to initial)
0
10
20
30
40
50
Time (Days)
0
1
2
3
4
5
6
7
0%
1%
2%
3%

Fig. 2

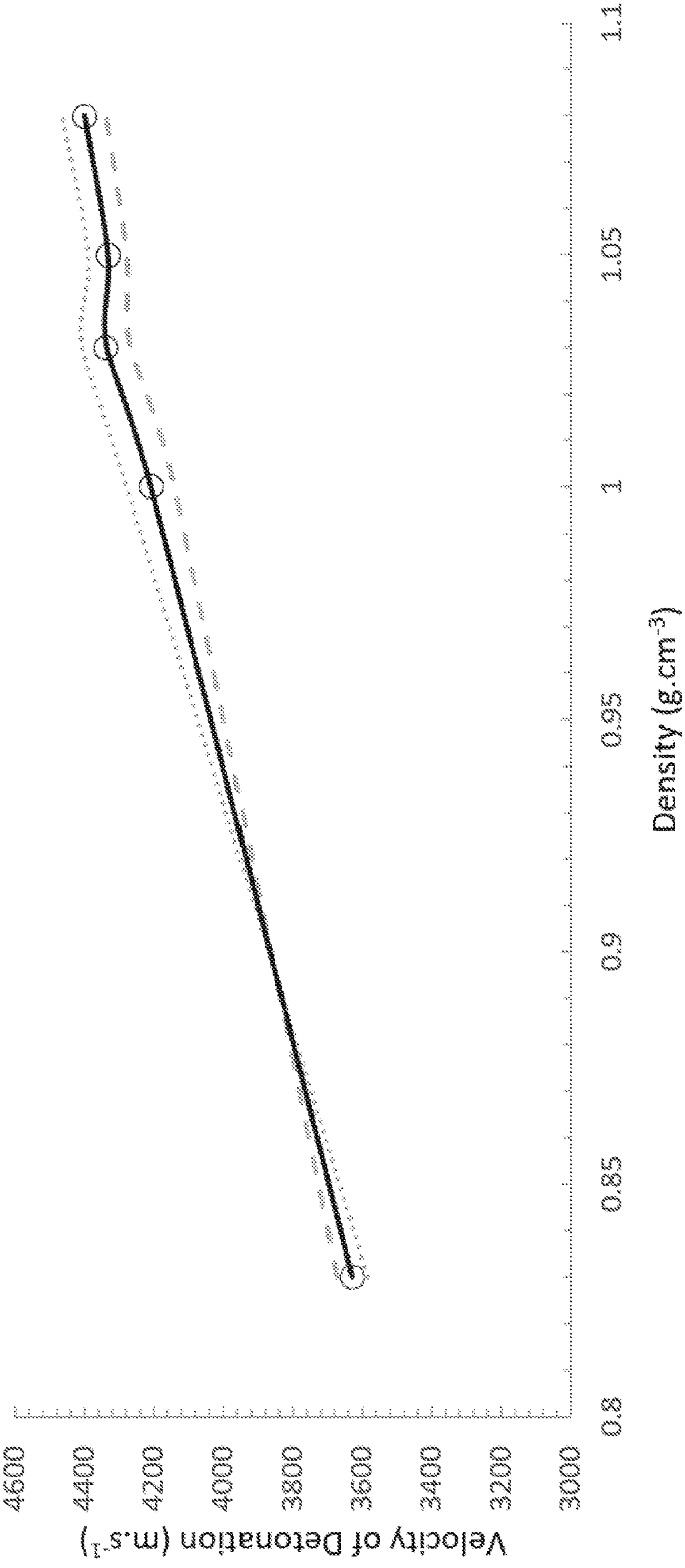

Velocity of Detonation (m.s-1)
4600
4400
4200
4000
3800
3600
3400
3200
3000
Density (g.cm-3)
0.8
0.85
0.9
0.95
1
1.05
1.1

Fig. 3

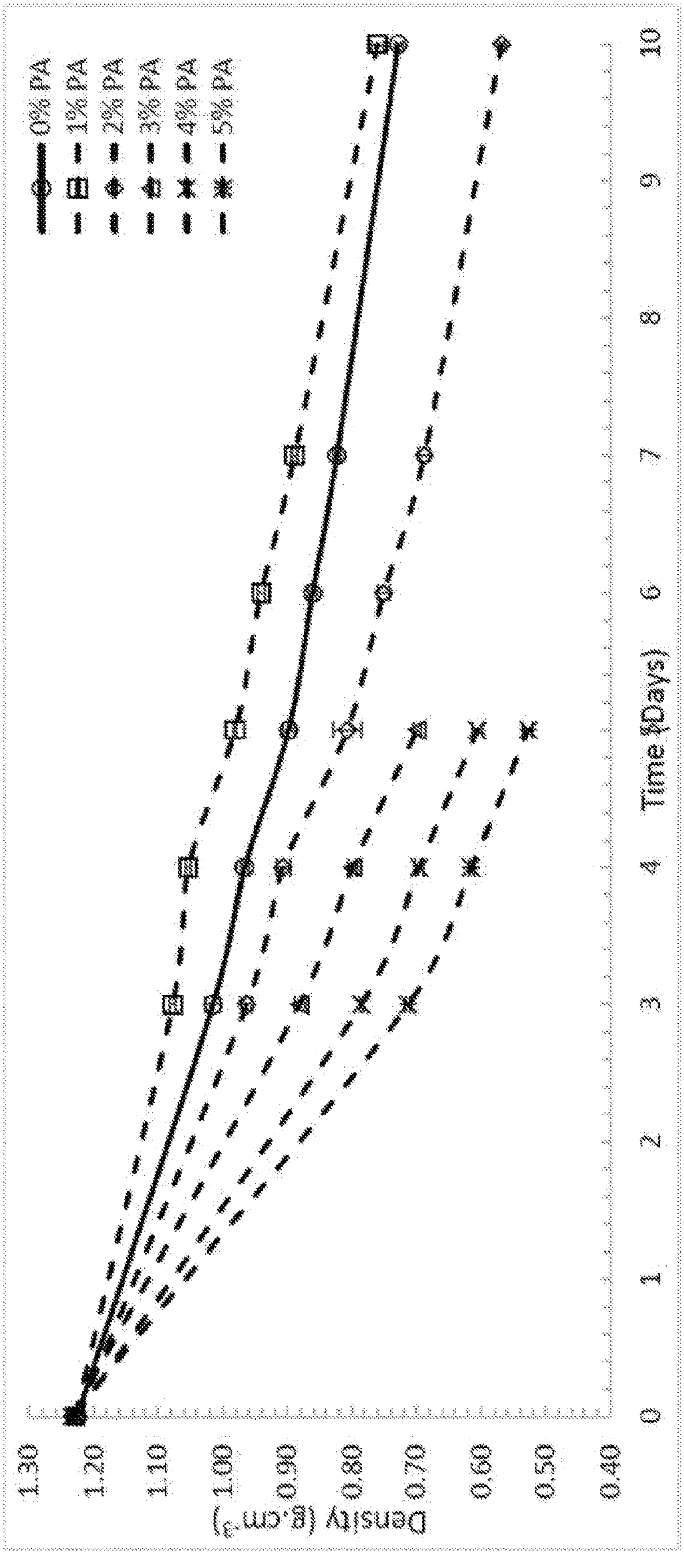

0% PA
1% PA
2% PA
3% PA
4% PA
5% PA
Density (g.cm-3)
1.30
1.20
1.10
1.00
0.90
0.80
0.70
0.60
0.50
0.40
0
1
2
3
4
5
6
7
8
9
10
Time (Days)

Fig. 4

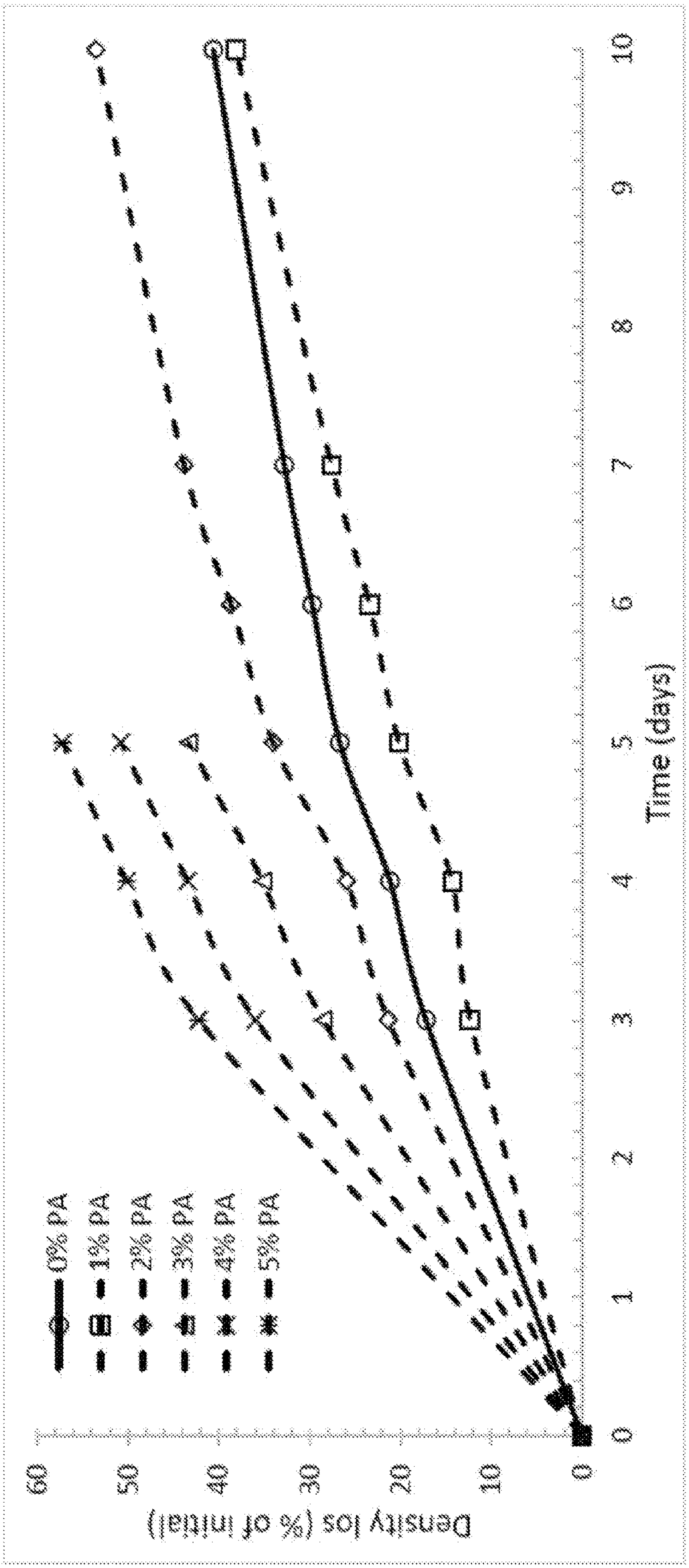

Density los (% of initial)
60
50
40
30
20
10
0
0
1
2
3
4
5
6
7
8
9
10
Time (days)
0% PA
1% PA
2% PA
3% PA
4% PA
5% PA

Fig. 5

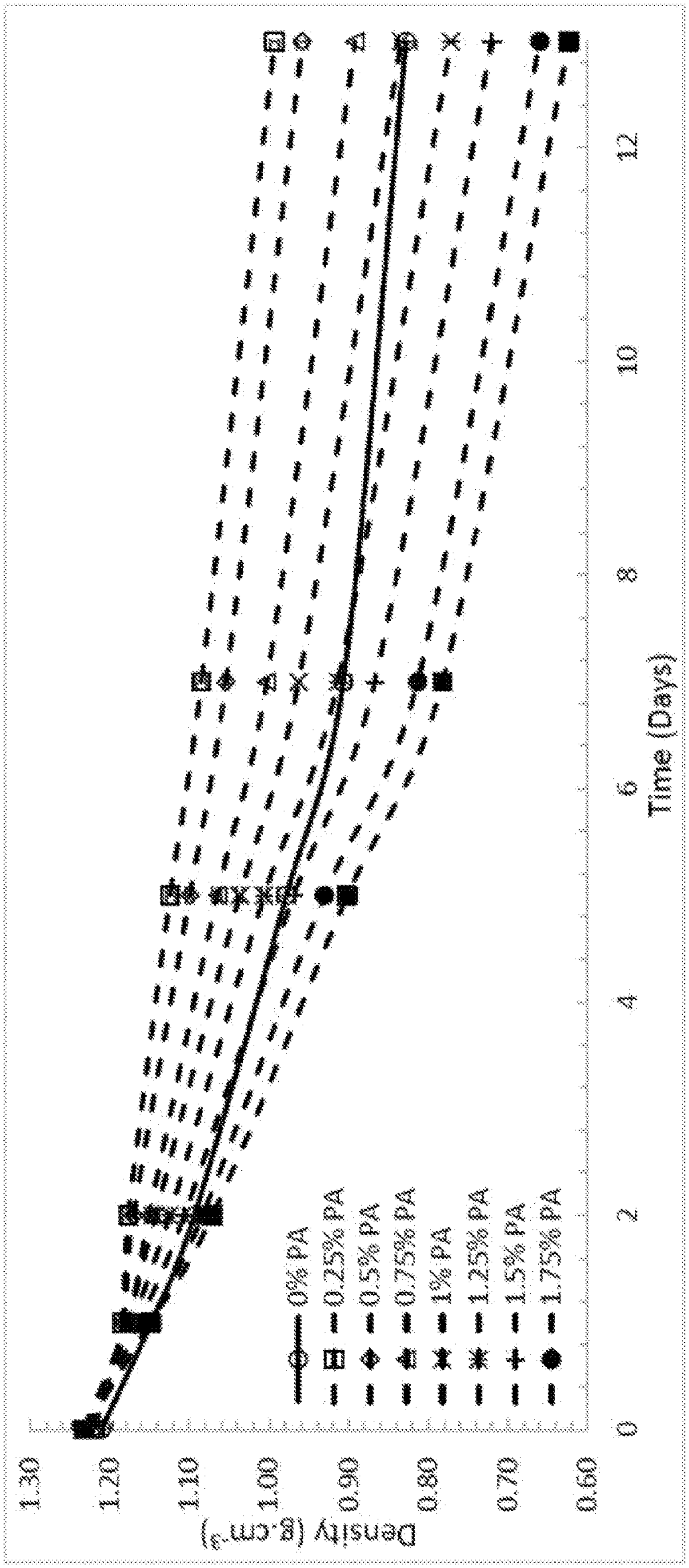

Density (g.cm⁻³)
1.30
1.20
1.10
1.00
0.90
0.80
0.70
0.60
0
2
4
6
8
10
12
Time (Days)
0% PA
0.25% PA
0.5% PA
0.75% PA
1% PA
1.25% PA
1.5% PA
1.75% PA

Fig. 6

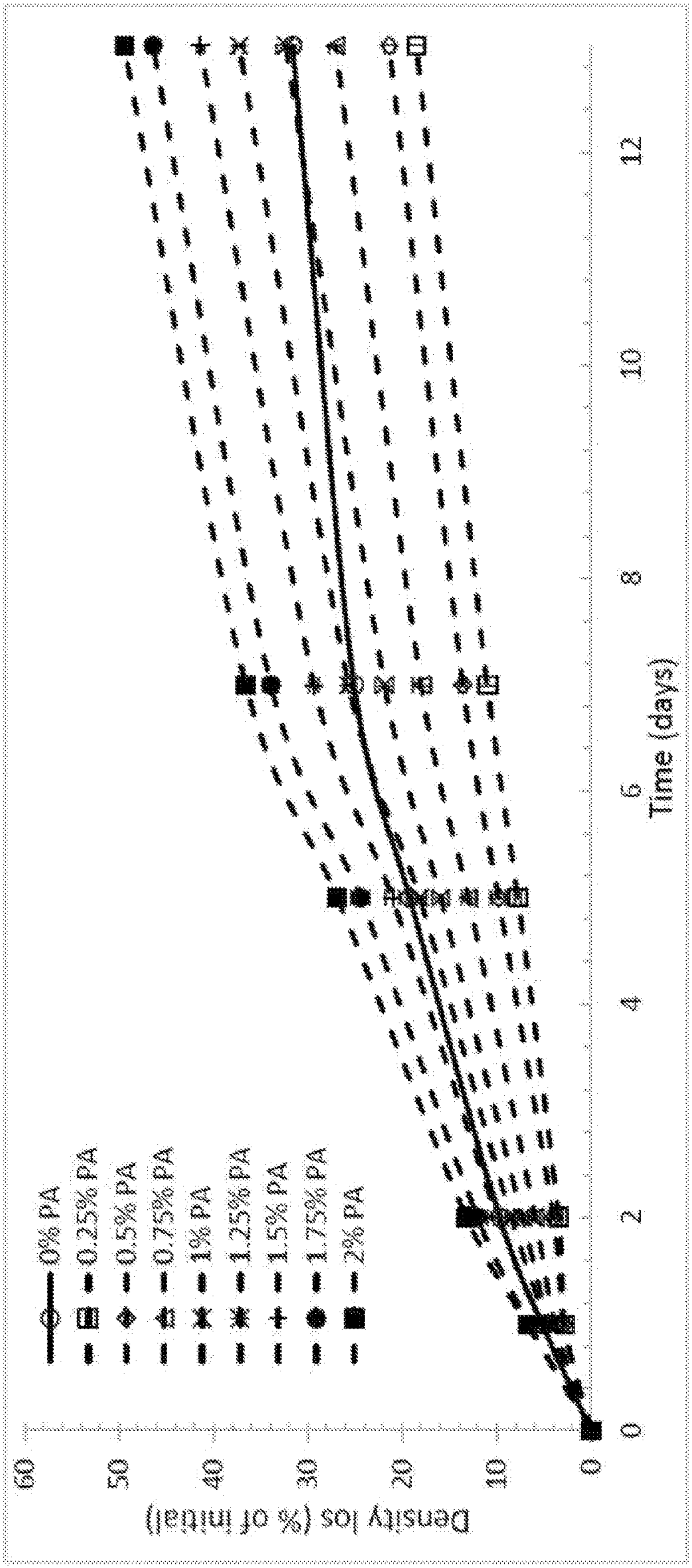

Density los (% of initial)
60
50
40
30
20
10
0
0
2
4
6
8
10
12
Time (days)
0% PA
0.25% PA
0.5% PA
0.75% PA
1% PA
1.25% PA
1.5% PA
1.75% PA
2% PA

Fig. 7

EXPLOSIVES BASED ON HYDROGEN PEROXIDE WITH IMPROVED SLEEP TIME

FIELD OF THE INVENTION

[0001] The present invention relates to improved hydrogen peroxide-based explosives. The invention has been developed primarily for use as a hydrogen peroxide/fuel-based explosive composition for use in mining applications and will be described hereinafter with reference to this application. However, it will be appreciated that the invention is not limited to this particular field of use.

