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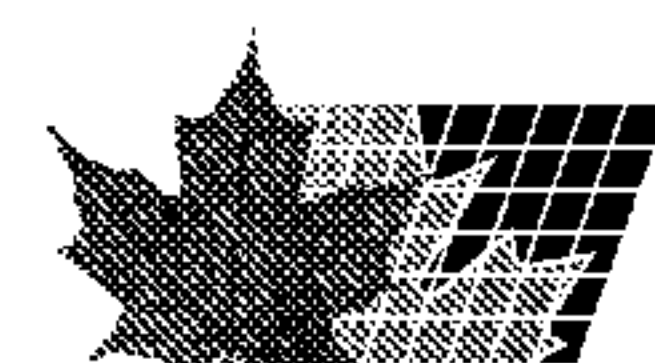
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(54) Titre : COMPOSITION EXPLOSIVE AMELIOREE
(54) Title: IMPROVED EXPLOSIVE COMPOSITION

(57) **Abrésumé/Abstract:**

An explosive composition comprising hydrogen peroxide and a sensitizer, wherein the sensitizer comprises a compressible material having one or more gas-filled voids and/or bubbles of gas. The sensitizer is included in a detonation-sensitive concentration, and the explosive composition is preferably adapted to retain the sensitizer in a substantially homogenous dispersion throughout. The invention also relates to a method of preparing an explosive composition comprising combining hydrogen peroxide and a sensitizer, wherein the sensitizer comprises a compressible material and/or bubbles of gas, and use of said explosive composition.



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(57) Abstract: An explosive composition comprising hydrogen peroxide and a sensitizer, wherein the sensitizer comprises a compressible material having one or more gas-filled voids and/or bubbles of gas. The sensitizer is included in a detonation-sensitive concentration, and the explosive composition is preferably adapted to retain the sensitizer in a substantially homogenous dispersion throughout. The invention also relates to a method of preparing an explosive composition comprising combining hydrogen peroxide and a sensitizer, wherein the sensitizer comprises a compressible material and/or bubbles of gas, and use of said explosive composition.

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IMPROVED EXPLOSIVE COMPOSITION

RELATED APPLICATIONS

The present application claims the benefit of Australian provisional patent application number 2011903076 filed on 27 July 2011, the disclosure of which is
5 incorporated herein by reference.

FIELD OF THE INVENTION

The present invention relates to an improved explosive composition. More particularly, the invention relates to a peroxide-based explosive composition which provides several advantages over the prior art, such as a reduction in the production of
10 toxic nitrogen oxides (NO_x) in the after-blast fumes. The invention has been developed primarily for use as a hydrogen peroxide-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.

15 BACKGROUND OF THE INVENTION

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
20 that such prior art is widely known or forms part of common general knowledge in the field.

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

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
30 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, other salts (calcium nitrate, sodium nitrate, etc) to depress the crystallisation point of the AN solution, and other additives

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such as guar gum (as thickener) and fuel (diesel). 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
5 compositions to slurries, however, crosslinkers can be added to enhance the water resistance of the product. Watergels can be aerated or gassed with bubbles chemically generated *in situ* or mixed with glass/plastic microspheres to lower the density, improve sensitivity and change the levels of energy delivered to the ground being blasted.

One of the drawbacks of watergels and slurries is that there is a limit of AN
10 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 US Patent No. 3,447,978). 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.
15 Emulsions can also be blended with ANFO in different ratios. Watergels can be aerated, gassed with bubbles chemically generated *in situ* or mixed with glass/plastic microspheres to lower the density, improve sensitivity velocity of detonation (VOD) and change the levels of energy delivered to the ground being blasted.

Despite the development of AN emulsions, AN slurries and watergels, however,
20 there is still a need to develop improved explosives, which are preferably more cost effective compared to existing explosive compositions and are capable of being produced in large quantities to meet the high demand from industry. Preferably any explosive composition which can be substituted for an AN-based explosive is insensitive to misfires and is not desensitised by wet blast holes. Furthermore, preferably any AN
25 substitute is a sustainable raw material which has a relatively low carbon footprint, and which can be manufactured relatively easily and preferably near the actual mine site to minimise transport issues. In addition, preferably any AN substitute can be produced on an as-needs basis to minimise the need for stockpiling and to increase safety. Further still, preferably any AN substitute can be used in slurry or in emulsion form so that
30 existing equipment can be used, and when in slurry form or is emulsified such that the viscosity enables pumping without difficulty. 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 cross linkable *in-situ* to increase viscosity down the blast hole.

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Despite of the advances on the types of composition 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 eliminate NO_x emissions or preferably reduces the production of NO_x.

One material that is also an oxidiser and that has the potential to meet at least some of these needs is hydrogen peroxide (HP). Use of HP as a liquid explosive has been patented by Shanley (US Patent No. 2,452,074) in which HP was mixed with glycerol and water, and initiated with a detonator. US '074 teaches that to achieve detonation the explosive compositions can only contain up to 52 wt% water. In 1962 a patent was granted to Baker (US Patent No. 3,047,441) in which HP was mixed with a range of different combustibles (wood products, hulls, metals, etc). Mixtures of HP and gelforming materials (corn starch) were also disclosed. The mixtures were sensitive to detonation with No. 6 blasting caps, but no velocities of detonation (VOD) were disclosed.

More recently, in 1990 mixtures of HP and water soluble resins were patented by Bouillet as a packaged explosive (US Patent No. 4,942,800). Examples provided in the patent show that some of the mixtures detonated at velocities above 6,000 m/s (in 33 mm diameter, unconfined blasts). Also, work published by Shell Co. (*Concentrated Hydrogen peroxide, summary of research data on safety limitations*, 1961) presents the detonation limits of the system HP-acetic acid-water in a ternary diagram. In 2004 an investigation into the detonation properties of HP and alcohols was published (*"Investigation of explosive hazard of mixtures containing hydrogen peroxide and different alcohols"*, *Journal of Hazardous Materials*, A108 pp. 1-7, 2004).

Despite these prior art examples of HP-based explosives, there is still a need to develop improved explosive compositions. In particular, there is a need to develop HP-

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fuel-water explosive compositions in which the sensitivity, density, velocity of detonation (VOD) and the delivery of the energy can be controlled.

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.

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SUMMARY OF THE INVENTION

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. 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.

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According to a first aspect the present invention provides an explosive composition comprising hydrogen peroxide and a sensitiser, wherein the sensitiser comprises a compressible material and/or bubbles of gas. Preferably the compressible material includes one or more gas-filled voids.

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Preferably the composition further includes other additives, such as fuel, water, stabilisers (either thickeners or emulsifiers), 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.

25

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, either as complete or partial replacements of HP. Non-limiting examples include nitrates salts, perchlorates salts, sodium/potassium peroxide, etc.

30

The preferred concentration of HP in the composition of the invention is between about 25% to 85% by weight. By way of example only, a concentrated HP 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 HP concentration in the composition is around 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, or 85% (w/w). Preferably the HP concentration in the composition is around between about 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

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80, or 80 to 85 % (w/w).

The present invention relies on sensitisation of a hydrogen peroxide 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. Sensitisation of AN-based explosive compositions is known in the art. In particular, it is known to sensitise by the addition of solid materials, high explosives, and the addition of micro balloons and gas bubbles. However, sensitisation of peroxide-based compositions is not commonly practiced in the art. Without wishing to be bound by theory, it is believed that because HP in high concentration may detonate as it is relatively unstable to impact or friction, explosive engineers have steered away from its use. However, it has been found that lower concentrations of HP (safer to impact or friction) can be formulated which can be made explosive by sensitisation. It has been surprisingly found that sensitisation of HP by use of compressible or low density materials containing gas-filled voids, or bubbles of gas provides explosive compositions which are superior to those taught in the prior art.

Preferably the explosive composition of the invention is adapted to retain the sensitiser in a substantially homogenous dispersion. It will be appreciated that a variety of techniques can be utilised to achieve this property, as discussed further below.

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 a preferred pre-determined explosive range. Preferably the final density is controlled with sensitiser to around 1.25 to 1.3 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 final density of the composition is formulated to be 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, or 1.3 to 1.4 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.

The skilled person will appreciate that a mathematical conversion will be required to convert the weight of glass/plastic micro balloons to yield a certain density, to volume (for gas bubbles). However, irrespective of the type of sensitisation, it will be

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appreciated that the final density is controlled to a predetermined value to yield an explosive composition and to thereby control the parameters discussed above.

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 HP, which is a sustainably-produced raw 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 or emulsion form. It will also be appreciated that the inventive compositions of the invention produce reduced amounts of NO_x, and in preferred forms of the invention no NO_x at all.

Sensitisers

The explosive compositions of the present invention comprise a discontinuous gaseous component to sensitise the composition. Once the explosive is sensitised, it can be easily initiated by a primer, 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. The gaseous component is incorporated into the compositions of the present invention as fine gas bubbles dispersed throughout the composition. Alternatively, hollow gas-filled compressible particles such as micro balloons, or porous particles, or mixtures thereof are included. 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.

Suitable chemicals for the *in situ* generation of gas bubbles include HP itself which can be decomposed with 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. 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. Examples of porous materials include expanded minerals such as perlite, fly ash or hollow particles that are a by-product of

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coal fired power stations

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 0.1 to 1.4 g/cm³.

5 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
10 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 large 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
15 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.

As discussed above, the introduction of gas bubbles can be provided by a variety of techniques, which are all applicable to the present invention. In one embodiment the
20 bubbles may be 'trapped' during the preparation of the explosive composition or by their formation through a chemical reaction. In US Patent 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 stabilization is described. US Patent No. 3,582,411 describes a watergel explosive formulation which contains a foaming agent of the guar
25 gum type modified by hydroxy groups. In US Patent 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. Incorporation of gas bubbles by means of their generation as a result of a chemical reaction is also described in the following
30 prior art (see for example US Patent No.'s 3,706,607; 3,711,345; 3,713,919; 3,770,522; 3,790,415 and 3,886,010).

Various gases in bubble form have been used to sensitise blasting agents, for example nitrogen (see US Patent No.'s 4,875,951; 4,305,766; and 3,390,030), carbon dioxide (see US Patent No.'s 3,288,658 and 3,390,032), oxygen (see US Patent No.'s

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3,706,607; 5,397,399; 4,081,299 and 3,617,401), and hydrogen (see US Patent No. 3,711,345). It is also known to directly inject air or gas into the explosive mixture (see for example US Patent No.'s 6,537,399; 3,582,411 and 3,642,547).

As discussed above, in other embodiments the compressible material is hollow
5 microspheres such as glass or plastic micro balloons, which are suspended in the composition. Preferably the microspheres/micro balloons contain gas such as pentane, etc. In alternative embodiments, the compressible material is a cellular material, such as expanded polystyrene (EPS), polyurethane foam, cotton seeds, expanded pop corn, husks, etc. In related embodiments the compressible material is any low density
10 material which has a specific gravity $< 1.0 \text{ g/cm}^3$. In brief summary, examples of glass balloons can be seen in US Patent No.'s 4,326,900 and 3,447,978, and plastic micro balloons in US Patent No.'s 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 US Patent No.'s 5,470,407 and 5,271,779. Other types of
15 sensitising materials can be used in the compositions of the invention, e.g. TNT, HMX, RDX and aluminium or silicon powder.