BACKGROUND OF THE INVENTION

[0002] The following discussion of the prior art is provided to place the invention in an appropriate technical context and enable the advantages of it to be more fully understood. It should be appreciated, however, that any discussion of the prior art throughout the specification should not be considered as an express or implied admission that such prior art is widely known or forms part of common general knowledge in the field.

[0003] Nearly all commercial and mining explosives used in the world today are based on ammonium nitrate (AN) or combinations of AN with smaller quantities of other alkaline and/or alkaline earth nitrate salts, e.g. sodium nitrate (SN) or calcium nitrate (CN). AN, which is a strong oxidiser, has been used as the base of commercial explosives for at least the last 50-60 years. Most explosives of this type rely on the energetic reaction of nitrogen compounds incorporated within the explosive to provide the necessary explosive power.

[0004] Initially, mining companies used AN as an explosive on its own. However, they soon realised that the addition of diesel increased the energy output without a large increase on costs (ammonium nitrate-fuel oil, now commonly referred to as ‘ANFO’). However, the water resistance of ANFO is quite poor, which limited its use in wet blast holes. To ameliorate this issue, slurries and watergels were developed. Slurries typically comprise AN dissolved/dispersed in water, and other salts such as calcium nitrate, sodium nitrate, amine nitrates, perchlorates, etc. and other additives such as guar gum (as thickener) and water soluble or insoluble fuels (glycerol, MMAN, diesel, etc). They can also be blended with ANFO depending on the characteristics of the ground being blasted. Slurries also typically include solid sensitisers (aluminium and high explosives such as TNT, RDX, etc) to enable the slurry to detonate and to minimise misfires. Watergels have similar compositions to slurries, however, crosslinkers can be added to enhance the water resistance of the product.

[0005] One of the drawbacks of watergels and slurries is that there is a limit of AN which can be incorporated into the solution. This drawback was overcome by the development of water-in-oil emulsions. These emulsions can contain AN in high concentration (see U.S. Pat. No. 3,447,978) as emulsions are manufactured at high temperatures. Water-in-oil emulsions are made of a hot aqueous phase (composed of AN, other nitrate salts, perchlorate salts, etc.) dispersed into an organic fuel. The aqueous-organic mixture is stabilised by the use of an emulsifier. Emulsions can also be blended with ANFO in different ratios so suit the ground to be blasted.

[0006] Despite the development of AN emulsions, AN slurries, and watergels, however, there is still a need to develop improved explosives, which are more cost effective compared to existing explosive compositions and are capable of being produced in large quantities to meet the high demand from industry. It would be advantageous to use less AN in the formulation and instead use other types of nitrates to provide alternatives to the usage of AN. Additionally, such substitutes should preferably be safer, have a relatively low carbon footprint, able to be manufactured nearby the point of use to minimise the transport on public roads, able to be manufactured on an as-needs basis to minimise the need for stockpiling and to increase safety, allow for the use of existing delivery equipment, and/or produce a lower amount of (or no) toxic nitrogen oxide fumes (NO_x) upon detonation, etc. It would also be ideal if there are no onerous regulatory requirements for such a substitute, thereby reducing administrative costs. It would also be preferable for the explosive composition to be crosslinkable in-situ to increase viscosity down the blast-hole.

[0007] Despite the advances on the types of compositions that can be manufactured from ammonium nitrate, one of the disadvantages is that during the detonation NO_x fumes can be generated, due to the presence of nitrogen compounds in the explosive composition (from nitrates). These NO_x fumes are toxic and can affect the health of mine site personnel. Therefore, the emission of NO_x fume after blasting is a safety issue and, in countries like Australia, there are now strict regulatory controls in place to manage such emissions. See for example “Queensland Guidance Note: Management of oxides of nitrogen in open cut blasting” issued by the regulator in Queensland, Australia, 2011. Likewise, explosive manufacturers in Australia have also issued a code of practice to manage the NO_x fumes after blasting (AEISG Code of Practice, Prevention and Management of Blast Generated NO_x Gases in Surface Blasting, 2011). Therefore, there is a need to find explosive compositions that substantially reduce the production of NO_x.

[0008] One material that is also an oxidiser and that has the potential to meet at least some of these needs is hydrogen peroxide (H_2O_2). H_2O_2/fuel-based explosives for mining operations generally consist of the combination of H_2O_2 with about 5 to about 15 percent of its weight of a liquid carbon-based fuel such as glycerol, fuel oil, and the like. However, it has been observed that, in some cases, H_2O_2-based explosives are less than ideal where sleep-time above 24 hours is required, as it has been observed that the density changes over time, which can affect parameters such as the velocity of detonation (VOD).

[0009] It is an object of the present invention to overcome or ameliorate one or more of the disadvantages of the prior art, or at least to provide a useful alternative.

[0010] It is an object of preferred forms of the invention to provide a H_2O_2/fuel-based explosive that has improved sleep time. Preferred explosive compositions of the invention have substantially maintained sensitivity, density, and VOD over an extended sleep time, which can be in the range of 24 to 48 hours, or even longer. The improved explosive compositions of the invention can be safely employed in mines due to extended sleep-time, and in some embodiments enable blasts to be undertaken that are not possible with prior art H_2O_2-based explosive compositions that do not have the extended sleep time as per the compositions of the present invention. In particular, compositions of the invention enable much larger blasts to be undertaken, as the inventive explosive compositions described herein have substantially maintained VOD over an extended period of time in the blast hole.

[0011] A preferred objective of an embodiment of the present invention is to provide an explosive composition which meets one or more of the following objectives: is conveniently prepared, has improved density stability over time in situ, can use large amounts of sustainable fuels (which lowers the carbon footprint of the explosive), and in some preferred embodiments can use large amount of nitrates other than AN (which lowers the dependency on AN), and enables much larger blasts due to extended sleep time.

[0012] A further preferred objective of the present invention is to substantially maintain the density of the explosive composition when loaded into the blast hole, thereby substantially maintaining the sleep time for days, and potentially for weeks.

SUMMARY OF THE INVENTION

[0013] The present invention relates to explosives for use in commercial, construction, civil, agriculture, mining, and similar fields. However, it will be appreciated that the invention could be utilised in other related fields.

[0014] It has now surprisingly been discovered that H_2O_2-based explosive compositions, when treated or modified with density stabilisers (i.e., phosphonates), display improved sleep time over prior art H_2O_2-based explosive compositions. Further, it has been surprisingly found that only relatively small quantities of phosphonates provide the improved density stability and sleep time. Without wishing to be bound by any theory, the inventor considers that the density stabiliser employed in the present invention acts to prevent additional bubbles of entrained sensitiser gas to spontaneously form, whereas without a density stabiliser existing sensitiser bubbles tend to increase in volume and number over time.

[0015] In the practice of the present invention, phosphonates, usually in liquid form, are added to the H_2O_2 prior to the addition of fuel. Thickeners may be added to the combination of the oxidiser/fuel mixture.

[0016] Generally, one or more density stabilisers are incorporated in an amount of up to about 15% w/w of the explosives composition, for example about 0.01% w/w to about 10% w/w, e.g. about 1 to about 5% w/w, such as about 1 to about 3% w/w. Thereafter, the density-stabilised H_2O_2-based explosive can be handled, loaded, and fired in identical fashion to other explosives.

[0017] According to a first aspect, the present invention provides an explosive composition comprising:

[0018] a. H_2O_2;

[0019] b. fuel; and

[0020] c. one or more density stabilisers.

[0021] According to a second aspect, the present invention provides a method of preparing an explosive composition according to the first aspect, the method comprising: combining H_2O_2, fuel and one or more density stabilisers and optionally one or more other oxidisers and/or a sensitiser.

[0022] According to a third aspect, the present invention provides use of an explosive composition according to the first aspect to break and move ground, e.g. in mining operations.

[0023] According to a fourth aspect, the present invention provides the use of one or more density stabilisers to improve the sleep time of an explosive composition in reactive or metalliferous ground, wherein the explosive composition comprises H_2O_2 and fuel.

[0024] In a related aspect, the present invention consists of a method of treating an explosive composition to improve its long-term stability (sleep time), the method comprising the step of combining a density stabiliser with said explosive composition to stabilise the density of the explosive composition, wherein the explosive composition comprises H_2O_2 and fuel. In a related aspect, the present invention comprises the use of a density stabiliser for improving the long-term stability of an explosive composition. The density stabiliser is used in a density-stabilising concentration.

[0025] The present invention relates to an explosive which substantially avoids the release of unwanted NO_x fumes upon detonation into the atmosphere surrounding the blasting site. A preferred objective of the present invention is to reduce and preferably eliminate nitrogen containing ingredients from the explosive composition. It will be appreciated that with little or no nitrogen present in the explosive virtually no NO_x is released into the atmosphere, or a substantially reduced amount is released. The present invention relates to explosives for use in commercial, construction, agriculture, mining, and similar fields. However, it will be appreciated that the invention could be utilised in other related fields.

[0026] The density is maintained by including a density stabiliser. The density stabiliser retains the density of the explosive composition to within +/−0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 14, 16, 18, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 35, 40, or 50% of its initial density, and/or the density of the explosive composition within 5, 10, 15, 20, 30 or 60, 90 or 120 minutes of being loaded into the blast hole. The density is preferably maintained (or stabilised) over a period of up to 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, or 14 days. The density stabiliser preferably maintains the VOD to within +/−0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 14, 16, 18, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 35, 40, or 50% of the initial VOD, or the VOD of the explosive composition within 5, 10, 15, 20, 30, 60, 90 or 120 minutes of being loaded into the blast hole. The VOD is preferably maintained over a period of up to 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, or 14 days.

[0027] The compositions of the invention have a predictable and controllable change in density and VOD over time. For example, at certain concentrations of density stabiliser, the density reduces by around 5% per day to around 10% per day, causing a corresponding drop of around 5% to 10% per day in VOD. This enables the drill and blast engineer to provide a predetermined VOD after a certain sleep time, as the quantity of density stabiliser can be selected to control change in density over that sleep time. It will be appreciated that, in some prior art compositions, the density reduces by around 10% per day to around 30% per day, causing a corresponding drop of around 10% to 30% per day in VOD.

[0028] Preferably the composition further includes other additives, such as fuel, water, thickeners, emulsifiers, mechanical sensitisation, chemically-derived sensitisation, injected gases, etc, as discussed further below. In one preferred embodiment the composition comprises no components which lead to the production of NO_x in the after-blast fumes. However, in other embodiments components are added which result in minimal NO_x in the after-blast fumes.

[0029] Whilst the preferred explosive oxidiser of the invention is hydrogen peroxide, it will be appreciated that other oxidiser salts or peroxide derivatives can be used with the invention, as partial replacements of H_2O_2. Non-limiting examples include nitrates salts, perchlorates salts, sodium/potassium peroxide, etc.

Definitions

[0030] In describing and claiming the present invention, the following terminology will be used in accordance with the definitions set out below. It is also to be understood that the terminology used herein is for the purpose of describing particular embodiments of the invention only and is not intended to be limiting. Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one having ordinary skill in the art to which the invention pertains.

[0031] Unless the context clearly requires otherwise, throughout the description and the claims, the words 'comprise', 'comprising', and the like are to be construed in an inclusive sense as opposed to an exclusive or exhaustive sense; that is to say, in the sense of 'including, but not limited to'.

[0032] Other than in the operating examples, or where otherwise indicated, all numbers expressing quantities of ingredients or reaction conditions used herein are to be understood as modified in all instances by the term 'about'. The examples are not intended to limit the scope of the invention. In what follows, or where otherwise indicated, '%' will mean 'weight %', 'ratio' will mean 'weight ratio' and 'parts' will mean 'weight parts'.

[0033] Unless the context clearly indicates otherwise, all references to a component being present at a certain % w/w are with respect to the entire explosive composition. For example, an explosive composition comprising 2-25% w/w hydrogen peroxide refers to an explosive composition comprising 2-25 g hydrogen peroxide per 100 g of the explosive composition.

[0034] The term H_2O_2 is an abbreviation for hydrogen peroxide.

[0035] The term AN means ammonium nitrate.

[0036] CN means calcium nitrate tetra hydrate.

[0037] CAN means calcium ammonium nitrate

[0038] SN is an abbreviation for sodium nitrate.

[0039] ANFO is an abbreviation for ammonium nitrate fuel oil.

[0040] Amine nitrates is an abbreviation for monomethylamine or ethyl amine or propyl amine nitrate.

[0041] Sensitiser means an additive that introduces voids in the composition. Sensitisers enable and increase the sensitivity to detonation of energetic materials. The sensitiser can be chemically generated voids (gas bubbles) or can enclose or entrap a gas (examples of which include ceramic/glass microballoons, EPS and polyurethane foams).

[0042] GMB is an abbreviation for glass micro balloons.

[0043] EPS is an abbreviation for expanded polystyrene.

[0044] TNT means trinitrotoluene.

[0045] HMX refers to octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine.

[0046] RDX refers to 1,3,5-trinitroperhydro-1,3,5-triazine.

[0047] VOD refers to velocity of detonation in m/sec.

[0048] OB means oxygen balance.

[0049] The term g/cm^3 is has the same meaning as g/ml.

[0050] Phosphonates are organic compounds with C-P bonds, such as $C—PO(OH)_2$ or $C—PO(OR)_2$ groups. "Phosphonate" as used herein also includes phosphonate salts comprising phosphonate anions with counter-cations (e.g. sodium salts). "Phosphonate" includes mono-phosphonates as well as bis-phosphonates and higher phosphonates. The R group of a phosphonate is not limited to alkyl and can, for example, include heteroatoms (e.g. N).

[0051] DTPMPA.Na.x mean diethylenetriamine pentamethylene phosphonic acid sodium salt ($C_9H_{28-x}N_3O_{15}P_5Na_x$, CAS no. 22042-96-2).

[0052] The term phosphate refers to chemical derivatives of phosphoric acid. The phosphate ion (PO_{43}—) is the conjugate base of phosphoric acid and can form many different salts. Organophosphates have the general structure $O=P(OR)_3$, wherein the R groups can be the same or different. R includes alkyl and aryl. Phosphates comprise COP bonds and lack the C-P bonds present in phosphonates.

[0053] The term "stannate" refers to compounds containing tin (II), (IV) or (VI) and oxygen.

[0054] Sleep time is understood as the time between explosives being loaded into a blast hole and their initiation. The period is typically days.

[0055] The terms 'preferred', 'preferably' and 'suitably' refer to embodiments of the invention that may afford certain benefits, under certain circumstances. However, other embodiments may also be preferred, under the same or other circumstances.

[0056] Furthermore, the recitation of one or more preferred embodiments does not imply that other embodiments are not useful, and is not intended to exclude other embodiments from the scope of the invention.

[0057] The terms 'a', 'an' and 'the' mean 'one or more', unless expressly specified otherwise. The terms 'an embodiment', 'embodiment', 'embodiments', 'the embodiment', 'the embodiments', 'an embodiment', 'some embodiments', 'an example embodiment', 'at least one embodiment', 'one or more embodiments' and 'one embodiment' mean 'one or more (but not necessarily all) embodiments of the present invention(s)' unless expressly specified otherwise.

[0058] The terms "subterranean" or "sub-surface" refers to areas below exposed earth and areas below earth covered by water such as fresh water and salt water.

[0059] The term "optionally substituted" as used throughout the specification denotes that the group may or may not be further substituted or fused (so as to form a condensed polycyclic system), with one or more non-hydrogen substituent groups. In certain embodiments the substituent groups are one or more groups independently selected from the group consisting of halogen, $=O$, $=S$, $—CN$, $—NO_2$, $—CF_3$, $—OCF_3$, alkyl, alkenyl, alkynyl, haloalkyl, haloalkenyl, haloalkynyl, heteroalkyl, cycloalkyl, cycloalkenyl, heterocycloalkyl, heterocycloalkenyl, aryl, heteroaryl, cycloalkylalkyl, heterocycloalkylalkyl, heteroarylalkyl, arylalkyl, cycloalkylalkenyl, heterocycloalkylalkenyl, arylalkenyl, heteroarylalkenyl, cycloalkylheteroalkyl, heterocycloalkylheteroalkyl, arylheteroalkyl, heteroarylheteroalkyl, hydroxy, hydroxyalkyl, alkyloxy, alkyloxyalkyl, alkyloxycycloalkyl, alkyloxyheterocycloalkyl, alkyloxyaryl, alkyloxyheteroaryl, alkyloxycarbonyl, alkylaminocarbonyl, alkenyloxy, alkynyloxy, cycloalkyloxy, cycloalkenyloxy, heterocycloalkyloxy, heterocycloalkenyloxy, aryloxy, phenoxy, benzyloxy, heteroaryloxy, arylalkyloxy, amino, alkylamino, acylamino, aminoalkyl, arylamino, sulfonylamino, sulfinylamino, sulfonyl, alkylsulfonyl, arylsulfonyl, aminosulfonyl, sulfinyl, alkylsulfinyl, arylsulfinyl, aminosulfinylaminoalkyl, —C(═O)OH, —C(═O)R^e, —C(═O)OR^e, C(═O)NR^eR^f, C(═NOH)R^e, C(═NR^e)NR^fR^g, NR^eR^f, NReC(═O)R^f, NR^eC(═O)OR^f, NR^eC(═O)NR^fR^g, NR^eC(═NR^f)NR^gR^h, N$R^e$$SO_2$$R^f$, —S$R^e$, SO_2NR^eR^f, —OR^e, OC(═O)NR^eR^f, OC(═O)R^e and acyl,

[0060] wherein R^e, R^f, R^g and R^h are each independently selected from the group consisting of H, C_1-C_{12}alkyl, C_1-C_{12}haloalkyl, C_2-C_{12}alkenyl, C_2-C_{12}alkynyl, C_1-C_{10}heteroalkyl, C_3-C_{12}cycloalkyl, C_3-C_{12}cycloalkenyl, C_1-C_{12}heterocycloalkyl, C_1-C_{12}heterocycloalkenyl, C_6-C_{18}aryl, C_1-C_{18}heteroaryl, and acyl, or any two or more of Ra, R^b, R^c and R^d, when taken together with the atoms to which they are attached form a heterocyclic ring system with 3 to 12 ring atoms.