Watergel-technology for HP-based explosive compositions

Fuels for watergels

HP-based watergels can be prepared with either water-miscible or water
20 immiscible fuels. Water-soluble fuels which can be used with the present invention can be selected from the group consisting of: glycerol, sugar, amine nitrates, hexamine and urea. Water-insoluble fuels which can be used with the present invention can be selected from the group consisting of: include aliphatic, alicyclic and aromatic compounds and mixtures thereof which are in the liquid state at the formulation
25 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
30 liquid hydrocarbons generally referred to as petroleum distillates such as gasoline, kerosene, fuel oils, paraffin oils and vegetable oils or mixture thereof.

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

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concentration of about 5, 10, 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).

Thickeners and crosslinkers

5 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 HP-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
10 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
15 sensitising material in a homogeneously dispersed state throughout the composition.

 If desired the aqueous solution of the compositions of the present invention may comprise thickening agents which optionally may be crosslinked. The thickening agents, 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
20 or xantham gum or guar gum or derivatives thereof such as hydroxypropyl guar gum. 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 thickening agents
25 include synthetic polymeric materials and in particular synthetic polymeric materials which are derived, at least in part, from the monomer acrylamide.

 Typically, the thickening agent component of the compositions of the present invention comprises from 0 to 5% by weight of the total composition.

 As indicated above, when used in the compositions of the present invention, the
30 thickening agent may be crosslinked. 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.

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Typically, the crosslinking agent component of the compositions of the present invention comprises from 0 to 0.5% and preferably from 0 to 0.1% by weight of the total composition.

Emulsion-technology for HP-based explosive compositions

5 Fuels for emulsions

HP-based emulsions can be prepared with water-immiscible fuels. 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 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..

Typically, the organic fuel or continuous phase of the HP-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).

Emulsifier/Stabiliser

HP-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 emulsifying agents. The emulsifying agent is adapted or chosen to maintain phase separation.

The emulsifying agent component of the composition of the present invention may be chosen from the wide range of emulsifying agents known in the art for the preparation of water-in-oil emulsion explosive compositions. Examples of such emulsifying agents 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

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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. Among the preferred emulsifying agents 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.

Typically, the emulsifying agent component of the composition of the present invention comprises up to 5% by weight of the total composition. Higher proportions of the emulsifying agent 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 emulsifying agent 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 emulsifying agent and for reasons of economy it is preferable to keep to amount of emulsifying agent used to the minimum required to have the desired effect. The preferred level of emulsifying agent used is in the range from 0.1 to 2.0% by weight of the total composition.

Secondary fuels for watergels and emulsions

If desired, other optional fuel materials, hereinafter referred to as secondary fuels, may be incorporated into the compositions of the present invention in addition to the water-immiscible organic fuel phase. Examples of such secondary fuels include finely divided solids, and water-miscible organic liquids. Examples of solid secondary fuels include finely divided materials such as: 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. Typically, the optional secondary fuel component of the compositions of the present invention comprise from 0 to 20% by weight of the total composition.

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Other oxidisers for watergel and emulsion HP-based explosive compositions

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

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

pH

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 preferably 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.

Preparation of composition

The HP-based compositions of the present invention may be prepared by a number of methods.

In one preferred method of manufacture the HP-based watergel type compositions may be prepared by combining hydrogen peroxide with 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. Finally, sensitising agents are mixed into said watergel capable in an amount capable to sensitise said watergel.

In one preferred method of manufacture the HP-based emulsion type compositions may be prepared by: combining hydrogen peroxide with said water-immiscible organic phase, a water-in-oil emulsifying agent, with rapid mixing to form a water-in-oil emulsion; then mixing until the emulsion is uniform. Once the emulsion is

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formed, solid ingredients (fuels, energy diluting agents, etc) are optionally mixed into said watergel. Finally, sensitising agents are mixed into said watergel in an amount capable of sensitising said watergel.

Viscosity of the HP-based compositions

5 The viscosity of the HP-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. 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
10 greater than 10Pa*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 35Pa*s. The range 10 to 25Pa*s provides the most efficient entrainment of gas bubbles by mechanical mixing.

Energy diluents(optional)

15 In the context of this invention, energy diluting agents 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 hydrogen peroxide-based explosive. In some cases these energy diluting agents are able
20 to reduce the density of the HP-based composition without increasing the sensitivity. Examples of these diluents materials are granulated/shredded rubber (from tyres), cotton seeds, saw dust, husk, expanded pop corn, plastic beads, wool meal, saw dust, bagasse, peanut and oat husks, peanut shells etc. US Patent No. 5,409,556 describes some example of these energy reducing agents. These materials could also be used in
25 combination with sensitising agents to offer more flexibility as far as the performance properties of the hydrogen peroxide-based explosive is concerned. Therefore another advantage of the HP-based explosive is that the performance properties of the explosive can be altered to suit the characteristics of the blasting site.

30 Possible variations of this general procedure will be evident to those skilled in the art of the preparation of emulsion explosive compositions. In one preferred embodiment the HP-based explosive compositions of the invention comprise the following components: HP:fuel:water in the range between 25%:5%:70% to 73%:11%:16%.

Table 1 lists the components of explosive systems discussed herein and provides typical ranges for each.

	Watergel	Emulsion
HP (% by weight)	From 25 to 64	From 27 to 80
Other oxidiser (% by weight)	From 0 to 60	From 0 to 60
Sensitiser (% by volume)	From 1 to 800*	From 1 to 800*
Fuels (% by weight)	From 8 to 12	From 7 to 12
Secondary fuels (% by weight)	From 0.1 to 11	From 0.1 to 11
Water (% by weight)	From 21 to 67	From 8 to 71
Thickeners (% by weight)	From 0.5 to 5	N/A
Emulsifiers (% by weight)	N/A	From 0.5 to 5
Additives (% by weight)	0.1 to 5	0.1 to 5
Energy diluting agents (% by volume)	From 1 to 300**	From 1 to 300**
Oxygen Balance	From 3 to -10	From 3 to -10
Final densities (g/ml)	0.1 to 1.40	0.1 to 1.40

Table 1: components for explosive systems discussed herein with typical ranges for each. NOTE: it will be appreciated that the volume can be increased by 8x (*), and 3x(**), respectively.