[0061] In some embodiments each optional substituent is independently selected from the group consisting of: halogen, ═O, ═S, —CN, —NO_2, —CF_3, —OCF_3, alkyl, alkenyl, alkynyl, haloalkyl, haloalkenyl, haloalkynyl, heteroalkyl, cycloalkyl, cycloalkenyl, heterocycloalkyl, heterocycloalkenyl, aryl, heteroaryl, hydroxy, hydroxyalkyl, alkyloxy, alkyloxyalkyl, alkyloxyaryl, alkyloxyheteroaryl, alkenyloxy, alkynyloxy, cycloalkyloxy, cycloalkenyloxy, heterocycloalkyloxy, heterocycloalkenyloxy, aryloxy, heteroaryloxy, arylalkyl, heteroarylalkyl, arylalkyloxy, amino, alkylamino, acylamino, aminoalkyl, arylamino, sulfonyl, alkylsulfonyl, arylsulfonyl, aminosulfonyl, aminoalkyl, —COOH, —SH, and acyl.

[0062] Examples of particularly suitable optional substituents include F, C, Br, I, CH_3, CH_2CH_3, OH, OCH_3, CF_3, OCF_3, NO_2, NH_2, and CN.

[0063] In the definitions of a number of substituents below it is stated that "the group may be a terminal group or a bridging group". This is intended to signify that the use of the term is intended to encompass the situation where the group is a linker between two other portions of the molecule as well as where it is a terminal moiety. Using the term alkyl as an example, some publications would use the term "alkylene" for a bridging group and hence in these other publications there is a distinction between the terms "alkyl" (terminal group) and "alkylene" (bridging group). In the present application no such distinction is made and most groups may be either a bridging group or a terminal group.

[0064] "Acyl" means an R—C(═O)— group in which the R group may be an alkyl, cycloalkyl, heterocycloalkyl, aryl or heteroaryl group as defined herein. Examples of acyl include acetyl and benzoyl. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the carbonyl carbon.

[0065] "Acylamino" means an R—C(═O)—NH— group in which the R group may be an alkyl, cycloalkyl, heterocycloalkyl, aryl or heteroaryl group as defined herein. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the nitrogen atom.

[0066] "Alkenyl" as a group or part of a group denotes an aliphatic hydrocarbon group containing at least one carbon-carbon double bond and which may be straight or branched preferably having 2-12 carbon atoms, more preferably 2-10 carbon atoms, most preferably 2-6 carbon atoms, in the normal chain. The group may contain a plurality of double bonds in the normal chain and the orientation about each is independently E or Z. The alkenyl group is preferably a 1-alkenyl group. Exemplary alkenyl groups include, but are not limited to, ethenyl, propenyl, butenyl, pentenyl, hexenyl, heptenyl, octenyl and nonenyl. The group may be a terminal group or a bridging group.

[0067] "Alkenyloxy" refers to an alkenyl-O— group in which alkenyl is as defined herein. Preferred alkenyloxy groups are C_1-C_6 alkenyloxy groups. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the oxygen atom.

[0068] "Alkyl" as a group or part of a group refers to a straight or branched aliphatic hydrocarbon group, preferably a C_1-C_{12} alkyl, more preferably a C_1-C_{10} alkyl, most preferably C_1-C_6 unless otherwise noted. Examples of suitable straight and branched C_1-C_6 alkyl substituents include methyl, ethyl, n-propyl, 2-propyl, n-butyl, sec-butyl, t-butyl, hexyl, and the like. The group may be a terminal group or a bridging group.

[0069] "Alkylamino" includes both mono-alkylamino and dialkylamino, unless specified. "Mono-alkylamino" means an Alkyl-NH— group, in which alkyl is as defined herein. "Dialkylamino" means a $(alkyl)_2N$— group, in which each alkyl may be the same or different and are each as defined herein for alkyl. The alkyl group is preferably a C_1-C_6alkyl group. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the nitrogen atom.

[0070] "Alkylaminocarbonyl" refers to a group of the formula $(Alkyl)_x(H)_y$NC(═O)— in which alkyl is as defined herein, x is 1 or 2, and the sum of X+Y=2. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the carbonyl carbon.

[0071] "Alkyloxy" refers to an alkyl-O— group in which alkyl is as defined herein. Preferably the alkyloxy is a C_1-C_6alkyloxy. Examples include, but are not limited to, methoxy and ethoxy. The group may be a terminal group or a bridging group.

[0072] "Alkyloxyalkyl" refers to an alkyloxy-alkyl- group in which the alkyloxy and alkyl moieties are as defined herein. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the alkyl group.

[0073] "Alkyloxyaryl" refers to an alkyloxy-aryl- group in which the alkyloxy and aryl moieties are as defined herein. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the aryl group.

[0074] "Alkyloxycarbonyl" refers to an alkyl-O—C(═O)— group in which alkyl is as defined herein. The alkyl group is preferably a C_1-C_6 alkyl group. Examples include, but are not limited to, methoxycarbonyl and ethoxycarbonyl. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the carbonyl carbon.

[0075] "Alkyloxycycloalkyl" refers to an alkyloxy-cycloalkyl- group in which the alkyloxy and cycloalkyl moieties are as defined herein. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the cycloalkyl group.

[0076] "Alkyloxyheteroaryl" refers to an alkyloxy-heteroaryl- group in which the alkyloxy and heteroaryl moieties are as defined herein. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the heteroaryl group.

[0077] "Alkyloxyheterocycloalkyl" refers to an alkyloxy-heterocycloalkyl- group in which the alkyloxy and heterocycloalkyl moieties are as defined herein. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the heterocycloalkyl group.

[0078] "Alkylsulfinyl" means an alkyl-S—(═O)— group in which alkyl is as defined herein. The alkyl group is preferably a C_1-C_6 alkyl group. Exemplary alkylsulfinyl groups include, but not limited to, methylsulfinyl and ethylsulfinyl. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the sulfur atom.

[0079] "Alkylsulfonyl" refers to an alkyl-S(═O)$_2$— group in which alkyl is as defined above. The alkyl group is preferably a C_1-C_6alkyl group. Examples include, but not limited to methylsulfonyl and ethylsulfonyl. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the sulfur atom.

[0080] "Alkynyl" as a group or part of a group means an aliphatic hydrocarbon group containing a carbon-carbon triple bond and which may be straight or branched preferably having from 2-12 carbon atoms, more preferably 2-10 carbon atoms, more preferably 2-6 carbon atoms in the normal chain. Exemplary structures include, but are not limited to, ethynyl and propynyl. The group may be a terminal group or a bridging group.

[0081] "Alkynyloxy" refers to an alkynyl-O— group in which alkynyl is as defined herein. Preferred alkynyloxy groups are C_1-C_6alkynyloxy groups. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the oxygen atom.

[0082] "Aminoalkyl" means an NH_2-alkyl- group in which the alkyl group is as defined herein. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the alkyl group.

[0083] "Aminosulfonyl" means an NH_2—S(═O)$_2$— group. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the sulfur atom.

[0084] "Aryl" as a group or part of a group denotes (i) an optionally substituted monocyclic, or fused polycyclic, aromatic carbocycle (ring structure having ring atoms that are all carbon) preferably having from 5 to 12 atoms per ring. Examples of aryl groups include phenyl, naphthyl, and the like; (ii) an optionally substituted partially saturated bicyclic aromatic carbocyclic moiety in which a phenyl and a C_{5-7}cycloalkyl or C_{5-7}cycloalkenyl group are fused together to form a cyclic structure, such as tetrahydronaphthyl, indenyl or indanyl. The group may be a terminal group or a bridging group. Typically an aryl group is a C_6-C_{18} aryl group.

[0085] "Arylalkenyl" means an aryl-alkenyl- group in which the aryl and alkenyl are as defined herein. Exemplary arylalkenyl groups include phenylallyl. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the alkenyl group.

[0086] "Arylalkyl" means an aryl-alkyl- group in which the aryl and alkyl moieties are as defined herein. Preferred arylalkyl groups contain a C_{1-5}alkyl moiety. Exemplary arylalkyl groups include benzyl, phenethyl, 1-naphthalenemethyl and 2-naphthalenemethyl. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the alkyl group.

[0087] "Arylalkyloxy" refers to an aryl-alkyl-O— group in which the alkyl and aryl are as defined herein. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the oxygen atom.

[0088] "Arylamino" includes both mono-arylamino and di-arylamino unless specified. Mono-arylamino means a group of formula arylNH—, in which aryl is as defined herein. Di-arylamino means a group of formula (aryl)$_2$N— where each aryl may be the same or different and are each as defined herein for aryl. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the nitrogen atom.

[0089] "Arylheteroalkyl" means an aryl-heteroalkyl- group in which the aryl and heteroalkyl moieties are as defined herein. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the heteroalkyl group.

[0090] "Aryloxy" refers to an aryl-O— group in which the aryl is as defined herein. Preferably the aryloxy is a C_6-C_{18}aryloxy, more preferably a C_6-C_{10}aryloxy. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the oxygen atom.

[0091] "Arylsulfonyl" means an aryl-S(═O)$_2$— group in which the aryl group is as defined herein. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the sulfur atom.

[0092] A "bond" is a linkage between atoms in a compound or molecule. The bond may be a single bond, a double bond, or a triple bond.

[0093] "Cycloalkenyl" means a non-aromatic monocyclic or multicyclic ring system containing at least one carbon-carbon double bond and preferably having from 5-10 carbon atoms per ring. Exemplary monocyclic cycloalkenyl rings include cyclopentenyl, cyclohexenyl or cycloheptenyl. The cycloalkenyl group may be substituted by one or more substituent groups. A cycloalkenyl group typically is a C_3-C_{12} alkenyl group. The group may be a terminal group or a bridging group.

[0094] "Cycloalkyl" refers to a saturated monocyclic or fused or spiro polycyclic, carbocycle preferably containing from 3 to 9 carbons per ring, such as cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl and the like, unless otherwise specified. It includes monocyclic systems such as cyclopropyl and cyclohexyl, bicyclic systems such as decalin, and polycyclic systems such as adamantane. A cycloalkyl group typically is a C_3-C_{12} alkyl group. The group may be a terminal group or a bridging group.

[0095] "Cycloalkylalkyl" means a cycloalkyl-alkyl- group in which the cycloalkyl and alkyl moieties are as defined herein. Exemplary monocycloalkylalkyl groups include cyclopropylmethyl, cyclopentylmethyl, cyclohexylmethyl and cycloheptylmethyl. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the alkyl group.

[0096] "Cycloalkylalkenyl" means a cycloalkyl-alkenyl- group in which the cycloalkyl and alkenyl moieties are as defined herein. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the alkenyl group.

[0097] "Cycloalkylheteroalkyl" means a cycloalkyl-heteroalkyl- group in which the cycloalkyl and heteroalkyl moieties are as defined herein. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the heteroalkyl group.

[0098] "Cycloalkyloxy" refers to a cycloalkyl-O— group in which cycloalkyl is as defined herein. Preferably the cycloalkyloxy is a C_1-C_6cycloalkyloxy. Examples include, but are not limited to, cyclopropanoxy and cyclobutanoxy. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the oxygen atom.

[0099] "Cycloalkenyloxy" refers to a cycloalkenyl-O— group in which the cycloalkenyl is as defined herein. Preferably the cycloalkenyloxy is a C_1-C_6cycloalkenyloxy. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the oxygen atom.

[0100] "Haloalkyl" refers to an alkyl group as defined herein in which one or more of the hydrogen atoms has been replaced with a halogen atom selected from the group consisting of fluorine, chlorine, bromine and iodine. A haloalkyl group typically has the formula $C_nH_{(2n+1-m)}X_m$ wherein each X is independently selected from the group consisting of F, Cl, Br and I. In groups of this type n is typically from 1 to 10, more preferably from 1 to 6, most preferably 1 to 3. m is typically 1 to 6, more preferably 1 to 3. Examples of haloalkyl include fluoromethyl, difluoromethyl and trifluoromethyl.

[0101] "Haloalkenyl" refers to an alkenyl group as defined herein in which one or more of the hydrogen atoms has been replaced with a halogen atom independently selected from the group consisting of F, Cl, Br and I.

[0102] "Haloalkynyl" refers to an alkynyl group as defined herein in which one or more of the hydrogen atoms has been replaced with a halogen atom independently selected from the group consisting of F, Cl, Br and I.

[0103] "Halogen" represents chlorine, fluorine, bromine or iodine.

[0104] "Heteroalkyl" refers to a straight- or branched-chain alkyl group preferably having from 2 to 24 carbons, 2 to 18 carbons, 2 to 14 carbons, 2 to 12 carbons, 2 to 6 carbons in the chain, in which one or more of the carbon atoms (and any associated hydrogen atoms) are each independently replaced by a heteroatomic group selected from S, O, P and NR' where R' is selected from the group consisting of H, optionally substituted C_1-C_{12}alkyl, optionally substituted C_3-C_{12}cycloalkyl, optionally substituted C_6-C_{18}aryl, and optionally substituted C_1-C_{18}heteroaryl. Exemplary heteroalkyls include alkyl ethers, secondary and tertiary alkyl amines, amides, alkyl sulfides, and the like. Examples of heteroalkyl also include hydroxyC_1-C_6alkyl, C_1-C_6alkyloxyC_1-C_6alkyl, aminoC_1-C_6alkyl, C_1-C_6alkylaminoC_1-C_6alkyl, and di(C_1-C_6alkyl)aminoC_1-C_6alkyl. The group may be a terminal group or a bridging group.

[0105] "Heteroalkyloxy" refers to a heteroalkyl-O— group in which heteroalkyl is as defined herein. Preferably the heteroalkyloxy is a C_2-C_6heteroalkyloxy. The group may be a terminal group or a bridging group.

[0106] "Heteroaryl" either alone or part of a group refers to groups containing an aromatic ring (preferably a 5 or 6 membered aromatic ring) having one or more heteroatoms as ring atoms in the aromatic ring with the remainder of the ring atoms being carbon atoms. Suitable heteroatoms include nitrogen, oxygen and sulphur. The group may be a monocyclic or bicyclic heteroaryl group. Examples of heteroaryl include thiophene, benzothiophene, benzofuran, benzimidazole, benzoxazole, benzothiazole, benzisothiazole, naphtho[2,3-b]thiophene, furan, isoindolizine, xantholene, phenoxatine, pyrrole, imidazole, pyrazole, pyridine, pyrazine, pyrimidine, pyridazine, tetrazole, indole, isoindole, 1H-indazole, purine, quinoline, isoquinoline, phthalazine, naphthyridine, quinoxaline, cinnoline, carbazole, phenanthridine, acridine, phenazine, thiazole, isothiazole, phenothiazine, oxazole, isooxazole, furazane, phenoxazine, 2-, 3- or 4-pyridyl, 2-, 3-, 4-, 5-, or 8- quinolyl, 1-, 3-, 4-, or 5- isoquinolinyl 1-, 2-, or 3- indolyl, and 2-, or 3-thienyl. A heteroaryl group is typically a C_1-C_{18}heteroaryl group. The group may be a terminal group or a bridging group.

[0107] "Heteroarylalkyl" means a heteroaryl-alkyl group in which the heteroaryl and alkyl moieties are as defined herein. Preferred heteroarylalkyl groups contain a lower alkyl moiety. Exemplary heteroarylalkyl groups include pyridylmethyl. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the alkyl group.

[0108] "Heteroarylalkenyl" means a heteroaryl-alkenyl- group in which the heteroaryl and alkenyl moieties are as defined herein. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the alkenyl group.

[0109] "Heteroarylheteroalkyl" means a heteroaryl-heteroalkyl- group in which the heteroaryl and heteroalkyl moieties are as defined herein. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the heteroalkyl group.

[0110] "Heteroaryloxy" refers to a heteroaryl-O— group in which the heteroaryl is as defined herein. Preferably the heteroaryloxy is a C_1-C_{18}heteroaryloxy. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the oxygen atom.

[0111] "Heterocyclic" refers to saturated, partially unsaturated or fully unsaturated monocyclic, bicyclic or polycyclic ring system containing at least one heteroatom selected from the group consisting of nitrogen, sulfur and oxygen as a ring atom. Examples of heterocyclic moieties include heterocycloalkyl, heterocycloalkenyl and heteroaryl.

[0112] "Heterocycloalkenyl" refers to a heterocycloalkyl group as defined herein but containing at least one double bond. A heterocycloalkenyl group typically is a C_2-C_{12}heterocycloalkenyl group. The group may be a terminal group or a bridging group.

[0113] "Heterocycloalkyl" refers to a saturated monocyclic, bicyclic, or polycyclic ring containing at least one heteroatom selected from nitrogen, sulfur, oxygen, preferably from 1 to 3 heteroatoms in at least one ring. Each ring is preferably from 3 to 10 membered, more preferably 4 to 7 membered. Examples of suitable heterocycloalkyl substituents include pyrrolidyl, tetrahydrofuryl, tetrahydrothiofuranyl, piperidyl, piperazyl, tetrahydropyranyl, morphilino, 1,3-diazapane, 1,4-diazapane, 1,4-oxazepane, and 1,4-oxathiapane. A heterocycloalkyl group typically is a C_2-C_{12}heterocycloalkyl group. The group may be a terminal group or a bridging group.

[0114] "Heterocycloalkylalkyl" refers to a heterocycloalkyl-alkyl- group in which the heterocycloalkyl and alkyl moieties are as defined herein. Exemplary heterocycloalkylalkyl groups include (2-tetrahydrofuryl)methyl, (2-tetrahydrothiofuranyl) methyl. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the alkyl group.

[0115] "Heterocycloalkylalkenyl" refers to a heterocycloalkyl-alkenyl- group in which the heterocycloalkyl and alkenyl moieties are as defined herein. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the alkenyl group.

[0116] "Heterocycloalkylheteroalkyl" means a heterocycloalkyl-heteroalkyl- group in which the heterocycloalkyl and heteroalkyl moieties are as defined herein. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the heteroalkyl group.

[0117] "Heterocycloalkyloxy" refers to a heterocycloalkyl-O— group in which the heterocycloalkyl is as defined herein. Preferably the heterocycloalkyloxy is a C_1-C_6heterocycloalkyloxy. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the oxygen atom.

[0118] "Heterocycloalkenyloxy" refers to a heterocycloalkenyl-O— group in which heterocycloalkenyl is as defined herein. Preferably the Heterocycloalkenyloxy is a C_1-C_6 Heterocycloalkenyloxy. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the oxygen atom.

[0119] "Hydroxyalkyl" refers to an alkyl group as defined herein in which one or more of the hydrogen atoms has been replaced with an OH group. A hydroxyalkyl group typically has the formula $C_nH_{(2n+1-x)}(OH)_x$. In groups of this type n is typically from 1 to 10, more preferably from 1 to 6, most preferably 1 to 3. x is typically 1 to 6, more preferably 1 to 3.

[0120] "Sulfinyl" means an R—S(═O)— group in which the R group may be OH, alkyl, cycloalkyl, heterocycloalkyl; aryl or heteroaryl group as defined herein. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the sulfur atom.

[0121] "Sulfinylamino" means an R—S(═O)—NH— group in which the R group may be OH, alkyl, cycloalkyl, heterocycloalkyl; aryl or heteroaryl group as defined herein. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the nitrogen atom.

[0122] "Sulfonyl" means an R—S(═O)$_2$— group in which the R group may be OH, alkyl, cycloalkyl, heterocycloalkyl; aryl or heteroaryl group as defined herein. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the sulfur atom.

[0123] "Sulfonylamino" means an R—S(═O)$_2$—NH— group. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the nitrogen atom.

[0124] The prior art referred to in this specification is incorporated herein by reference.

BRIEF DESCRIPTION OF THE DRAWINGS

[0125] Preferred embodiments of the invention will now be described, by way of example only, with reference to the accompanying drawings in which:

[0126] FIG. **1** is a graph showing the results of Example 1, showing the change of gel density ($g\cdot cm^{-3}$) over time (days) with range of density-stabilised H_2O_2 employing the phosphonate, DTMPMA.Na.X (% w/w).

[0127] FIG. **2** is a graph showing the results of Example 1, showing loss of gel density (% to initial) compared to initial density over time (days) with range of density-stabilised H_2O_2 employing the phosphonate, DTMPMA.Na.X (% w/w).

[0128] FIG. **3** is a graph showing the results of Example 2, showing averaged Velocity of Detonation (VOD) for varying densities of 3% w/w DTMPMA enhanced H_2O_2/glycerol-based explosive formula in unconfined detonations (n=3) in 47 mm diameter tubing, sensitised with 3M™ K15 Glass Micro-Balloons, and initiated with a 25 g Pentex D Booster. Two VOD monitors, VOD1 (dotted line) and VOD2 (dashed line) were attached to each shot, average for VOD data displayed as solid line.

[0129] FIG. **4** is a graph showing the change in gel density ($g\cdot cm^{-3}$) over ten days between 0-5% w/w PA. Error bars are Standard Deviation (n=4). 3, 4, & 5% w/w PA formulations collapsed at 5 days.

[0130] FIG. **5** is a graph showing the loss of gel density (%) compared to initial density over 10 days between 0-5% w/w PA. Error bars are Standard Deviation (n=4). 3, 4, & 5% w/w PA formulations collapsed at 5 days.

[0131] FIG. **6** is a graph showing the change in gel density ($g\cdot cm^{-3}$) over 13 days between 0-2% w/w PA. Error bars are Standard Deviation (n=4).

[0132] FIG. **7** is a graph showing the loss of gel density (%) compared to initial density over 13 days between 0-2% w/w PA. Error bars are Standard Deviation (n=4).

DETAILED DESCRIPTION OF THE INVENTION

[0133] The present invention provides an explosive composition comprising:

[0134] a. H_2O_2;

[0135] b. fuel; and

[0136] c. one or more density stabilisers.

[0137] In one embodiment, the compositions of the invention are formulated as watergels. In an alternative embodiment, the compositions of the invention are formulated as emulsions.

Hydrogen Peroxide (H_2O_2)

[0138] The preferred concentration of H_2O_2 in the composition of the invention is between about 2% to 85% by weight. By way of example only, a concentrated H_2O_2 solution can be sourced (70% w/w) and diluted down to 25% w/w for use in the composition. Other possibilities will be apparent to the skilled person. Preferably the H_2O_2 concentration in the composition is around 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, or 85% (w/w). Preferably the H_2O_2 concentration in the composition is around between about 2 to 3, 3 to 5, 5 to 10, 10 to 15, 15 to 20, 20 to 25, 25 to 30, 30 to 35, 35 to 40, 40 to 45, 45 to 50, 50 to 55, 55 to 60, 60 to 65, 65 to 70, 70 to 75, 75 to 80, or 80 to 85% (w/w).

[0139] It will be understood that the % w/w of hydrogen peroxide present in the composition refers the amount of pure hydrogen peroxide. As hydrogen peroxide is provided in the form of an aqueous solution having an H_2O_2 concentration of less than 100%, for example, having an H_2O_2 concentration of 50% w/w, or 35% w/w, or 30% w/w, the skilled person will readily understand the need and manner by which they can adjust the amount of diluted H_2O_2 solution required to ensure the explosive compositions of the invention comprise 2 to 25% w/w H_2O_2. To take an example for the avoidance of doubt, if a composition of the invention contains 20% of a 50% w/w solution of H_2O_2, the composition contains 10% w/w H_2O_2. The skilled person will also appreciate that the 2 to 85% w/w concentration of H_2O_2 is the final H_2O_2 concentration in the explosive composition, and thus account must be taken of the diluting effects of any other components (e.g., fuels, oxidisers, thickeners, etc.) added to the composition during formulation.

Water

[0140] The explosive compositions described herein may comprise water. In one embodiment, the explosive composition may comprise less than 50% w/w of water, or 40% w/w or less of water, or 30% w/w or less of water, for example 25% w/w or less, 20% w/w or less, 15% w/w or less or 10% w/w or less. In one embodiment, the explosive composition may comprise 5% w/w or more of water, for example 10% w/w or more. The composition may thus comprise between 5 and 50% w/w water, or between 5 and 20% w/w water, or between 15 and 30% w/w water, or between 10 and 40% w/w water, or 50, 45, 40, 35, 30, 25, 20, 15, 10, 5 or 1% w/w water.

Sensitisers

[0141] The explosive composition according to the invention may comprise one or more sensitisers dispersed in the composition to produce voids which improve sensitivity to detonation. In addition, H_2O_2 may itself act as both a sensitiser and an oxidiser. Alternatively, H_2O_2 itself may act as the sensitiser and no other sensitisers may be used.

[0142] Sensitisers include gas bubbles generated in situ or injected air or air/gas entrapped material. Another example of sensitisation is the combination of both gas bubbles (chemically generated and or injected) and air entrapped material.

[0143] The explosive compositions of the present invention comprise a discontinuous gaseous component to sensitise the composition.

[0144] The present invention relies on sensitisation of a H_2O_2-based composition to result in an explosive composition, and to control key factors such as explosive sensitivity, density, velocity of detonation (VOD) and the delivery of the energy.

[0145] Preferably the explosive composition of the invention is adapted to retain the sensitiser in a substantially homogenous dispersion (e.g. by a thickener or an emulsifier in the case of a watergel or an emulsion, respectively). It will be appreciated that a variety of techniques can be utilised to achieve this property, as discussed further below.

[0146] Preferably a minimum concentration of sensitiser is included into the composition to cause it to be explosive. Preferably the sensitiser is included in a detonation-sensitive concentration or amount. The sensitiser is also preferably maintained in a detonation-sensitive dispersion/distribution throughout the composition. Preferably the final density of the composition is controlled into an initial preferred predetermined explosive range. Preferably the final density is controlled with sensitiser to about 0.6 to about 1.15 g/ml. Preferably the density of the composition is formulated to be around 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1, 1.1, 1.2, 1.3, or 1.4 g/ml. Preferably the density of the composition is formulated to be initially between around 0.1 to 0.2, 0.2 to 0.3, 0.3 to 0.4, 0.4 to 0.5, 0.5 to 0.6, 0.6 to 0.7, 0.7 to 0.8, 0.8 to 0.9, 0.9 to 1.0, 1.0 to 1.1, 1.1 to 1.2, 1.2 to 1.3, 1.3 to 1.4, or 1.4 to 1.5 g/ml. However, it will be appreciated that for some applications other high density additives can specifically be included to increase the density, up to 1.6, 1.7, 1.8, 1.9 or 2.0 g/ml. Preferably the density is maintained or stabilised as discussed above over an extended period of time, thereby increasing sleep time compared to the explosive composition not including a density stabiliser as discussed herein.

[0147] The skilled person will appreciate that a mathematical conversion will be required to convert the weight of mechanical sensitisers, such as ceramic/glass/plastic micro balloons or expanded polystyrene spheres or the amount of chemical to be decomposed into bubbles to yield a certain density, to volume (for void spaces). However, irrespective of the type of sensitisation, it will be appreciated that the final density is controlled to a predetermined value to yield an explosive composition and to thereby control the parameters discussed above.

[0148] Many advantages result from the inventive explosive compositions taught herein. For example, certain formulations of the compositions of the invention are more cost effective compared to existing explosive compositions, and are capable of being produced in large quantities to meet the demand from the mining industry. The explosive compositions of the invention utilise H_2O_2, which is a sustainably-produced material that has a relatively low carbon footprint compared to other types oxidisers used in the art. The explosive compositions of the invention can also be formulated into slurry, prilled, beaded, or emulsion form. It will also be appreciated that the compositions of the invention produce reduced amounts of NO_x, and in preferred forms of the invention no NO_x at all. Other advantages include the stabilisation of density over an extended period of time (compared to not including a density stabiliser as described herein), thereby improving sleep time and enabling blasts to be conducted that are not possible with H_2O_2-based explosive compositions that do not include a density stabiliser.

[0149] Once the explosive is sensitised, it can be initiated by a primer/booster, which as the skilled person will be aware is an explosive which generates a high detonation pressure which then initiates detonation of the sensitised explosive.

[0150] The introduction of voids into the composition can be provided by a variety of techniques (by entrapping gas bubbles when mixing, by using gas bubbles chemically generated in situ, by injecting gas bubbles, or mixing the composition with gas entrapped material), which are all applicable to the present invention.

[0151] Examples of air entrapped material for sensitisation for hydrogen peroxide-based explosives that can be used in conjunction with gas bubbles are glass or plastic microballoons, expanded polystyrene beads, polyurethane foam, etc.

[0152] Preferably the void component is incorporated into the compositions of the present invention as fine gas bubbles dispersed throughout the composition. Hollow gas-filled compressible particles such as micro balloons, or porous particles, or mixtures thereof can also be included.

[0153] The discontinuous phase of fine gas bubbles may be incorporated into the compositions of the present invention by mechanical agitation, injection by bubbling the gas through the composition, or by in situ generation of the gas by chemical means.

[0154] Suitable chemicals for the in situ generation of gas bubbles include H_2O_2 itself which can be decomposed with manganese (Mn) salts, yeast, iodide salts, etc; nitrogen-based compounds such as, for example, sodium nitrite, nitrosoamines such as, for example, N,N'dinitrosopentamethylenetetramine; boron-based compounds such as, for example, sodium borohydride; carbonates such as, for example, sodium carbonate. Decomposition in situ of a portion of the hydrogen peroxide with permanganates (or the like) forms oxygen gas bubbles. Decomposition of carbonates with acid in situ to forms carbon dioxide bubbles.

[0155] Examples of suitable hollow particles include small hollow microspheres of glass and resinous materials such as phenol-formaldehyde, poly(vinylidene chloride)/poly(acrylonitrile) copolymers and ureaformaldehyde. Examples of suitable hollow particles include Q-Cel, Cenospheres, Expancel, 3M, Extendospheres, etc.

[0156] Examples of porous materials include expanded minerals such as perlite, fly ash or hollow particles that are a by-product of coal fired power stations Typically, sufficient void space/gas bubbles (potentially also including hollow particles and/or porous particles) are used in the compositions of the present invention to give an explosive composition having a density in the range of from 0.1 to 1.4 g/cm^3. In preferred embodiments, the sensitisation is provided entirely from gas bubbles, with the proviso that there are no hollow gas-filled compressible particles.

[0157] Using conventional mixing techniques to provide bubbles in emulsion explosive compositions often produce bubbles with a range of bubble sizes. For example, the bubbles often have diameters up to 2000 microns and average bubble diameters of less than 50 microns are also common. By choice of suitable surfactants bubbles of smaller or larger diameters can be produced. Thus, by choice of an appropriate surfactant at a desired concentration the mean gas bubble diameter in the discontinuous gas phase may be controlled, and bubbles of 50 to 200 microns are possible. It will be appreciated that the bubble size influences the overall density, and if low densities are required 50 to 100 microns gas bubbles are preferred. For emulsified explosives the density range is preferably around 0.60-1.20 g/ml, and for watergels the density range is preferably between 0.2-1.2 g/ml. In an emulsified system the gas bubbles are preferably 10-100 times larger than the disperse phase droplets. The oily phase is likely to be in contact the gas bubble, whereas the oxidiser (or discontinuous phase) does not.

[0158] As discussed above, the introduction of gas bubbles can be provided by a variety of techniques, which are all applicable to the present invention.

[0159] In one embodiment the bubbles may be ‘trapped’ during the preparation of the explosive composition or by their formation through a chemical reaction. In U.S. Pat. No. 3,400,026 a formulation which uses protein in solution (albumin, collagen, soy protein, etc.) in order to favour the formation of bubbles and their stabilisation is described. U.S. Pat. No. 3,582,411 describes a watergel explosive formulation which contains a foaming agent of the guar gum type modified by hydroxy groups. In U.S. Pat. No. 3,678,140 a process for the incorporation of air by means of the use of protein solution is described, by passing the composition through a series of openings at pressures from 40 to 200 psi and simultaneously introducing air through eductors.

[0160] Incorporation of gas bubbles by means of their generation as a result of a chemical reaction is also described in the prior art. Wherein in situ generation of gas bubbles is provided by the decomposition of chemicals compounds, the decomposition suitably produces O_2, CO_2, N_2, H_2, or combinations thereof.

[0161] Various gases in bubble form have been used to sensitise blasting agents, for example nitrogen, carbon dioxide, oxygen, and hydrogen. It is also known to directly inject air or gas into the explosive mixture. Suitable gases for injection include air, oxygen, nitrogen, carbon dioxide, hydrogen, and noble gases (such as Argon).

[0162] Alternatively, hollow gas-filled compressible particles such as glass or plastic micro balloons, or porous particles, or expanded polystyrene (EPS) or mixtures thereof are included. In related embodiments the compressible material is any low-density material which has a specific gravity <1.0 g/cm^3. In brief summary, examples of glass balloons can be seen in U.S. Pat. Nos. 4,326,900 and 3,447,978, and plastic micro balloons in U.S. Pat. Nos. 4,820,361 and 4,547,234. These balloons are typically 0.05 mm in diameter and have a bulk density of 100 g/L. Use of expanded polystyrene can be seen for example in U.S. Pat. Nos. 5,470,407 and 5,271,779.

[0163] In one embodiment, the compressible material is gas-filled and selected from small hollow microspheres of ceramic, glass or resinous materials or porous materials, and combinations thereof, such as perlite or fly ash.

[0164] Preferably the microspheres/micro balloons contain gas such as pentane, etc.

[0165] Suitably the microspheres are sized between about 20 to 2000 micron and have a bulk density of less than 1000 g/L.

[0166] In alternative embodiments, the compressible material is a cellular material, such as expanded polystyrene (EPS), polyurethane foam, cotton seeds, expanded pop corn, husks, and combinations thereof.

[0167] Examples of suitable hollow particles include small hollow microspheres of ceramic, glass and resinous materials such as phenol-formaldehyde, poly(vinylidene chloride)/poly(acrylonitrile) copolymers and ureaformaldehyde. Examples of suitable hollow particles include Q-Cel, Envirospheres®, Cenospheres®, Expancel®, 3M, Extendospheres®, etc. Examples of porous materials include expanded minerals such as perlite, fly ash. A further example of a porous material is hollow particles that are a by-product of coal fired power stations.

[0168] Typically, sufficient bubbles and/or hollow particles and/or porous particles are used in the compositions of the present invention to give an explosive composition having a density in the range of from 0.3 to 1.4 g/cm^3.