According to a second aspect the present invention provides a method of preparing an explosive composition comprising combining hydrogen peroxide 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.

According to a third aspect the present invention provides use of an explosive composition comprising hydrogen peroxide 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.

According to a fourth aspect the present invention provides a sensitised explosive composition comprising hydrogen peroxide and compressible material and/or bubbles of gas.

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In some embodiments the present invention consists essentially of hydrogen peroxide and a sensitiser, wherein the sensitiser comprises a compressible material and/or bubbles of gas. In other embodiments the present invention consists essentially of hydrogen peroxide, a sensitiser, a thickener and/or crosslinker, wherein the sensitiser
5 comprises a compressible material and/or bubbles of gas. In other embodiments the present invention consists essentially of hydrogen peroxide, a sensitiser, fuel, 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 hydrogen peroxide, a sensitiser, fuel, surfactant/emulsifier, a thickener and/or
10 crosslinker, wherein the sensitiser comprises a compressible material and/or bubbles of gas.

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.

15

BRIEF DESCRIPTION OF THE DRAWINGS

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

Figure 1 is a schematic outlining the preparation of a HP-based watergel explosive composition according to the invention; and

Figure 2 is a schematic outlining the preparation of a HP-based water-in-oil emulsion explosive composition according to the invention.

DEFINITIONS

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.

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'.

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'.

The terms 'preferred' and 'preferably' 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. 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.

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.

As used herein the term "sensitiser" is meant to define voids that can increase the sensitivity to detonation of energetic materials. Examples are air bubbles, entrapping air, and material like micro balloons/spheres.

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

PREFERRED EMBODIMENT OF THE INVENTION

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.

The present invention relates to a peroxide-based explosive composition that is preferably prepared as watergel or water-in-oil emulsion, and is sensitised. Typical components for each type of explosive technology are listed in Table 2.

Element	Explosive technology	
	Watergel	Water-In-oil emulsion
Oxidiser agent	hydrogen peroxide optionally nitrate salts and /or perchlorate salts and/or sodium / potassium peroxide	hydrogen peroxide optionally nitrate salts and /or perchlorate salts and/or sodium / potassium peroxide
Sensitiser	gas bubbles (chemically generated or injected bubbles) and/or compressible materials	gas bubbles (chemically generated or injected bubbles)and/or compressible materials
Fuel	water soluble fuels or water- insoluble fuels	water soluble fuels or water- insoluble fuels
Stabilisers	thickeners	emulsifiers
Additives	cross linking agents, catalysts for gassing, pH adjusters	cross linking agents, catalysts for gassing, pH adjusters
Energy diluents (optional)	Granulated / shredded rubber, expanded popcorn, expanded rice, plastic beads	Granulated / shredded rubber, expanded popcorn, expanded rice, plastic beads

Table 2: Typical components of the present invention for each type of explosive technology.

Preparation of watergel HP-based explosive composition

Watergel explosive compositions made according to the present invention preferably include HP in concentrations between 25 – 64% by weight.

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

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.

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.

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

It will be appreciated that for an HP-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. In accordance with the present invention this may be achieved by formulating the explosive as a stable watergel. Formation of such forms of 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.

As discussed above, any conventional thickening agent may be used with the present invention. The thickener may be selected from natural gums, such guar gum,

xanthan gum, sodium alginate, carboxymethylcellulose, 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.

Crosslinkers can also used with the present invention. Thickening agents in
5 combination with crosslinkers can improve the water resistance and mechanical strength of the HP-based explosive. Examples of crosslinkers are those from antimony, calcium, titanium, chromium, borate salts and dichromate salts, etc.

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

10 Preparation of water-in-oil HP-based explosive composition

Water-in-oil explosive compositions made according to the present invention include hydrogen peroxide in concentration between 25 – 85% by weight. It will also be appreciated that other oxidisers can be combined with HP, as discussed above. For example nitrate salts, perchlorate salts, amine nitrates, sodium / potassium
15 peroxide, etc., can be also incorporated in combination with HP.

The fuel can be any fuel such as diesel fuel. 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.

Secondary fuels may be a solid hydrocarbon, such as coal and recycled plastic
20 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.

Preferably the amount of these fuels materials in the formulation can be adjusted
25 so the HP-based composition has an oxygen balance between 3 and -10 and the HP-based composition can be easily pumped..

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.
30 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).

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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.

5 Sensitisation of watergel or water-in-oil emulsions HP-based compositions

The present invention relates to the use of HP-based composition and a specific class of sensitisers. As discussed above, sensitising agents include gas bubbles generated in situ or injected air or air/gas entrapped material. A further example of sensitisation for hydrogen peroxide-based explosives is the decomposition *in situ* of a portion of the
10 hydrogen peroxide with permanganates (or other ions) to form oxygen gas bubbles. Another example to produce gas bubbles is the decomposition of carbonates with acid in situ to form carbon dioxide bubbles. Examples of air entrapped material for sensitisation for hydrogen peroxide-based explosives are glass or plastic microballoons, expanded polystyrene beads, polyurethane foam, etc, as discussed above. Another example of
15 sensitisation is the combination of both gas bubbles (chemically generated and or injected) and air entrapped material.

Watergel or water-in-oil HP-based explosive compositions made according to the present invention include sensitisers in concentration between 1 – 800% by volume. (i.e. the volume can be increased by 8x).