[0169] For example, an explosive composition of the invention may have a density of up to 1.4 g/cm^3, up to 1.3 g/cm^3, up to 1.2 g/cm^3, up to 1.1 g/cm^3, up to 1.0 g/cm^3, etc. An explosive composition of the invention may have a density of from 0.3 g/cm^3, from 0.4 g/cm^3, from 0.5 g/cm^3, etc. Using conventional mixing techniques to provide bubbles in emulsion explosive compositions often produce bubbles with a range of bubble sizes. For example, the bubbles often have diameters up to 2000 microns and average bubble diameters of less than 300 microns are also common. By choice of suitable surfactants bubbles of smaller or larger diameters can be produced. Thus by choice of an appropriate surfactant at a desired concentration the mean gas bubble diameter in the discontinuous gas phase may be controlled, and bubbles of 50 to 300 microns are possible. For emulsified explosives the density range is suitably around 0.60-1.30 g/cm^3, and for watergels the density range is suitably between 0.2-1.40 g/cm^3. In an emulsified system the gas bubbles are suitably 10-100 times larger than the disperse phase droplets. The oily phase is likely to be in contact the gas bubble, whereas the oxidiser (or discontinuous phase) does not.

[0170] Other types of sensitising materials can be used in the compositions of the invention, e.g. TNT, HMX, RDX, aluminium powder and silicon powder and combinations thereof (e.g. TNT, HMX, RDX and aluminium powder and combinations thereof).

Density Stabilisers

[0171] The explosive compositions of the present invention comprise at least one density stabiliser.

[0172] Generally, one or more density stabilisers are incorporated in an amount of up to about 15% w/w of the explosives composition, for example about 0.01% w/w to about 10% w/w, e.g. about 1 to about 5% w/w, such as about 1 to about 3% w/w. The one or more density stabilisers are preferably present in a concentration of about 0.01, 0.05, 0.1, 0.25, 0.5, 0.75, 1, 1.25, 1.5, 1.75, 2, 2.25, 2.5, 2.75, 3, 3.25, 3.5, 3.75, 4, 4.25, 4.5, 4.75, 5, 5.25, 5.5, 5.75, 6, 6.25, 6.5, 6.75, 7, 7.25, 7.5, 7.75, 8, 8.25, 8.5, 8.75, 9, 9.25, 9.5, 9.75, 10, 11, 12, 13, 14 or 15% w/w. The one or more density stabilisers are preferably present in a concentration of around 0.01 to 0.05, 0.05 to 0.1, 0.1 to 0.5, 0.5 to 1, 1 to 1.5, 1.5 to 2, 2 to 2.5, 2.5 to 3, 3 to 3.5, 3.5 to 4, 4 to 4.5, 4.5 to 5, 5 to 5.5, 5.5 to 6, 6 to 6.5, 6.5 to 7, 7 to 7.5, 7.5 to 8, 8 to 8.5, 8.5 to 9, 9 to 9.5, 9.5 to 10, 10 to 11, 11 to 12, 12 to 13, 13 to 14 or 14 to 15% w/w.

[0173] Preferably the density stabiliser is present at about 0.01% w/w to about 10% w/w, e.g. about 1 to about 5% w/w, such as about 1 to about 3% w/w.

[0174] Preferred density stabilisers are phosphonates.

Phosphonates

[0175] Preferably the phosphonate(s) are in liquid form (e.g. dissolved in solution).

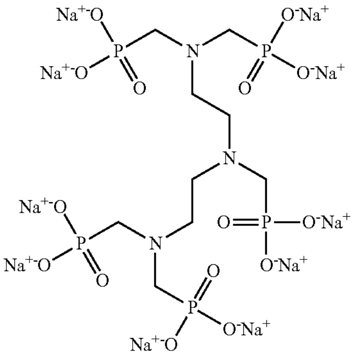
[0176] The phosphonate may have 1, 2, 3, 4, 5 or 6 pendant phosphonate groups, or more than 6 groups. In some embodiments, the phosphonate may have 1, 2, 3, 4, 5, 6, 7, 8, 9 or 10 pendant phosphonate groups. Preferably the phosphonate has at least 3 pendant phosphonate groups, more preferably 5 pendant phosphonate groups.

[0177] In certain embodiments, the phosphonate has the structure $X—(PO_3Y_2)_n$, where X is selected from the group consisting of an optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cycloalkyl, optionally substituted heterocycloalkyl, optionally substituted alkenyl; optionally substituted aryl, optionally substituted heteroaryl; Y is H or a water-soluble cation; and n is 1 to 10 (i.e., 1, 2, 3, 4, 5, 6, 7, 8, 9, 10). Suitable optional substituents can be selected from the group consisting of —OH, —COOH, halogen, —NH$_2$, —SH. In preferred embodiments, the phosphonate has the structure $X—(PO_3Y_2)_n$, where X is an optionally substituted heteroalkyl, optionally substituted heterocycloalkyl or an optionally substituted heteroaryl having at least two nitrogen atoms, preferably at least three nitrogen atoms, more preferably three nitrogen atoms; Y is H or a water-soluble cation; and n is 1 to 10 (i.e., 1, 2, 3, 4, 5, 6, 7, 8, 9, 10). Suitable optional substituents can be selected from the group consisting of —OH, —COOH, halogen, —NH$_2$, —SH.

[0178] In some preferred embodiments the phosphonates suitable for use in the invention are amine based, more preferably tertiary amine based.

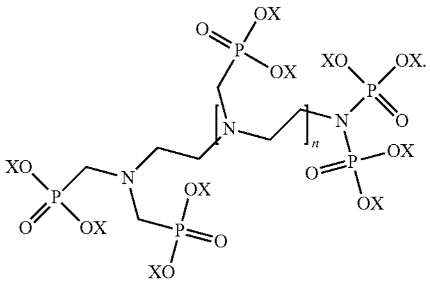
[0179] Suitable water soluble-cations for phosphonate anions include alkali metals (e.g. lithium, sodium, potassium), ammonium, substituted ammonium and alkaline earth metals (e.g. calcium, magnesium). Preferred compounds have n=1 to 2 and preferably Y is hydrogen, ammonium, sodium or potassium or mixtures thereof. In one preferred embodiment, the density stabiliser is a phosphonate which is diethylenetriamine pentamethylene phosphonic acid sodium salt (DTPMPA.Na.x, $C_9H_{28-x}N_3O_{15}P_5Na_x$)—see Formula I.

Formula I



[0180] Examples of other suitable phosphonates include those falling within the scope of Formula II:

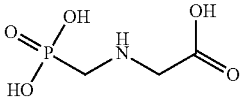
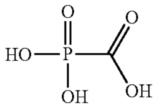
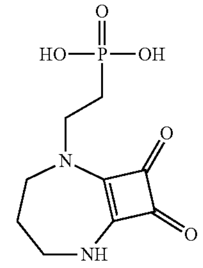
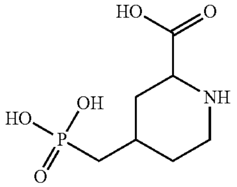
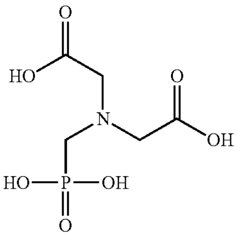
Formula II



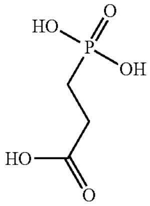
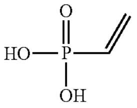
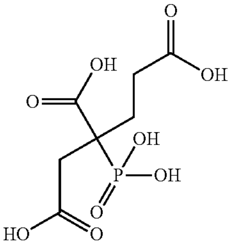
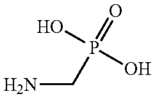
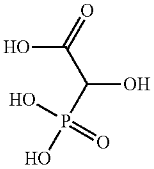
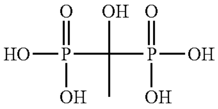
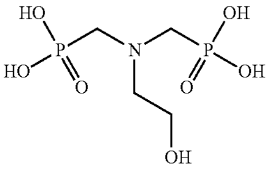
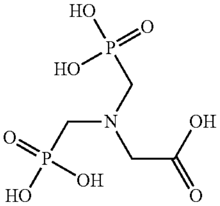
wherein n = 1-4; and X = H or a water-soluble cation

[0181] The various X groups may be the same or different.

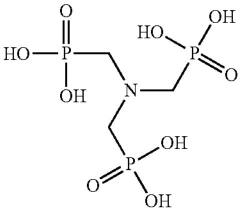
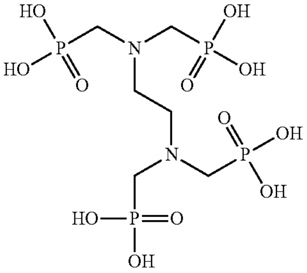
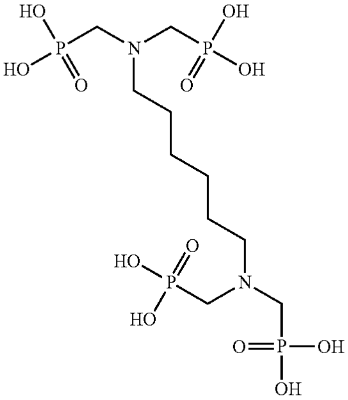
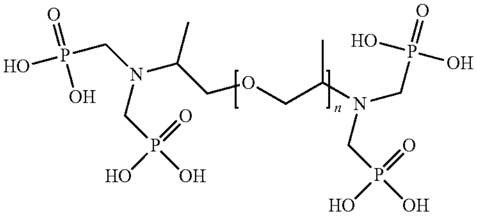
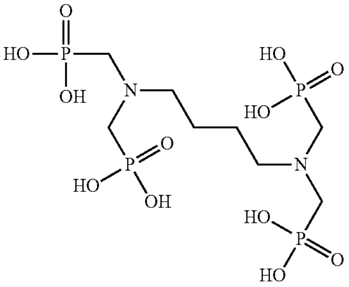
[0182] Examples of other suitable phosphonates include:

Phosphonate (number of phosphonate groups)	Structure
Glyphosate (1)	
Foscarnet (1)	
Perzinfotel (1)	
Selfotel (1)	
N-(phosphonomethyl)iminodiacetic acid (PMIDA) (1)	

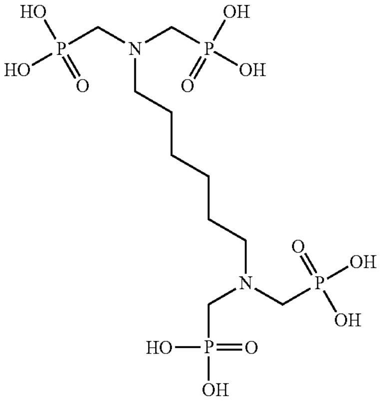
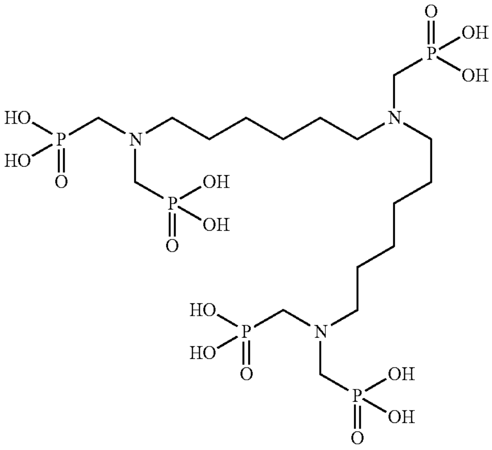
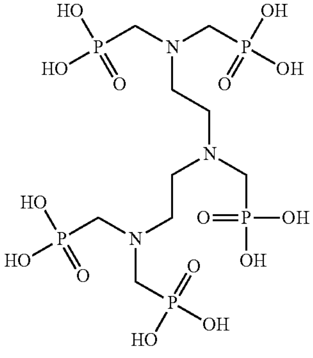
-continued

Phosphonate (number of phosphonate groups)	Structure
2-carboxyethyl phosphonic acid (CEPA) (1)	
vinylphosphonic acid (1)	
2-phosphonobutane-1,2,4-tricarboxylic acid (PBTC) (1)	
aminomethylphosphonic acid (AMPA) (1)	
2-hydroxyphosphonoacetic acid (HPAA) (1)	
hydroxyethylidene-1,1-diphosphonic acid (HEDP) (2)	
hydroxyethylamino-di(methylene phosphonic acid) (HEMPA) (2)	
N,N-bis(phosphonomethyl)glycine (BPMG) (2)	

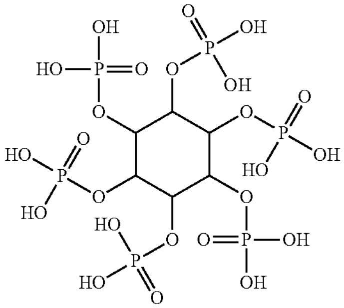
-continued

Phosphonate (number of phosphonate groups)	Structure
aminotris(methylenephosphonic acid) (ATMP) (3)	
ethylenediamine tetra(methylene phosphonic acid) (EDTMP) (4)	
hexamethylene diamine tetra (methylene phosphonic acid) (HMDTMP) (4)	
polyamino polyether methylene phosphonic acid (PAPEMP) (4)	
tetramethylenediaminetetra (methylenephosphonic acid) (TDTMP) (4)	

-continued

Phosphonate (number of phosphonate groups)	Structure
hexamethylenediaminetetra (methylenephosphonic acid) (HDTMP) (4)	
bis(hexamethylene triamine penta (methylene phosphonic acid)) (BHMTPMP) (5)	
diethylenetriamine penta(methylene phosphonic acid) (DTPMP) (5)	

-continued

Phosphonate (number of phosphonate groups)	Structure
Phytic acid (6)	

[0183] and salts, solvates, dimers, stereoisomers thereof.

[0184] Without being bound by any one theory, the inventor contemplates that suitable phosphonates for use in the invention provide density stabilisation via chelation or sequestration of impurities inherently present within the explosive compositions contemplated herein (i.e., providing "internal" stability). Additionally, suitable phosphonates for use in the invention provide density stabilisation via chelation or sequestration of impurities that arise when the explosive composition is loaded into the blasthole and exposed to rock (i.e., providing "external" stability). It will be appreciated that the explosives of the invention can be used in a wide range of surface and subsurface applications, and in a range of different types of rock having different metalliferous minerals. One or more phosphonates described herein can be selected for use depending on the type of impurity (metal ion) present in the rock to be blasted and/or whether the application is in hot reactive ground, which can affect the solubility of metal ions and/or the pH.

Composition Stabilisers

[0185] Other composition stabilisers can also be used with the present invention.

[0186] Suitable composition stabilisers may be selected from the group consisting of phosphates, stannates and sulfites.

[0187] Suitable composition stabilisers also include EDTA and nitrates (e.g. sodium nitrate or potassium nitrate).

[0188] For example, stannates, sulphites, and nitrates, either as a separate entity or as a component of the density stability system such as, for example, a mixture of phosphonates and nitrates.

[0189] Typically, the other composition stabiliser component(s) of the compositions of the present invention are incorporated in an amount of up to about 15% w/w, for example about 0.01% w/w to about 10% w/w, e.g. about 1 to about 5% w/w, such as about 1 to about 3% w/w of the total composition.

Fuels for Watergels

[0190] The explosive compositions of the invention may comprise one or more fuels.

[0191] H_2O_2-based watergels can be prepared with either water-miscible or water immiscible fuels.

[0192] The skilled person will appreciate that there are many options available for use as a fuel. For example, depending on their origin, the fuel may be a product of vegetable origin, such as sugars, molasses, vegetable oils or alcohols. Such fuels may be regarded as sustainable fuels. Other fuels can be sourced from the petrochemical industry, as for example diesel, paraffinic oils or mineral oil, organic acids, ethers, esters, amine nitrates, urea, hexamine, etc. Other fuels may be silicone oils, etc. Suitable fuels for use in the compositions of the invention are glycerol, sugar, syrup, alcohol, carbon, ground coal, waxes, oils such as corn, cottonseed, olive, peanut, or fatty acid oils. Suitable sustainable fuels for use in the compositions of the invention may include, sugar molasses, vegetable oil, alcohol, oils such as corn, cottonseed, olive, peanut, fatty acid oils, or gums. Other fuels may be selected from ethylene glycol, glycerol, propylene glycol, and/or formamide Preferably, the sustainable fuel is glycerol. The composition may comprise between 15 and 25% w/w sustainable fuel, e.g., between 15 and 20%, or between 20 and 25% w/w. The composition may alternatively comprise less than 40% w/w sustainable fuel, less than 30%, less than 25%, or less than 20% w/w sustainable fuel, e.g., 5%, 10%, 15%, 20%, 25%, 30%, 35% or 40% w/w sustainable fuel. Alternatively, the above fuels can also split into water-soluble and water-insoluble fuels.

[0193] Water-miscible fuels which can be used with the present invention can be selected from the group consisting of: glycerol, sugar, amine nitrates, hexamine and urea.

[0194] Water immiscible fuels which can be used with the present invention can be selected from the group consisting of: aliphatic, alicyclic and aromatic compounds and mixtures thereof which are in the liquid state at the formulation temperature. Suitable organic fuels may be chosen from fuel oil, diesel oil, distillate, kerosene, naphtha, waxes, (e.g. microcrystalline wax, paraffin wax and slack wax) paraffin oils, benzene, toluene, xylenes, asphaltic materials, polymeric oils such as the low molecular weight polymers of olefins, vegetable oils, animal oils, fish oils, and other mineral, hydrocarbon or fatty oils, and mixtures thereof. Preferred organic fuels are liquid hydrocarbons generally referred to as petroleum distillates such as gasoline, kerosene, fuel oils, paraffin oils and vegetable oils or mixture thereof.

[0195] Typically, the water miscible or water-immiscible fuel of the watergel composition of the present invention comprises from 5 to 30% by weight and preferably 10 to 25% by weight of the total composition. Preferably the fuel is included in a concentration of about 5, 7, 8, 10, 12, 15, 20, 25, 30, 35, 40, 45, or 50% (w/w). Preferably the fuel is included in a concentration of between about 5 to 10, 10 to 15, 15 to 20, 20 to 25, 25 to 30, 30 to 35, 35 to 40, 40 to 45, or 45 to 50% (w/w).

[0196] In one embodiment, the water-immiscible fuel is included at 7 to 25% w/w of the total composition.

[0197] In one embodiment, the water-miscible fuel is included at 8 to 25% w/w of the total composition.

Fuels for Emulsions

[0198] The explosive compositions of the invention may comprise one or more fuels.

[0199] H_2O_2-based emulsions can be prepared with water-immiscible fuels.

[0200] The fuel can be any fuel such as diesel fuel, and/or oil distillates. Alternatively, it can be paraffinic, mineral, olefinic, naphthenic, animal, vegetable, fish and silicone oils. Other types of fuels are benzene, toluene, xylenes, asphaltic materials and the likes. The fuel may be a sustainable fuel. Suitable sustainable fuels for use in emulsions may include vegetable oil, oils such as corn, cottonseed, olive, peanut, or fatty acid oils. The composition may comprise between 15 and 25% w/w sustainable fuel, e.g., between 15 and 20%, or between 20 and 25% w/w. The composition may alternatively comprise less than 40% w/w sustainable fuel, less than 30%, less than 25%, or less than 20% w/w sustainable fuel, e.g., 5%, 10%, 15%, 20%, 25%, 30%, 35% or 40% w/w sustainable fuel.

[0201] The water-immiscible organic phase component of the composition of the present invention comprises the continuous "oil" phase of the water-in-oil emulsion and is the fuel. Suitable organic fuels include aliphatic, alicyclic and aromatic compounds and mixtures thereof which are in the liquid state at the formulation temperature. Suitable organic fuels may be chosen from recycled lubricant distillates, recycled oil distillates, fuel oil, diesel oil, distillate, kerosene, naphtha, waxes, (e.g. microcrystalline wax, paraffin wax and slack wax) paraffin oils, benzene, toluene, xylenes, asphaltic materials, polymeric oils such as the low molecular weight polymers of olefins, vegetable oils, animal oils, fish oils, and other mineral, hydrocarbon or fatty oils, and mixtures thereof. Preferred organic fuels are liquid hydrocarbons generally referred to as petroleum distillates such as gasoline, kerosene, fuel oils, paraffin oils and vegetable oils or mixture thereof.

[0202] Typically, the organic fuel or continuous phase of the H_2O_2-based emulsion composition of the present invention comprises from 2 to 20% by weight and preferably 3 to % 20% by weight of the total composition. Preferably the organic fuel is included in a concentration of about 2, 4, 6, 8, 10, 12, 14, 16, 18, or 20% (w/w). Preferably the organic fuel is included in a concentration of between about 2 to 4, 4 to 6, 6 to 8, 8 to 10, 10 to 12, 12 to 14, 14 to 16, 16 to 18, or 18 to 20% (w/w).

Secondary Fuels for Watergels and Emulsions

[0203] If desired, other optional fuel materials, hereinafter referred to as secondary fuels, may be incorporated into the compositions of the present invention.

[0204] Examples of secondary fuels include finely divided solids. Examples of secondary fuels also include water-miscible organic liquids. Examples of solid secondary fuels include sulfur; aluminium; and carbonaceous materials such as gilsonite, comminuted coke or charcoal, carbon black, resin acids such as abietic acid, vegetable products such as starch, nut meal, grain meal and wood pulp and combinations thereof. Examples of secondary fuels include sugars such as glucose and dextrose. Examples of secondary fuels further include recycled plastic waste.

[0205] Typically, the optional secondary fuel component of the compositions of the present invention comprise from 0 to 20% w/w of the total composition, e.g. at 0.1 to 12% w/w.

Thickeners

[0206] The explosive compositions of the invention may comprise one or more thickeners. More particularly, the watergel explosive compositions of the invention may comprise one or more thickeners.

[0207] Because bubbles of gas and materials enclosing gas have a relatively low density, they will tend to migrate towards the surface of the column of explosive if the viscosity of the H_2O_2-based explosive composition is not capable of maintaining the sensitising material homogeneously dispersed throughout. Migration of the sensitising material towards the surface is undesirable as it may render the explosive too insensitive to initiation, and therefore the explosive composition may not deliver the energy and gases needed to break and move the rock as required or even worst, the explosive may undergo a misfire. One way to ameliorate this issue is to formulate the explosive composition into a watergel. These types of compositions can be formulated with different levels of viscosity by using a thickener. Viscosities can be selected to generally retain the sensitising material in a homogeneously dispersed state throughout the composition.

[0208] If desired the aqueous solution of the compositions of the present invention may comprise thickeners which optionally may be crosslinked. Any conventional thickener may be used with the present invention. The thickeners, when used in the compositions of the present invention, are suitably polymeric materials, especially gum materials typified by the galactomannan gums such as locust bean gum or xanthan gum or alginate gum or derivates of alginate gum or guar gum or derivatives thereof such as hydroxypropyl guar gum. The thickener may be selected from gums including natural gums, such guar gum, xanthan gum, sodium alginate, carboxymethylcellullose, methylcellulose and the like. Other useful, but less preferred, gums are the so-called biopolymeric gums such as the heteropolysaccharides prepared by the microbial transformation of carbohydrate material, for example the treatment of glucose with a plant pathogen of the genus *Xanthomonas* typified by *Xanthomonas campestris*. Other useful thickeners include synthetic polymeric materials and in particular synthetic polymeric materials which are derived, at least in part, from the monomer acrylamide. An example of a synthetic thickener is polyacrylamide. Inorganic thickeners, such as fumed silica, clays and carbosil, may also be used, or a combination thereof. Suitably the thickener is selected from locust bean gum, guar gum, hydroxypropyl guar gum, sodium alginate and heteropolysaccharides, and combinations thereof.

[0209] Typically, the thickener component of the compositions of the present invention comprises from 0 to 5% by weight of the total composition, e.g. from 0.5 to 5% w/w, e.g. from 0 to 2% w/w of the total composition, e.g. from 0.1 to 2% by weight of the total composition.

Crosslinkers

[0210] Crosslinkers can also be used with the present invention.

[0211] Thickeners in combination with crosslinkers can improve the water resistance and mechanical strength of the explosive. It is convenient for this purpose to use conventional crosslinking agents such as zinc chromate or a dichromate either as a separate entity or as a component of a redox system such as, for example, a mixture of potassium dichromate and potassium antimony tartrate. Salts of Ca, Ti, Sb can also be used as crosslinkers.

[0212] In one embodiment the crosslinker is selected from salts containing zinc, calcium, titanium, antimony, chromium, borate and dichromate and combinations thereof.

[0213] Typically, the crosslinker component of the compositions of the present invention comprises from 0 to 3% w/w, e.g. from 0 to 0.1% w/w of the total composition, e.g. from 0.1 to 1% w/w of the total composition, e.g. from 1 to 2% w/w of the total composition, e.g. from 2 to 3% w/w of the total composition.

Emulsifiers

[0214] The explosive compositions of the invention, when prepared as emulsion form, may comprise one or more emulsifiers.

[0215] H_2O_2-based emulsion compositions are made of a discontinuous phase of oxidising material that is dispersed in a continuous phase of an organic fuel in the presence of one or more emulsifiers. The emulsifier is adapted or chosen to maintain phase separation.

[0216] The emulsifier component of the composition of the present invention may be chosen from the wide range of emulsifiers known in the art for the preparation of water-in-oil emulsion explosive compositions. Examples of such emulsifiers include polyisobutylene succinic anhydride (PIBSA) reacted with amines; other emulsifiers examples are alcohol alkoxylates, phenol alkoxylates, poly(oxyalkylene) glycols, poly(oxyalkylene) fatty acid esters, amine alkoxylates, fatty acid esters of sorbitol and glycerol, fatty acid salts, sorbitan esters, poly(oxyalkylene) sorbitan esters, fatty amine alkoxylates, poly(oxyalkylene) glycol esters, fatty acid amides, fatty acid amide alkoxylates, fatty amines, quaternary amines, alkyloxazolines, alkenyloxazolines, imidazolines, alkyl-sulfonates, alkylarylsulfonates, alkylsulfosuccinates, alkylphosphates, alkenylphosphates, phosphate esters, lecithin, copolymers of poly(oxyalkylene) glycols and poly(12-hydroxystearic acid), and mixtures thereof.

[0217] Among the preferred emulsifiers are the 2-alkyl- and 2-alkenyl-4,4'-bis (hydroxymethyl) oxazoline, the fatty acid esters of sorbitol, lecithin, copolymers of poly(oxyalkylene) glycols and poly(12-hydroxystearic acid), and mixtures thereof, and particularly sorbitan mono-oleate, sorbitan sesquioleate, 2-oleyl- 4,4'-bis (hydroxymethyl) oxazoline, mixture of sorbitan sesquioleate, lecithin and a copolymer of poly(oxyalkylene glycol and poly (12-hydroxystearic acid), and mixtures thereof.

[0218] Typically, the emulsifier component of the composition of the present invention comprises up to 5% by weight of the total composition. Higher proportions of the emulsifier may be used and may serve as a supplemental fuel for the composition but in general it is not necessary to add more than 5% by weight of emulsifier to achieve the desired effect. One of the advantages of the compositions of the present invention is that stable emulsions can be formed using relatively low levels of emulsifier and for reasons of economy it is preferable to keep the amount of emulsifier used to the minimum required to have the desired effect. The preferred level of emulsifier used is in the range from 0.1 to 2.0% by weight of the total composition.

Surfactants

[0219] The explosive compositions of the invention when formulated as watergels may comprise one or more surfactants. In particular, one or more surfactants may be employed when the explosive composition comprises a diesel-like fuel.

[0220] The surfactant component of the composition of the present invention may be chosen from the wide range of surfactants known in the art for the preparation of watergels and water-in-oil emulsion explosive compositions. Examples of such surfactants include Sodium Lauryl Sulphate, Betaine CAB30, Sodium Coco Sulphate (Sodium Mono-C12-C18-Alkyl Sulfate), Alpha Olefin Sulphonate 46, Coconut diethanolamide, APG0810 (Octyldecyl glucoside), and Cocamidopropyl Betaine.

[0221] Typically, the surfactant component of the composition of the present invention comprises up to about 0.5% by weight of the total composition, with about 0.25% w/w. used for Cocamidopropyl Betaine. Other oxidisers for watergel and emulsion H_2O_2-based explosive compositions

[0222] It lies within the invention that there may also be incorporated into the H_2O_2-based watergel/emulsion compositions hereinbefore described one or more other substances or mixtures of substances which are themselves suitable as explosive materials.

[0223] As a typical example of such a modified compositions reference is made to compositions wherein there is added to and mixed with an watergel/emulsion composition as hereinbefore described up to 90% w/w of an oxidizing salt such as ammonium nitrate or an explosive composition comprising a mixture of an oxidizing salt such as ammonium nitrate and fuel oil and commonly referred to by those skilled in the art as “ANFO”. The compositions of “ANFO” are well known and have been described at length in the literature relating to explosives.

[0224] In particular, the explosive compositions of the invention optionally comprise one or more other oxidisers (e.g. one other oxidiser, e.g. two other oxidisers). Any suitable oxidiser can be used. For example, the one or more other oxidiser(s) are suitably selected from the group consisting of nitrate salts, perchlorate salts, sodium peroxide and potassium peroxide and optionally nitric acid.

[0225] Nitrate salts may be selected from the group consisting of ammonium nitrate, sodium nitrate, calcium ammonium nitrate, calcium nitrate, potassium nitrate, barium nitrate and magnesium nitrate.

[0226] Perchlorate salts may be selected from the group consisting of ammonium perchlorate, sodium perchlorate, potassium perchlorate, barium perchlorate, magnesium perchlorate and calcium perchlorate (e.g. ammonium perchlorate and sodium perchlorate).

[0227] In one embodiment the one or more other oxidiser (s) are selected from the group consisting of nitrate salts and perchlorate salts. In one embodiment the one or more other oxidiser(s) are selected from nitrate salts. In one embodiment the one or more other oxidiser(s) are selected from the group consisting of AN, CAN and SN. In one embodiment the one or more other oxidiser(s) are selected from the group consisting of CAN, CN and SN. In one embodiment the one or more other oxidiser(s) are selected from the group consisting of CAN and SN. In one embodiment the other oxidiser is CAN. In one embodiment the other oxidiser is SN. In one embodiment the other oxidiser is CN. In one embodiment, the one or more other oxidiser(s) do not include AN. In other words, in one embodiment, the explosive composition is devoid of AN.

[0228] The compositions of the invention comprise from greater than 0 and up to about 90% w/w of one or more other oxidisers, such as from about 0.1% to about 75% w/w. For example, compositions of the invention may comprise from greater than 0, from 0.1%, from 1%, from 10%, from 20%, from 30%, from 40%, from 50%, or from 60% w/w up to 90% w/w of one or more other oxidisers, e.g., compositions of the invention may comprise from 1 to 20%, from 20 to 40%, from 15 to 35%, from 35 to 55%, from 30 to 70%, from 40 to 70%, or from 50 to 80% w/w of the one or more other oxidisers. For example, compositions of the invention may comprise up to 90%, 80%, 75%, 70%, 65%, 60%, 50%, 40%, 30%, 20% w/w, etc of one or more other oxidisers, or may comprise about 90%, 80%, 75%, 70%, 65%, 60%, 55%, 50%, 45%, 40%, 30%, or 20% w/w of one or more other oxidisers. It will be understood that the explosive compositions herein comprise one or more oxidisers according to the foregoing amounts or ranges in total, and as such, where more than one oxidiser is used, each oxidiser may be present in any suitable amount within the foregoing amounts or ranges such that the total mass of the oxidisers adds up to the specified amount or range.

[0229] It will be appreciated that the oxidiser can be in the form of a mixture of solid and liquids. To explain, typically the oxidiser will be solubilised in water when used at a relatively low concentration, and if present at higher concentrations beyond the solubility of the oxidiser, then the oxidiser will be solubilised and in a solid form. In some embodiments, the oxidiser is fully solubilised (or substantially fully solubilised) in the composition. In such embodiments, excess solid oxidiser, e.g., in the form of prills, may be added. In other embodiments, the oxidiser is only partially solubilised in the composition, in which case solid oxidiser (e.g., in the form of solid prills) may be added just prior to detonation such that there is insufficient time for the prills to solubilise substantially. The oxidiser can be in a liquid:solid ratio of between 100:0 to 20:80, and any ratio in between. For example, the liquid:solid ratio may be between 100:0 and 70:30, or between 80:20 and 60:40, or between 70:30 and 40:60, or between 5:50 and 30:70, or of 100:0, 70:30, 60:40, 50:50, 45:55, 40:60; or 20:80.

[0230] It also lies within the invention to have as a further explosive component of the composition well known explosive materials comprising one or more of for example trinitrotoluene, nitroglycerine or pentaerythritol tetranitrate.

[0231] It will also be appreciated that these other oxidisers can be used to partially replace H_2O_2 in the H_2O_2 compositions. Examples of such oxidisers are nitrate salts, perchlorate salts, sodium/potassium peroxide, etc.

Ratios of Oxidisers:Fuel

[0232] In one embodiment, the explosive composition may comprise a ratio of H_2O_2:one or more other oxidisers in the range between 100:1 to 30:70.

[0233] In one embodiment, the explosive composition may comprise a ratio of H_2O_2 (or H_2O_2+one or more oxidisers):fuel in the range between 87:13 to 64:36.

[0234] In one embodiment, the explosive composition may comprise a ratio of H_2O_2 (or H_2O_2+one or more oxidisers):fuel:water in the range between 60:20:20 to 72:24:4.

Energy Deferments

[0235] The explosive compositions of the invention may optionally comprise one or more energy deferments. Energy deferments include metal oxides such as aluminium oxide.

Energy Diluents

[0236] The explosive compositions of the invention may optionally comprise one or more energy diluents.

[0237] In the context of this invention, energy diluents are inert materials that have minimal contribution to the detonation process and can be used to replace part of the energetic material in the composition and therefore reduce the energy output of the H_2O_2-based explosive.

[0238] In some cases these energy diluents may increase, decrease or not alter the density of the H_2O_2-based composition. In some cases, these energy diluting agents are able to reduce the density of the H_2O_2-based composition without increasing the sensitivity.

[0239] Examples of these diluents materials are EPS (with particle size larger than 2 mm in diameter), granulated/shredded rubber (from tyres), cotton seeds, saw dust, husk, expanded popcorn, plastic beads, wool meal, bagasse, peanut and oat husks, peanut shells etc. U.S. Pat. No. 5,409,556 describes some example of these energy reducing agents. In one embodiment the energy diluting agent is selected from granulated/shredded tyres, rubber, expanded rice, expanded popcorn, expanded wheat, and combinations thereof. These materials could also be used in combination with sensitisers to offer more flexibility (as shown in U.S. Pat. No. 5,470,407) as far as the performance properties of the H_2O_2-based explosive is concerned.

[0240] Therefore, another advantage of the H_2O_2-based explosive is that the performance properties of the explosive can be altered to suit the characteristics of the blasting site.

[0241] Possible variations of this general procedure will be evident to those skilled in the art of the preparation of emulsion explosive compositions.

[0242] Watergel or emulsion H_2O_2-based explosive compositions made according to the present invention include energy diluents in concentration between 0-800% by volume (i.e. the volume can be increased by 8×). As a result, the use of the additives (sensitiser and energy diluents), provides a better control of the density, VOD and energy delivery in the ground being blasted.

[0243] Therefore, an additional advantage of the H_2O_2-based explosive is that it could be used in a range of density between about 0.1 g/ml to about 1.4 g/ml (e.g. between about 0.3 g/cm^3 to about 1.4 g/cm^3.