20 Energy-diluting agents

In the context of this invention, diluting agents could be used to replace part of the mass of the HP-based composition and thus reduce the energy output. These energy-diluting agents may increase, decrease or not alter the density of the HP-based composition. Examples of these energy-diluting energy agents are granulated shredded
25 rubber (from tyres), plastic beads, cotton seeds, saw dust, husk, expanded pop corn, plastic beads, wool meal, saw dust, bagasse, peanut and oat husks, peanut shells etc. These diluents material could also be used in combination with sensitising agents to offer more flexibility as far as the performance properties of the HP-based explosive is concerned. Therefore another advantage of the HP-based explosive is that the
30 performance properties of the explosive can be altered to suit the characteristics of the blasting site.

Watergel or water-in-oil HP-based explosive compositions made according to the present invention include energy-diluting agents in concentration between 0 – 800% by volume. As a result, the use of the additives (sensitising agent and energy-diluting

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agents), provides a better control of the density, VOD and energy delivery in the ground being blasted. Therefore an additional advantage of the HP-based explosive is that it could be used in a range of density between 0.1 g/ml to 1.40 g/ml.

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

Examples

In example 1 to 3 suspensions of various gelling agents in glycerol were formed by gently stirring the ingredients, and then a solution of hydrogen peroxide 50% by
10 weight was added. Gentle stirring was applied until the mixture became a gel within 60 seconds.

In example 4 to 6, blends of gelling agents and sugar were prepared, followed by the addition of a solution of hydrogen peroxide 50% by weight with gentle stirring. The mixture became a gel within 5 minutes.

15 In Examples 7 to 8, fuels were heated up to 40°C and emulsifier added. The mixture was stirred for 1 minute to dissolve the emulsifier, and then the mixture was place in a container and mixed at 400 rpm. A solution of hydrogen peroxide 50% by weight was slowly added during mixing over about 8 minutes. The resulting product has a paste-like consistency. Compositions from 1 to 8 were stable over time.

20

Compositions (weight percent)									
water gel							water-in-oil emulsion		
	1	2	3	4	5	6	7	8	
hydrogen peroxide 50% w/w	82.6	82.6	81.0	82.0	82.0	81.0	91.6	93.0	
glycerol	14.4	14.4	16.0						
sugar				15.0	15.0	16.0			
guar gum	3.0			3.0					
xanthan gum		3.0			3.0				
sodium alginate			3.0			3.0			
vegetable oil (peanut)							6.4		
diesel								5.0	
P3000							2.0	2.0	
oxygen balance	-1.45	-1.34	-0.36	-0.88	-0.77	-1.14	-3.31	-1.42	
density (g/ml)	1.19	1.19	1.19	1.21	1.21	1.21	1.13	1.14	

Table 3: Explosive compositions prepared according to the invention.

P3000 is an emulsifier manufactured by Croda chemicals.

5 Detonation testing

Selected compositions were tested to determine detonation. PVC pipes 50 mm in diameter by 600 mm in length, sealed on one end were used. VOD was measured using the D' Autriche method.

	Composition				
	2	3	3	6	7
Sensitiser	air + EPS ⁽¹⁾	GMB ⁽²⁾	O ₂ ⁽³⁾	CO ₂ ⁽⁴⁾	GMB ⁽⁵⁾
Density (g/ml)	0.55	0.93	0.80	1.05	0.81
Primer	Booster 50 g	Booster 50 g	Booster 50 g	Booster 50 g	Booster 50 g
VOD (m/s)	2100	4200	2800	3600	2400

Table 4: Sensitised explosive compositions primed with a 50g booster and resulting VOD measurements.

Note (1) - Composition 2 had a density after entrapping air of 0.89 g/ml. A 0.1% by weight (or 25% by volume) of expanded polystyrene, density 4 g/L, was mixed into the composition, producing a final density of 0.55 g/ml.

Note (2) - Composition 3 was mixed with 2.5% (or 25% by volume) of glass micro balloons (GMB), from 3M, density 100 g/L.

Note (3) - Composition 3 was gassed using 5% of a KMnO₄ solution (0.3% w/w). Composition gassed quickly. Bubbles were lost when pouring into the testing pipe.

Note (4) - Composition 6 was sensitised with a combination of 1.8% of a citric acid solution (10% w/w) and 2% of a solution NaHCO₃ (4% w/w). The product was detonated 90 minutes after adding the gassing agents.

Note (5) - Composition 3 was mixed with 3.75% of glass micro balloons (GMB) (or 37.5% by volume) from 3M, density 100 g/L.

In order to tests whether or not samples were sensitive to detonation without the presence of sensitiser, sample 6 was initiated with a detonator and with a 50 g booster (see Table 5).

	Formula number	
	6	6
Sensitiser	none	none
Density (g/ml)	1.21	1.21
Primer	Detonator No. 8	Booster 50 g
VOD (m/s)	failed	failed

Table 5: Sample 6 with no sensitiser present and resulting VOD data.

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The examples above show that a HP-based explosive composition will not detonate unless sensitiser is incorporated into the composition. Accordingly, it is clear to the skilled person that the above examples fall within the scope of the claims.

Although the invention has been described with reference to specific examples, it
5 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.