[0244] In one preferred embodiment the H_2O_2-based explosive compositions of the invention comprise the following components: H_2O_2:fuel:water in the range between 25%:5%:70% to 73%:11%:16%.

Density of the Explosive Compositions

[0245] Suitably the final density is controlled with sensitiser to around 0.3 to 1.4 g/cm^3.

[0246] Suitably the density of the composition is formulated to be around 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1, 1.1, 1.2, 1.3, or 1.4 g/cm^3. Suitably the final density of the composition is formulated to be between around 0.3 to 0.4, 0.4 to 0.5, 0.5 to 0.6, 0.6 to 0.7, 0.7 to 0.8, 0.8 to 0.9, 0.9 to 1.0, 1.0 to 1.1, 1.1 to 1.2, 1.2 to 1.3, or 1.3 to 1.4 g/cm^3. In some embodiments the density is controlled to a predetermined target value by selection of the ratios of the components of the composition. For example, by balancing the concentration of a component which reduces the density, such as hollow microspheres, and one that has a relatively high density, such as nitrate prills.

pH of the Explosive Compositions

[0247] The pH of the emulsion explosive compositions of the present invention is not narrowly critical. However, in general the pH is between 0 and 8 and suitably the pH is between 1 and 6, and may be controlled by suitable addition of conventional additives, for example inorganic or organic acids and salts.

Viscosity of the H_2O_2-Based Compositions

[0248] The viscosity of the H_2O_2-based compositions (watergel or emulsion type) will be discussed in terms of apparent viscosity. Where used herein the term "apparent viscosity" refers to viscosity measure using a Brookfield RVT viscometer, #7 spindle at 50 r.p.m.

[0249] It is preferred in the process of the present invention that the explosive composition of the water-in-oil emulsion explosive particles have an apparent viscosity greater than 10 Pa*s (Pascal*second) prior to the entrainment of gas bubbles. Apparent viscosity is more preferably in the range 10 to 50 Pa*s. A more preferred viscosity range for the entrainment of gas bubbles by mechanical mixing is from 10 to 35 Pa*s. The range 10 to 25 Pa*s provides the most efficient entrainment of gas bubbles by mechanical mixing.

[0250] Preferably the explosive composition of the invention can be easily pumped.

Oxygen Balance of the Explosive Compositions

[0251] "Oxygen balance" (OB) is a term of the art which is used to indicate the degree to which an explosive can be oxidised. An OB close to zero is preferred when formulating mining explosives, such that no reactant is in excess during the detonation process, and therefore the expected products are nitrogen, water and carbon dioxide. If the oxygen balance is far from zero, some part of the reactant materials will not react and instead, those unreacted material absorb/sink heat from the detonation reaction, which in turn will cause the explosive to underperform. For example, some prior art compositions are unsuitable for combustion, as they lack fuel (and therefore the OB is too positive) and the composition cannot burn.

[0252] Suitably the amount of fuels materials in the explosive composition can be adjusted so the composition has a final oxygen balance between +10 and −10, e.g. between +5 and −5.

Preparation of Composition

[0253] According to a second aspect, the present invention provides a method of preparing an explosive composition according to the first aspect, the method comprising: combining H_2O_2, and fuel and one or more density stabilisers, and optionally one or more other oxidisers and/or, a sensitiser, and one or more density stabilisers.

[0254] The H_2O_2-based compositions of the present invention may be prepared by a number of methods.

[0255] In one preferred method of manufacture, the H_2O_2-based watergel type compositions may be prepared by combining H_2O_2 with a density stabiliser, water miscible fuels, and thickeners until the thickener starts increasing the viscosity of said composition. Once the watergel is formed, solid ingredients (fuels, energy diluting agents, etc) are optionally mixed into said watergel. Sensitisers can be mixed into said watergel capable in an amount capable to sensitise the watergel. Finally, sensitising agents can be mixed into the oxidiser component prior to mixing into said watergel.

[0256] In one preferred method of manufacture the H_2O_2-based emulsion type compositions may be prepared by: combining hydrogen peroxide with a density stabiliser, the water-immiscible organic phase, a water-in-oil emulsifier, with rapid mixing to form a water-in-oil emulsion; then mixing until the emulsion is uniform. Once the emulsion is formed, solid ingredients (fuels, energy diluting agents, etc) are optionally mixed into said watergel. Sensitisers are mixed into said emulsion in an amount capable of sensitising said watergel. Finally, sensitising agents can be mixed into the oxidiser component prior to mixing into said emulsion.

Preparation of Watergel H_2O_2-Based Explosive Composition

[0257] Watergel explosive compositions made according to the present invention preferably include H_2O_2 in concentrations between 10-64% by weight.

[0258] It will also be appreciated that other oxidisers can be combined with H_2O_2, as discussed above. For example nitrate salts, perchlorate salts, amine nitrates, sodium/potassium peroxide, etc., can be also incorporated in combination with H_2O_2.

[0259] The skilled person will appreciate that there are many options that are available for use as a fuel. For example the fuel may be a product of vegetable origin, such as sugars or molasses, alcohols, organic acids, ethers, esters, urea, hexamines, etc. Alternatively, it may be a product derived from crude oil such a diesel, paraffinic oils or mineral oil, etc. Other fuels may be silicone oils, etc.

[0260] Secondary fuels may be a solid hydrocarbon, such as coal and recycled plastic waste. It may also be a metallic fuel, such as aluminium/silicon, etc, or gilsonite, comminuted coke or charcoal, carbon black, resin acids such as abietic acid, vegetable products such as starch, nut meal, grain meal and wood pulp; or nitrogen compounds such as amides, amines, etc.

[0261] Preferably the amount of these fuels materials in the formulation can be adjusted so the H_2O_2-based composition has an oxygen balance between 3 and −10 and the H_2O_2-based composition can be easily pumped. The preferred fuels are oil distillates, diesel-like hydrocarbons, glycerol, sugar, syrup, alcohol, carbon, ground coal, waxes, oils such as corn, cottonseed, olive, peanut, or fatty acid oils.

[0262] It will be appreciated that for an H_2O_2-based composition in accordance with the invention to be functional, it is important that gas bubbles are homogeneously distributed throughout the composition. It is also important that once distributed throughout, the gas bubbles should be maintained in a homogenous distribution throughout the composition, i.e. little or no segregation or settling, and that the density be maintained or stabilised to increase the sleep time. In accordance with the present invention this may be achieved by formulating the explosive as a stable watergel and including a density stabiliser. Formation of watergel compositions is conventional in the art and one skilled in the art will be familiar with the various forms that may be produced. Typically this will involve the use of a thickener that acts on the liquid oxidant component of the composition. Herein the term "thickener" is also intended to include gelling agents, crosslinking agents, and the like.

[0263] As discussed above, any conventional thickener may be used with the present invention. The thickener may be selected from natural gums, such guar gum, xanthan gum, sodium alginate, carboxymethylcellullose, methylcellulose and the like. Synthetic thickeners, such polyacrylamide, may also be used. Inorganic thickeners, such as fumed silica, clays and carbosil, may also be used, or a combination thereof.

[0264] Crosslinkers can also used with the present invention. Thickeners in combination with crosslinkers can improve the water resistance and mechanical strength of the H_2O_2 -based explosive. Examples of crosslinkers are those from antimony, calcium, titanium, chromium, borate salts and dichromate salts, etc.

[0265] Various additional ingredients, familiar to those skilled in the art, may be employed in the formulation of the invention.

Preparation of Water-In-Oil H_2O_2-Based Explosive Composition

[0266] Water-in-oil explosive compositions made according to the present invention include hydrogen peroxide in concentration between 10-85% by weight. It will also be appreciated that other oxidisers can be combined with H_2O_2, as discussed above. For example nitrate salts, perchlorate salts, amine nitrates, sodium/potassium peroxide, etc., can be also incorporated in combination with H_2O_2.

[0267] The fuel can be any fuel such as diesel fuel, recycled oil distillates, and diesel-like distillates. Alternatively it can be paraffinic, mineral, olefinic, naphtenic, animal, vegetable, fish and silicone oils. Other types of fuels are benzene, toluene, xylenes, asphaltic materials and the likes.

[0268] Secondary fuels may be a solid hydrocarbon, such as coal and recycled plastic waste. It may also be a metallic fuel, such as aluminium/silicon, etc, or gilsonite, comminuted coke or charcoal, carbon black, resin acids such as abietic acid, vegetable products such as starch, nut meal, grain meal and wood pulp; or nitrogen compounds such as amides, amines, etc.

[0269] Preferably the amount of these fuels materials in the formulation can be adjusted so the H_2O_2-based composition has an oxygen balance between 3 and −10 and the H_2O_2-based composition can be easily pumped.

[0270] In relation to sensitisation, similar considerations apply to water-in-oil explosive compositions as the watergel explosive compositions discussed above, namely preferably the gas bubbles are homogeneously distributed throughout the composition. In accordance with the present invention this is achieved by formulating the explosive as a stable water-in-oil emulsion. Formation of emulsified explosives is conventional in the art and one skilled in the art will be familiar with the various forms may be produced. Typically this will involve the use of an emulsifier, which is adapted to keep the oxidiser dispersed throughout the continuous organic phase (fuel).

[0271] Emulsifiers commonly used in emulsion explosive compositions include sorbitan mono oleate, sorbitan sesquioleate, poly isobutylene succinic anhydrides (PIBSA) and amino derivatives of PIBSA, PIB-lactone and its amino derivatives, fatty acid salts, lecithin, etc.

Use of the Compositions

[0272] According to a third aspect, the present invention provides use of an explosive composition according to the first aspect to break and move ground, e.g. in mining operations.

[0273] According to a fourth aspect, the present invention provides the use of one or more density stabilisers to improve the sleep time of an explosive composition in reactive or metalliferous ground wherein the explosive composition comprises H_2O_2 and fuel.

FURTHER EMBODIMENTS OF THE INVENTION

[0274] According to an embodiment of the present invention, a method of preparing an explosive composition is provided comprising: combining hydrogen peroxide a density stabiliser and a sensitiser, wherein the sensitiser comprises a compressible material and/or bubbles of gas. It will also be appreciated that the invention relates to a method of preparing an explosive composition comprising combining hydrogen peroxide and one or more compounds which produce a sensitiser.

[0275] According to a further embodiment of the present invention, use of an explosive composition is provided comprising hydrogen peroxide and a density stabiliser and a sensitiser, wherein the sensitiser comprises a compressible material and/or bubbles of gas. It will be appreciated that the composition of the invention can be used for many purposes, but in particular to break and move ground in mining operations.

[0276] According to yet a further embodiment, the present invention provides a sensitised and sleep-time enhanced explosive composition that delays auto-sensitisation comprising H_2O_2, compressible material and/or bubbles of gas, and a density stabiliser.

[0277] In some embodiments the present invention consists essentially of H_2O_2, fuel, density stabiliser, and a sensitiser, wherein the sensitiser comprises a compressible material and/or bubbles of gas. In other embodiments the present invention consists essentially of H_2O_2, density stabiliser, fuel, a sensitiser, a thickener and/or crosslinker, wherein the sensitiser comprises a compressible material and/or bubbles of gas. In other embodiments the present invention consists essentially of H_2O_2, fuel, density stabiliser, a sensitiser, fuel, surfactant/emulsifier, a thickener and/or crosslinker, wherein the sensitiser comprises a compressible material and/or bubbles of gas.

[0278] In certain aspects, the present invention provides an explosive composition comprising: from about 2 to about 25% w/w H_2O_2; from greater than 0 and up to about 90% w/w one or more other oxidisers, and a density stabiliser.

[0279] In one embodiment, there is provided an explosive composition comprising: from about 2 to about 25% w/w H_2O_2; and from greater than 0 and up to about 90% w/w of one or more of other oxidisers; and from about 15 to about 25% w/w of fuels, preferably sustainable fuels, and a density stabiliser.

[0280] According to a preferred embodiment, the present invention provides an explosive composition comprising: from about 2 to about 25% w/w H_2O_2; from greater than 0 and up to about 90% w/w of one or more other oxidisers; a fuel phase; a thickener and/or crosslinker; a secondary fuel; a sensitiser, and a density stabiliser.

[0281] In some embodiments, the composition comprises from about 5 to about 25% w/w H_2O_2. Preferably the one or more other oxidiser(s) is a salt or acid selected from the group consisting of nitrate salts, perchlorate salts, peroxide salts, or nitric acid. For example, the one or more other oxidisers may be selected from the group consisting of nitrate salts, perchlorate salts, sodium peroxide, potassium peroxide and optionally nitric acid. The perchlorate salts may be selected from ammonium perchlorate and sodium perchlorate. Preferably the salts are selected from ammonium nitrate (AN), calcium nitrate (CN), calcium ammonium nitrate (CAN), sodium nitrate (SN), NH_4ClO_4, $NaClO_4$, Na_2O_2, K_2O_2 or mixtures thereof. For example, the nitrate salts may be selected from ammonium nitrate, calcium nitrate and sodium nitrate. By way of further example, the nitrate salts may be selected from calcium ammonium nitrate, calcium nitrate and sodium nitrate. In one embodiment, the explosive composition is devoid of AN. The one or more other oxidisers in the explosive composition may be selected from calcium nitrate and sodium nitrate. Preferably the explosive composition contains from 0.1 to 75% w/w of one or more other oxidisers. In one embodiment, the explosive composition contains from 0.1 to 75% w/w of dissolved salts. In a preferred embodiment, at least some of at least one of the one or more other oxidisers is not fully dissolved in the explosive composition but is present as a solid oxidiser, e.g., in the form of powder or prills. In such an embodiment, the one or more other oxidisers that is at least partially present as a solid may be selected from the group consisting of AN, SN, CN, CAN, or mixtures thereof. The composition may comprise a solid nitrate oxidiser, for example, in an amount of from contains from 0.1 to 70% w/w. The composition may comprise water. The solid nitrate oxidiser may be selected from the group of AN, SN, CAN or mixtures thereof.

[0282] In one embodiment, there is provided an explosive composition comprising:

[0283] from about 2 to about 85% w/w hydrogen peroxide; and

[0284] from about 2 to about 25% w/w of fuels, preferably sustainable fuels; and

[0285] from about 0.25 to about 5 of DTPMPA.Na.x

[0286] According to a preferred embodiment, the present invention provides an explosive composition comprising:

[0287] from about 2 to about 25% w/w hydrogen peroxide; and from greater than 0 and up to about 90% w/w of one or more other oxidisers; or from about 2 to about 85% w/w hydrogen peroxide;

[0288] from about 0.25 to about 3% w/w of DTPMPA.Na.x;

[0289] a fuel phase;

[0290] a thickener and/or crosslinker;

[0291] a secondary fuel; and

[0292] a sensitiser.

[0293] Preferably the composition comprises 50% w/w or less of water, or 30% w/w or less of water, or 25% w/w or less of water. The explosive composition may further comprise one or more other components selected from the group consisting of sensitisers, fuels, secondary fuels, water, thickeners, crosslinkers, emulsifiers, energy diluents and optionally other additives.

[0294] Preferably the explosive composition comprises a sensitiser. Preferably the sensitiser comprises a compressible material and/or bubbles of gas, or comprises a gas entrapped material. The bubbles of gas may be formed in situ and consist of N_2, O_2, CO_2, NO, or H_2 bubbles or a mixture thereof. The gas entrapped material may be selected from glass microballoons, ceramic microballoons, plastic microballoons or EPS with a particle size smaller than 2 mm. The explosive composition preferably has a density controlled by adding a sufficient amount of sensitiser such that the composition is detonation-sensitive. The density may be controlled to around 0.3 to 1.4 g/cm^3, or may be formulated to around 0.3 to 1.4 g/cm^3.

[0295] The composition may comprise a fuel, or it may comprise a fuel and a secondary fuel. The fuel may be a water soluble fuel. The water soluble fuel may be selected from an amine nitrate or urea or a mixture thereof. The explosive composition may contain from 0.1 to 30% w/w of water soluble fuel. The composition may contain between 13-25% w/w of the fuel phase. Preferably the fuel phase comprises one or more components selected from the group consisting of gums, glycerol, ethylene glycol, propylene glycol, sugar molasses, formamide or mixtures thereof. For example, the fuel phase may comprise one or more components selected from the group consisting of gums, glycerol, ethylene glycol, propylene glycol, formamide or mixtures thereof. The composition may comprise a sustainable fuel. The sustainable fuel may be present in the composition in an amount of between 15 and 25% w/w.

[0296] Preferably the composition is a watergel composition, in which case the composition may comprise a thickener or crosslinker. The composition may be a watergel composition comprising a thickener and a crosslinker. The thickener may be suspended in the fuel. The thickener may be selected from the group consisting of guar gum, xanthan gum, sodium alginate, polyacrylamides, and polyvinyl alcohols. The composition may comprise a crosslinker selected from the group of antimony salts, chromic salts, phosphoric acid or mixtures thereof. The fuel phase may comprise one or more water insoluble fuels selected from the group consisting of diesel, oils, vegetable oils, or mixtures thereof. Accordingly, the explosive composition may be formulated as an emulsion, in which case it may comprise an emulsifier. The emulsifier may be mixed in the fuel. The emulsifier may be selected from the group consisting of PIBSA-amine derivatives, SMO, lecithin or a mixture thereof.

[0297] Preferably the composition is formulated to have an oxygen balance between +10 to −10, e.g., the composition may have an oxygen balance of between +5 and −5. The explosive composition may contain from 1 to 800% v/v of an energy reducing agent (i.e., diluent material). The energy diluent material may be selected from the group consisting of EPS, crumb rubber tyre, popcorn, and plastic beads. The hydrogen peroxide, one or more other oxidisers and a fuel containing thickeners may be mixed until a thick material is formed, with a viscosity between 5-50 Pa*s. The composition may have a viscosity of from 5 to 50 Pa*s.

[0298] Many advantages result from the inventive explosive compositions taught herein. For example, certain formulations of the compositions of the invention may be more convenient to prepare, more cost effective compared to existing explosive compositions, safer to produce and to store, and/or capable of being produced in large quantities to meet the demand from the mining industry. Added safety and broader application is provided by the use of a density stabiliser to extend sleep-time. The present invention is therefore a significant advance in the art. The explosive compositions of the invention utilise H_2O_2, which is a sustainably-produced material that has a relatively low carbon footprint compared to other types oxidisers used in the art. The composition may also use sustainable fuels, as opposed to current technology used in the mining industry. To explain, current explosive compositions use a low concentration of fuel, which is typically sourced from the petrochemical industry. In contrast, the inventive explosive compositions disclosed herein are able to incorporate relative amounts of recycled fuel to commercially available or prior art explosive compositions. Accordingly, the recycled fuels from the petrochemical industry is a significant advance in the art. Additionally use of recycled fuels in the composition means that the amount of oxidiser material in the formulation can be balanced without affecting the detonation properties.

[0299] The present invention is counterintuitive to the common knowledge in the art. To explain, it is currently believed that it is impossible or very difficult to stabilise the density of compositions that has a relatively high concentration of H_2O_2. However, surprisingly, the present invention provides the ability to enhance the density stability of compositions that contain up to 42% w/w of H_2O_2. This aspect of the present invention is a significant advance in the art. The present invention also provides the ability to incorporate a relatively high amount of nitrates by making a watergel or emulsion, which already comprises H_2O_2/nitrate in the aqueous phase, with a further solid nitrate phase in the form of prills. Use of oxidiser in solid form enables some control over the density of the overall composition, and therefore provides some control over the VOD, as will be discussed below.

[0300] The explosive compositions of the invention may also be formulated into emulsion form. It will also be appreciated that the inventive compositions of the invention may produce low amounts of NO_x, and in some forms of the invention no NO_x at all.

[0301] The compositions of the invention are contemplated to provide several advantages over the prior art, such as better stability over time than explosive compositions comprising a higher percentage of H_2O_2. This is advantageous in the context of both safety, storage, and application. More specifically, the "sleep time" (i.e. the time over which an explosive deteriorates in situ such that its velocity of detonation decreases below a defined useful limit of such an explosive composition when it is in contact with rocks) is expected to be greater than an explosive comprising a higher percentage of H_2O_2. By way of example, a density-stabilised H_2O_2 composition according to the invention has been made and found to have a sleep time that is in excess of compositions without density stabilisers, and comparable/compatible for application in a commercially viable product, for example, a sleep time beyond 24 hours or more. It is therefore contemplated that larger blasts are possible because there is a longer time (e.g. several days) over which explosives can be loaded into many holes before the first-loaded explosive becomes unstable in its hole. More holes can therefore be loaded before detonation.

[0302] Another advantage is that these compositions detonate when density stabliisers are used. This is unexpected because of concerns that density-stabilised compositions may not detonate. There are also safety advantages contemplated in using density stabilised compositions.

[0303] The present invention relates to a peroxide-based explosive composition that is preferably prepared as watergel or water-in-oil emulsion and is sensitised.

[0304] Numerous embodiments are described in this patent application and are presented for illustrative purposes only. The described embodiments are not intended to be limiting in any sense. The invention is widely applicable to numerous embodiments, as is readily apparent from the disclosure herein.

[0305] Table 1 lists the components of explosive systems discussed herein and provides typical ranges for each:

TABLE 1

components for explosive systems discussed herein with typical ranges for each.

Component (in % by weight of total composition except where indicated otherwise)	Explosive technology	
	Watergel	Emulsion
H_2O_2	From 2 to 65	From 10 to 80
Density stabiliser	From 0.1 to 5	From 0.1 to 5
One or more other oxidiser	From 0 to 90	From 0 to 90
Sensitiser (% by volume)	From 0.5 to 800*	From 0.5 to 800*
Fuels	From 2 to 25	From 2 to 25
Secondary fuels	From 0.1 to 11	From 0.1 to 11
Water	From 5 to 40	From 5 to 40
Thickeners	From 0.5 to 5	N/A
Emulsifiers	N/A	From 0.5 to 5
Additives	0.1 to 5	0.1 to 5
Energy diluents (% by volume)	From 0.1 to 300**	From 0.1 to 300**
Oxygen Balance	From 5 to −5	From 5 to −5
Final densities (g/ml)	0.3 to 1.4	0.3 to 1.4

NOTE:
it will be appreciated that the volume can be increased by 8× (*), and 3× (**), respectively.

[0306] Typical components for each type of explosive technology are listed in Table 2:

TABLE 2

Typical components of the present invention for each type of explosive technology.

Component	Explosive technology	
	Watergel	Water-in-oil emulsion
Oxidiser(s)	hydrogen peroxide (H_2O_2) optionally nitrate salts and/or perchlorate salts and/or sodium/potassium peroxide	hydrogen peroxide (H_2O_2) optionally nitrate salts and/or perchlorate salts and/or sodium/potassium peroxide
Sensitiser	gas bubbles (chemically generated or injected bubbles) and/or gas	gas bubbles (chemically generated or injected bubbles) and/or gas

TABLE 2-continued

Typical components of the present invention for each type of explosive technology.

Component	Explosive technology Watergel	 Water-in-oil emulsion
	entrapped compressible materials	entrapped compressible materials
Fuel	Water miscible fuels, water immiscible fuels, water soluble fuels or water-insoluble fuels	Water miscible fuels, water immiscible fuels, water soluble fuels or water-insoluble fuels
Surfactant	water soluble surfactants or fuel-soluble surfactants	water soluble surfactants or fuel-soluble surfactants
Density stabiliser	e.g., Phosphonates	e.g., Phosphonates.
Composition stabiliser	Phosphates, Stannates, etc.	Phosphates, Stannates, etc
Additives	crosslinkerss, catalysts for gassing, pH adjusters, thickeners	crosslinkers, catalysts for gassing, pH adjusters, emulsifiers
Energy diluents (optional)	Granulated/shredded rubber, expanded popcorn, expanded rice, plastic beads, EPS >5 mm	Granulated/shredded rubber, expanded popcorn, expanded rice, plastic beads, EPS >5 mm
Energy deferments (optional)	Metal oxides	Metal oxides

EXAMPLES

[0307] The present invention can be used for a variety of forms of explosives provided of course that the principles of the invention as described herein are observed. The invention is further illustrated with reference to the following examples.

Example 1

[0308] Hydrogen peroxide/fuel-based hydrogel formulations, containing a glycerol fuel phase, were calculated and hand-made containing 0-3% w/w DTMPMA.Na.X material (See Table 3 below).

[0309] DTMPMA.Na.X was first suspended in the oxidiser phase, then mixed with the fuel phase of the formulation. Plastic pots (58 mL) were used to store the gels (n=4) on laboratory benches at room temperature (25-35° C.). Formulation density vs DTMPMA.Na.X % w/w were determined for the range of 0-3% w/w. Over seven days, density measurements were taken and change in density was calculated. Tests were terminated when gels displayed compromised structure due to large gas bubble generation.

TABLE 3

Explosive compositions prepared according to the present invention.

Component (w/w %)	Composition (w/w % phosphonate) 0	 1	 2	 3
hydrogen peroxide (100% w.w.)	41.8	41.5	41.1	40.8
water	41.8	41.5	41.1	40.8
glycerol fuel	13.4	13	12.8	12.4
xanthan gum-based explosive compositions	3	3	3	3
diethylenetriamine pentamethylene phosphonic acid sodium salt (DTPMPA.Na.x)	0	1	2	3

[0310] The results are shown in FIG. **1** and FIG. **2**. Whilst 0% w/w DTMPMA.Na.X formulation degraded within two days, the tests were allowed to continue until decomposition of all gels was observed.

TABLE 4

Density ($g \cdot cm^{-3}$) vs time (days) for explosive compositions having varying levels of phosphonates.

Time (days)	Density ($g \cdot cm^{-3}$) at Composition (% w/w phosphonate) 0	 1	 2	 3
0	1.25	1.25	1.25	1.25
1	1.06	1.21	1.21	1.21
2	0.88	1.16	1.16	1.16
3	—	1.13	1.13	1.13
4	—	1.02	1.02	1.04
7	—	0.76	0.76	0.76

Note,
0% w/w phosphonate mixture collapsed by day 3.

TABLE 5

Density loss (% to initial) vs time for explosive compositions having varying levels of phosphonates.

Time (days)	Density loss (% to initial) at Composition (% w/w phosphonate) 0	 1	 2	 3
0	0	0	0	0
1	15.2	1.2	2.2	3
2	29.6	4	5.2	7
3	—	7.4	8.2	9.4
4	—	16.6	16.6	16.6
7	—	40	40	40

Note,
0% w/w phosphonate mixture collapsed by day 3.

[0311] Formulations without density-stabilised hydrogen peroxide degraded within 48 hours, whereas density-stabilised hydrogen peroxide compositions at the same time period exhibited approx. 7 percent density loss to the initial density. This is a significant and surprising improvement. This improvement to sleep time means that more blast holes can be loaded during a planned blast saving time and money, that the detonation performance of the product has enhanced reliability, and that the product has improved safety due to the reduced likelihood of density loss.

Example 2

[0312] Detonation performance analysis was carried out in field-range unconfined tests to assess the explosive capability and characteristics of density-stabilised hydrogen peroxide compositions 81.35% w/w hydrogen peroxide (50% w/w), 12.65% w/w glycerol fuel, 3% w/w xanthan gum, and 3% w/w DTPMPA.Na.x formulation, incorporating varying % w/w GMB (3M™ K15 Glass Bubbles) for required density (See table 4 below).

TABLE 6

Detonation testing of explosive compositions prepared according to the present invention.

	Density ($g \cdot cm^{-3}$)				
Component (w/w %)	0.83	1.0	1.03	1.05	1.08
hydrogen peroxide (100% w/w)	39.4	39.8	40	40	40.06
water	39.4	39.8	40	40	40.06
glycerol fuel	12.25	12.35	12.4	12.45	12.46
xanthan gum-based explosive compositions	2.9	2.9	2.925	2.9525	2.96
diethylenetriamine pentamethylene phosphonic acid sodium salt (DTPMPA.Na.x)	2.9	2.9	2.925	2.9525	2.96
GMB, (3M ™ K15)	3.15	2.25	1.75	1.6	1.5
Average Velocity of Detonation ($m \cdot s^{-1}$)	3628	4210	4337	4334	4401

[0313] Triplicate samples were prepared of explosive compositions.

[0314] The results are shown in FIG. **3**.

[0315] As can be seen from these examples, the density loss and instability of the hydrogen peroxide-based explosives was reduced, with the addition of phosphonates, increasing the sleep-time of the formulations. The use of hydrogen peroxide/fuel-based explosives prepared with the addition of phosphonates results in a substantial improvement in the art of hydrogen peroxide/fuel-based explosives. Importantly, the addition of density stabilisers as described herein does not adversely impact on the detonation performance of the explosive composition.

Detonation Testing

[0316] Selected compositions were tested to determine detonation. 47 mm diameter, clear high density (150 μm) polyethylene lay-flat tube by 1000 mm in length and sealed on one end were used for gels. Detonation was initiated with a 25 g Pentex D Booster.

[0317] Duplicate VOD was measured using a Time Domain Reflectometry (TRD)-based VOD instrument featuring a sample rate of under 4 uS and a nominal resolution of 90 Pico seconds. The VOD data indicate an acceptable detonation performance for mining applications.

Example 3

[0318] Stabilised-hydrogen peroxide/fuel-based hydrogel formulations, containing a glycerol fuel phase, were calculated and hand-made containing 0-2% w/w Phytic Acid (PA). PA was first suspended in the oxidiser phase, then mixed with the fuel phase (3% xanthan gum) of the formulation. Plastic pots (~58 mL) were used to store the gels (n=4) on laboratory benches at room temperature (20-25° C.). Product density vs PA % w/w were established for the range of 0-5% PA. Over 13 days, density measurements were taken and change in density was calculated. Tests were terminated when gels displayed compromised structure due to large gas bubble generation. Whilst 3-5% w/w PA degraded within 5 days, the tests were allowed to continue until decomposition of all gels was observed.

[0319] Over two tests, of 10 days and 13 days respectively, it was observed that all gels decreased in density. All initial gel densities were approx. 1.22 $g \cdot cm^3$. With increasing % w/w PA an associated increase in gel density was observed (FIG. **4** & FIG. **5**). Gels containing 3-5% w/w PA degraded within five days. At approximately seven days the rate of degradation of the nil-PA control appears to change, which may be an indicator of HP degradation nearing completion. Whilst 0.25% w/w PA displayed the least density loss over the time course (FIG. **6** & FIG. **7**), statistically significant loss over 13 days was not determined between nil-PA and 0.25% w/w PA gels (p-value=0.19). Over the measurement time, individual pot measurement standard deviations of replicants did not exceed 0.02 mL.

[0320] Formulations containing PA at concentrations of 0.25-0.75% w/w displayed increased gel stability over 13 days. However, PA at concentrations above about 0.75% accelerated decomposition. After 13 days of room temperature bench-top storage, all gels, including mixtures containing PA, had lost at least 18% gel density when compared to initial density.

[0321] The skilled addressee will understand that the invention comprises the embodiments and features disclosed herein as well as all combinations and/or permutations of the disclosed embodiments and features.

[0322] Although the invention has been described with reference to specific examples, it will be appreciated by those skilled in the art that the invention may be embodied in many other forms. In particular features of any one of the various described examples may be provided in any combination in any of the other described examples.

1. An explosive composition comprising:

H_2O_2;

fuel; and

one or more density stabilisers of about 0.01% to about 10% w/w.

2. The explosive composition according to claim **1**, wherein the H_2O_2 is between about 2% to about 85% by weight.

3. The explosive composition according to claim **1**, wherein the one or more density stabilisers are in an amount of about 1% to about 5% w/w.

4. The explosive composition according to claim **1**, wherein the one or more density stabilisers comprises a phosphonate having the structure X—$(PO_3Y_2)_n$, wherein:

X is selected from the group consisting of an optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cycloalkyl, optionally substituted heterocycloalkyl, optionally substituted alkenyl, optionally substituted aryl, and optionally substituted heteroaryl;

Y is H or a water-soluble cation; and

n is 1 to 10.

5. The explosive composition according to claim **4**, wherein the phosphonate is selected from the group consisting of: phytic acid, aminotris(methylenephosphonic acid), bis(hexamethylene triamine penta (methylene phosphonic acid)), diethylenetriamine penta(methylene phosphonic acid), tetramethylenediaminetetra(methylenephosphonic acid), hydroxyethylidene-1,1-diphosphonic acid, hydroxyethylamino-di(methylene phosphonic acid), hexamethylene diamine tetra (methylene phosphonic acid), 2-hydroxyphosphono acetic acid, nitrilotrimethyl-phosphonic acid, polyamino polyether methylene phosphonic acid, 2-phosphonobutane-1,2,4-tricarboxylic acid, glyphosate, foscarnet, perzinfotel, selfotel, N-(phosphonomethyl)iminodiacetic acid, 2-carboxyethyl phosphonic acid, vinylphosphonic acid, aminomethylphosphonic acid, N,N-bis (phosphonomethyl)glycine, and tetramethylenediaminetetra (methylenephosphonic acid), and salts, solvates, dimers, and stereoisomers thereof.

6. The explosive composition according to claim **4** wherein the phosphonate is diethylenetriamine pentamethylene phosphonic acid sodium salt.

7. The explosive composition according to claim **1**, wherein the density stabiliser retains the density of the explosive composition to within +/−10% of its initial density, and wherein the density is maintained over a period of up to 10 days.

8. (canceled)

9. The explosive composition according to claim **7**, wherein the density stabiliser maintains the velocity of detonation (VOD) to within +/−10% of the initial VOD, and wherein the VOD is maintained over a period of up to 14 days.

10. (canceled)

11. The explosive composition according to claim **1**, further comprising 50% w/w or less of water.

12. The explosive composition according to claim **1**, further comprising one or more components selected from the group consisting of: one or more other oxidisers, a sensitiser, a secondary fuel, a thickener, a crosslinker, an emulsifier, and an energy diluent.

13. The explosive composition according to claim **12**, wherein the sensitiser comprises a compressible material and/or bubbles of gas.

14. The explosive composition according to claim **13**, wherein the bubbles of gas are formed in situ and consist of N_2, O_2, CO_2, or H_2 bubbles, or a mixture thereof.

15. The explosive composition according to claim **13**, wherein the compressible material is gas-entrapped material which is selected from glass microballoons, ceramic microballoons, plastic microballoons or expanded polystyrene (EPS) with a particle size smaller than 2 mm.

16. The explosive composition according to claim **15**, wherein a sufficient amount of sensitiser is added such that the composition is detonation-sensitive, and wherein the density of the explosive composition is controlled to around 0.3 to 1.4 g/cm^3.

17. (canceled)

18. (canceled)

19. The explosive composition according to claim **13** comprising from about 0.1% to about 75% w/w one or more other oxidisers.

20. (canceled)

21. (canceled)

22. (canceled)

23. The explosive composition according to claim **12**, wherein the thickener is selected from the group consisting of guar gum, xanthan gum, sodium alginate, polyacrylamides, and polyvinyl alcohols.

24. (canceled)

25. (canceled)

26. The explosive composition according to claim **12**, wherein the composition is formulated as an emulsion or a watergel.

27. The explosive composition according to claim **1**, wherein the explosive composition contains from 2% to 25% w/w fuel, wherein the fuel comprises one or more water insoluble fuels selected from the group consisting of diesel, oils, paraffinic oils, naphthenic oils, and vegetable oils, or mixtures thereof.

28. (canceled)

29. (canceled)

30. (canceled)

31. (canceled)

32. A method of preparing an explosive composition, the method comprising combining H_2O_2, fuel and one or more density stabilisers of about 0.01% to about 10% w/w.

33. (canceled)

34. (canceled)

* * * * *