CLAIMS:

1. An explosive composition comprising hydrogen peroxide and a sensitiser included in a detonation-sensitive concentration, wherein the sensitiser comprises bubbles of gas incorporated by mechanical agitation, injection by bubbling said gas through said composition or by *in situ* generation of said gas by chemical means, wherein the concentration of hydrogen peroxide in the composition is between about 25% to 80% w/w.
2. A composition according to claim 1 further comprising nitrate salts and/or perchlorate salts and/or sodium/potassium peroxide.
3. A composition according to claim 1 or claim 2 wherein a sufficient amount of said sensitiser is included such that the density of said composition is between around 0.1 to 1.4 g/ml.
4. A composition according to any one of the preceding claims wherein *in situ* generation of gas bubbles is provided by the decomposition of chemicals compounds that can produce O₂, CO₂, N₂, H₂, NO or combinations thereof.
5. A composition according to any one of the preceding claims further comprising a gas-filled compressible material selected from small hollow microspheres of glass or resinous materials or porous materials, and combinations thereof.
6. A composition according to claim 5 wherein said microspheres are sized between about 20 to 2000 micron and have a bulk density of less than 1000 g/L.
7. A composition according to claim 5 or claim 6 wherein said gas-filled compressible material is perlite or fly ash.
8. A composition according to any one of claims 5 to 7 wherein said compressible material further comprises a cellular material selected from expanded polystyrene, polyurethane foam, and combinations thereof.
9. A composition according to any one of the preceding claims wherein an additional energetic material is included and is selected from TNT, HMX, RDX and aluminium powder and combinations thereof.
10. A composition according to any one of the preceding claims wherein said composition is formulated as a watergel or an emulsion.
11. A composition according to claim 10 further comprising a water-miscible fuel selected from the group consisting of glycerol, sugar, mono methyl ammonium nitrate, hexamine and urea.

12. A composition according to claim 11 wherein said water-miscible fuel is included at 5 to 25% by weight of the total composition.
13. A composition according to any one of claims 10 to 12 wherein said watergel composition is adapted to retain the sensitiser in a substantially homogenous dispersion.
14. A composition according to any one of the preceding claims further comprising a thickener and/or a crosslinker for retaining said sensitiser in a substantially homogenous dispersion.
15. A composition according to claim 14 wherein said thickener is selected from locust bean gum, guar gum, hydroxypropyl guar gum, sodium alginate, and heteropolysaccharides, and combinations thereof.
16. A composition according to any one of claims 14 to 15 wherein said thickener is included at from 0 to 5% by weight of the total composition.
17. A composition according to claim 14 wherein said crosslinker is selected from salts containing zinc, calcium, titanium, antimony, chrome, and combinations thereof.
18. A composition according to claim 17 wherein said crosslinker is included at from 0.1 to 0.5% by weight of the total composition.
19. A composition according to claim 10 further comprising a water-immiscible fuel selected from the group consisting of: fuel oil, diesel oil, distillate, kerosene, naphtha, waxes, paraffin oils, benzene, toluene, xylenes, asphaltic materials, low molecular weight polymers of olefins, animal oils, fish oils, and other mineral, hydrocarbon or fatty oils, and mixtures thereof.
20. A composition according to claim 19 wherein said water-immiscible fuel is included at 7 to 12% by weight of the total composition.
21. A composition according to any one of claims 19 to 20 wherein the emulsion composition is adapted to retain the sensitiser in a substantially homogenous dispersion by an emulsifier.
22. A composition according to claim 21 wherein said emulsifier is selected from polyisobutylene succinic acid (PIBSA) reacted with amines, PIB-lactone and its amino derivatives, 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.

23. A composition according to any one of claims 21 to 22 wherein said emulsifier is included at up to 5% by weight of the total composition.
24. A composition according to any one of the preceding claims further comprising a secondary fuel selected from sulphur, aluminium, gilsonite, comminuted coke or charcoal, carbon black, abietic acid, glucose or dextrose, starch, nut meal, grain meal, wood pulp, methanol, ethylene glycol, formamide and methylamine, and combinations thereof.
25. A composition according to claim 24 wherein said secondary fuel is included at 0.1 to 12% by weight of the total composition.
26. A composition according to any one of the preceding claims further comprising a secondary oxidiser selected from nitrate salts, perchlorate salts, sodium/potassium peroxide and combinations thereof.
27. A composition according to any one of claims 11 to 26 wherein the viscosity of the emulsion or watergel explosive composition is in the range 10 to 50 Pa*s.
28. A composition according to any one of the preceding claims further comprising an energy diluting agent selected from granulated/shredded tyres rubber, expanded rice, expanded pop corn, expanded wheat, and combinations thereof.
29. A composition according to any one of claims 14 to 28 wherein the explosive composition comprises hydrogen peroxide:fuel:water in the range between 24%:4%:72% to 73%:8.75%:18.25% (wt%).
30. A method of preparing an explosive composition comprising combining hydrogen peroxide and a sensitiser, said sensitiser being included in a detonation-sensitive concentration and wherein said sensitiser comprises bubbles of gas incorporated by mechanical agitation, injection by bubbling said gas through said composition or by *in situ* generation of said gas by chemical means, wherein the concentration of hydrogen peroxide in the composition is between about 25% to 80% w/w.

31. A method according to claim 30 wherein said concentration of said hydrogen peroxide is partially substituted with nitrate salts and/or perchlorate salts and/or sodium/potassium peroxide.
32. A method according to claim 30 or claim 31 further comprising the step of adding a sufficient amount of said sensitiser such that the density of said composition is between around 0.1 to 1.4 g/ml.
33. A method according to any one of claims 30 to 32 wherein said *in situ* generation of gas bubbles is provided by the decomposition of chemicals compounds that can produce O₂, CO₂, N₂, H₂, NO and combinations thereof .
34. A method according to any one of claims 30 to 33 wherein said composition further comprises gas-filled compressible material selected from small hollow microspheres of glass or resinous materials or porous materials, and combinations thereof.
35. A method according to claim 34 wherein said microspheres are sized between about 20 to 2000 micron and have a bulk density of less than 1000 g/L.
36. A method according to claim 34 or claim 35 wherein said gas-filled compressible material is perlite or fly ash.
37. A method according to any one of claims 34 to 36 wherein said compressible material further comprises a cellular material selected from expanded polystyrene, and polyurethane foam, and combinations thereof.
38. A method according to any one of claims 30 to 37 further comprising the step of adding an additional energetic material selected from TNT, HMX, RDX and aluminium powder and combinations thereof.
39. A method according to any one of claims 30 to 38 comprising the step of formulating said composition as a watergel or an emulsion.
40. A method according to claim 39 further comprising adding a water-miscible fuel selected from the group consisting of: glycerol, sugar, mono methyl ammonium nitrate, hexamine and urea.
41. A method according to claim 40 wherein said water-miscible fuel is included at 5 to 25% by weight of the total composition.
42. A method according to any one of claims 40 to 41 wherein the watergel composition is adapted to retain the sensitiser in a substantially homogenous dispersion.
43. A method according to claim 42 wherein said sensitiser is retained in a substantially homogenous dispersion by use of a thickener and/or a crosslinker.

44. A method according to claim 43 wherein said thickener is selected from locust bean gum, guar gum, hydroxypropyl guar gum, sodium alginate and heteropolysaccharides, and combinations thereof.
45. A method according to any one of claims 43 to 44 wherein said thickener is included at from 0.1 to 2% by weight of the total composition.
46. A method according to claim 43 wherein said crosslinker is selected from salts containing zinc, calcium, titanium, antimony, chrome and combinations thereof.
47. A method according to claim 46 wherein said crosslinker is included at from 0.1 to 0.5% by weight of the total composition.
48. A method according to claim 39 further comprising the step of adding a water-immiscible fuel selected from the group consisting of: fuel oil, diesel oil, distillate, kerosene, naphtha, waxes, paraffin oils, benzene, toluene, xylenes, asphaltic materials, low molecular weight polymers of olefins, animal oils, fish oils, and other mineral, hydrocarbon or fatty oils, and mixtures thereof.
49. A method according to claim 48 wherein said water-immiscible fuel is included at 7 to 12% by weight of the total composition.
50. A method according to claim 48 or claim 49 wherein said emulsion is adapted to retain said sensitiser in a substantially homogenous dispersion by use of an emulsifier.
51. A method according to claim 50 wherein said emulsifier is selected from polyisobutylene succinic acid (PIBSA) reacted with amines, PIB-lactone and its amino derivatives, 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.
52. A method according to any one of claims 50 to 51 wherein said emulsifier is included at up to 5% by weight of the total composition.

53. A method according to any one of claims 30 to 52 further comprising the step of adding a secondary fuel selected from sulphur, aluminium, gilsonite, comminuted coke or charcoal, carbon black, abietic acid, glucose or dextrose, starch, nut meal, grain meal, wood pulp, methanol, ethylene glycol, formamide and methylamine, and combinations thereof.
54. A method according to claim 53 wherein said secondary fuel is included at 0.1 to 12% by weight of the total composition.
55. A method according to any one of claims 30 to 54 further comprising the step of adding a secondary oxidiser selected from nitrate salts, perchlorate salts, sodium/potassium peroxide and combinations thereof.
56. A method according to any one of claims 39 to 55 wherein the viscosity of the emulsion or watergel explosive composition is in the range 10 to 50 Pa*s.
57. A method according to any one of the preceding claims 30 to 56 further comprising the step of adding an energy diluting agent selected from granulated/shredded tyres rubber, expanded rice, expanded pop corn, expanded wheat, and combinations thereof.
58. A method according to any one of claims 30 to 57 wherein the explosive composition comprises hydrogen peroxide:fuel:water in the range between 24%:4%:72% to 73%:8.75%:18.25% (wt%).
59. Use of an explosive composition comprising hydrogen peroxide and a sensitizer included in a detonation-sensitive concentration, wherein the sensitizer comprises bubbles of gas incorporated by mechanical agitation, injection by bubbling said gas through said composition or by *in situ* generation of said gas by chemical means, wherein the concentration of peroxide in the composition is between about 25% to 80% w/w.

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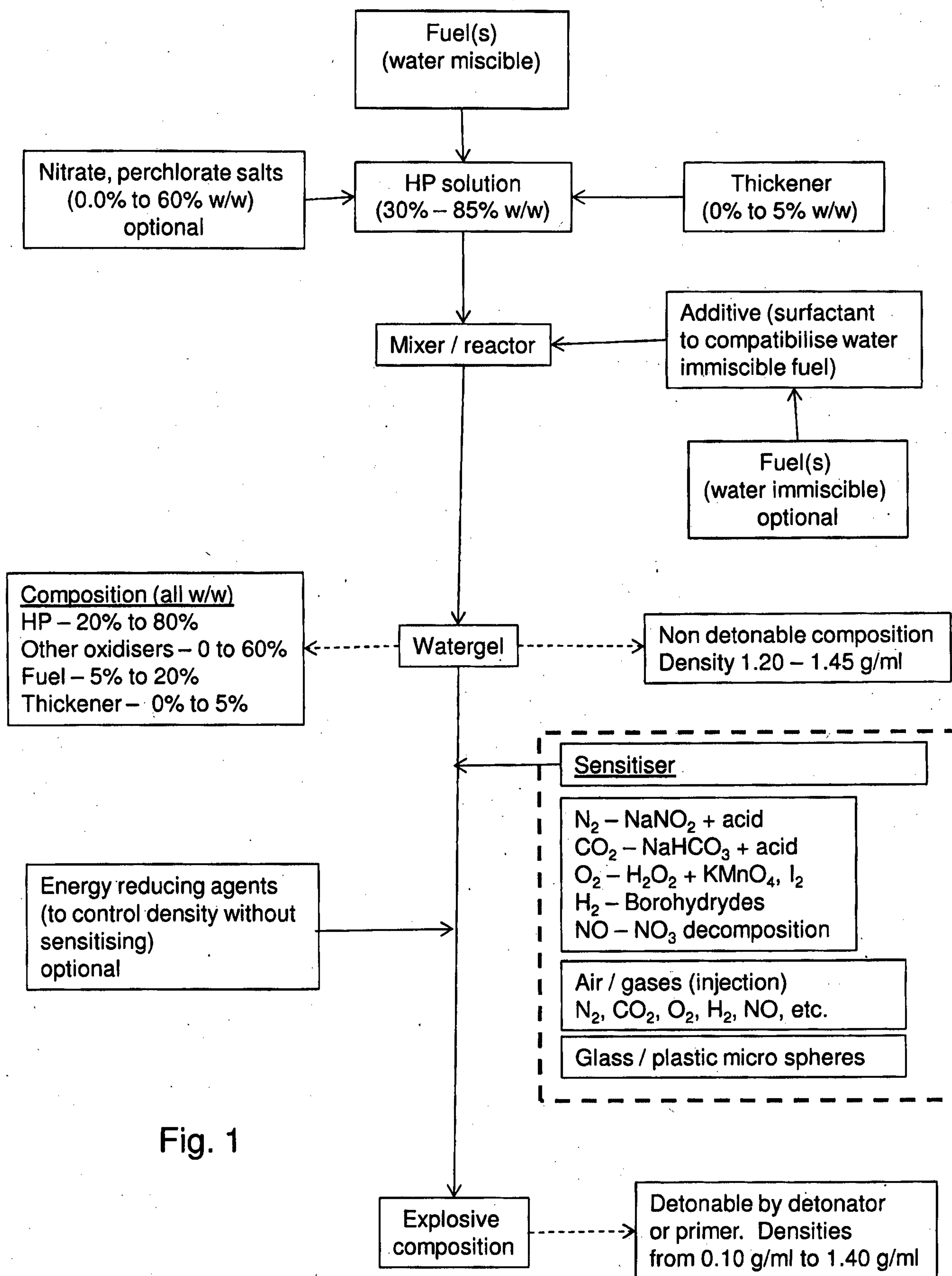


Fig. 1

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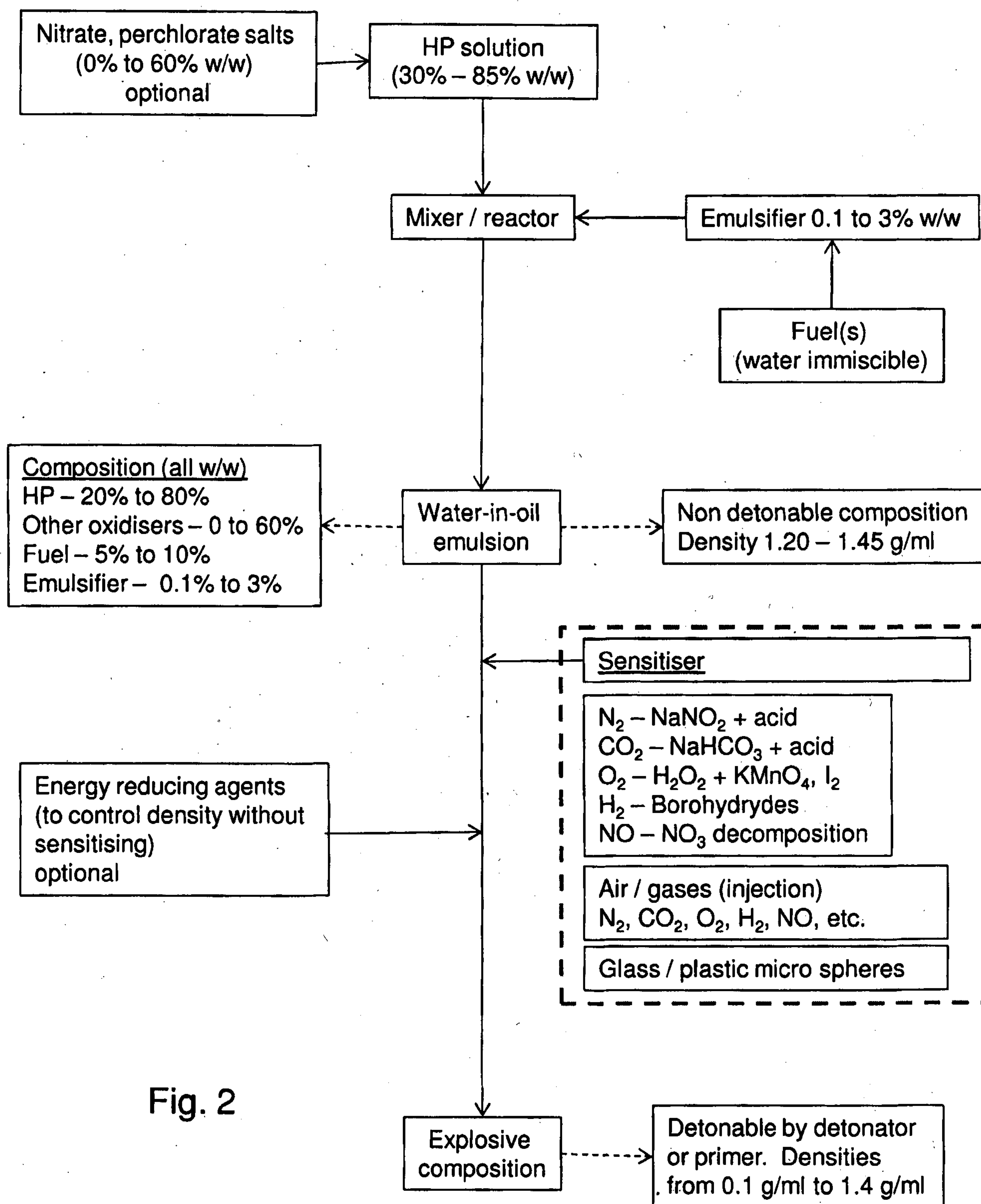


Fig. 2