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(54) **COMPOSITION FOR FORMING A HYDROGEN PEROXIDE BASED EMULSION EXPLOSIVE**

(57) A composition for forming a hydrogen peroxide-based emulsion explosive which composition comprises; an oxidizer-phase comprising at least 15% by weight of hydrogen peroxide and at least 15% by weight of water, a fuel-phase comprising at least one oil type

fuel, an emulsifier and at least one finely divided solid adsorbent, wherein the oxidizer-phase is discontinuously dispersed throughout the continuous fuel-phase. A method of preparing an emulsion type explosive composition is also disclosed.

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Description**Field of invention**

5 **[0001]** The present invention relates to a composition for forming an emulsion type hydrogen peroxide-based explosive. The invention also relates to a method of preparing such a composition. The composition may be used e.g. in mining, construction and similar applications for rock blasting. However, it will be appreciated that the invention is not limited to this particular field of use.

10 **Background of the invention**

[0002] The following background 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.

15 **[0003]** Civil explosives formulated as emulsions are well known in the art and are commonly used in the mining- and civil construction blasting industry, both in bulk and cartridge form. Emulsion explosives are normally water-in-oil type dispersions consisting of a discontinuous aqueous oxidizer phase normally consisting of nitrate salts dissolved in water and a continuous fuel phase consisting of various water insoluble fuels (normally oils) and emulsifiers. The two phases are combined in a continuous or batch mixing process which normally implements pressurized high shear mixing.

20 **[0004]** In practice, most available civil explosives are based on nitrate salts where Ammonium nitrate (AN) is predominantly used. It is well known that AN is a strong oxidizer and have been used in the industry for at least 60 years in various forms.

25 **[0005]** Upon detonating nitrate based explosives, large quantities of toxic nitrogen oxide (commonly referred to as NO_x) gas is produced in the post detonation fumes. These gases are lethal to humans and must be removed before personnel may enter the blast site post blast. The gases linger for an extended amount of time which leads to downstream issues such as contamination of ecological systems and pollution. Further, nitrate residues in the blasted rock or undetonated explosives forms nitrogen leaching which pollutes water based ecological systems and ground water. These problems are well known in the mining and construction industry and are directly related to the use of ammonium nitrate. It is therefore desirable to investigate the use of alternative oxidizers which preferably should be nitrogen free. Ideally these oxidizers should exhibit good detonation performance comparable to status quo and improve on the environmental and health aspects of the explosive.

30 **[0006]** Hydrogen peroxide (HP) is known to be a suitable candidate and prior art research proposes various explosive compositions. HP is nitrate free and decomposes to water and oxygen in the detonation process. The oxidizing properties of HP can also be used as a replacement for traditional nitrate salt oxidizers. The idea of using HP is not new; Baker & Groves where granted a patent for an HP based explosive composition (US7491279B1) and another was granted to Bouillet *et. al* in 1990 (US4942800A). For clarity, the use of the term HP denotes hydrogen peroxide in combination with water in various concentrations combined with known hydrogen peroxide stabilizers such as phosphonic acid.

35 **[0007]** PCT patent WO 2013/013272 (Araos) and PCT patent WO 2020/243788 A1 (Kettle) represents some of the most recent research in the field and proposes various types of water gel and emulsion type explosives bases on hydrogen peroxide. Araos and Kettle mainly focus on water gel technology and argues that HP based compositions could be a relevant alternative to AN based mining explosives. Kettle builds on Araos work and argues that the compositions proposed by Araos suffers from too low shelf life making them difficult to use practically. Kettle proposes the addition of density stabilizers which in the context are described as HP stabilizers (i.e., phosphonates). These have shown to have a stabilizing effect on the density of the HP based explosive compositions. Kettle (as Araos) does not give any insight nor results on emulsion formulations.

40 **[0008]** Commercially available HP is normally solved in water and is normally supplied with phosphonate acids or similar compounds as the stabilizing effects on HP are well known. As an example, US patent 8802613B2 (Bonislawski, Lovetro) from 2007 gives an example of the stabilizing characteristics of various phosphonic acids and other compounds when added into the HP solution. HP solutions with varying concentration of such stabilizers are readily available which implies that the HP stabilizer, i.e. phosphonic acid is de-facto added to the explosive via the HP solution.

45 **[0009]** As for HP based emulsion explosives, tests have shown that even if emulsifiers used therein are pre-heated and combined with viscous oils, emulsification is still difficult once the temperature decreases to sub 25 degrees, this is especially true if oxygen balance must be kept in a reasonable interval between +1 to -4%.

50 **[0010]** Another problematic aspect of the emulsion compositions is the process of sensitization. Test show that addition of glass hollow spheres (micro balloons) used as sensitizer for emulsion explosives, tend to quickly destabilize and separate these emulsions. If hydrogen peroxide decomposition catalysts are used as sensitizer, it has been found that controlling the gassed density is very difficult due to the movement capabilities of the catalyst particles inside the emulsion.

In practice, such emulsions are not practically applicable due to their inherent instability and sensitization incompatibility.

[0011] T. Halme argues in Development of nitrogen free environmentally friendly blasting explosive (Helsinki EFEE Conference Proceedings 2019, R. Holmberg *et al*) that HP has been the main alternative to nitrates in explosives and shows detonation and performance data from water gel HP explosives which are comparable to ANE compositions.

[0012] The properties of HP are well known. Among the known risks is the peroxide's highly reactive nature in combination with many materials commonly found in the mining and construction industry. HP decomposes to water and oxygen in an exothermic reaction which may lead to explosive type events. This decomposition can be aggressive and occur if impurities with catalytic behaviour enters the solution, in particular, alkaline materials, metals and some organic compounds may cause such reaction. Risk of aggressive reactivity which may lead to explosive events increases with higher concentration HP solutions (over 60%) and in particular if the HP solution is combined with organic fuels such as sugars, alcohols or similar which is the case for water gel type explosives.

[0013] Additional factors affect the decomposition reaction such as stabilizers in the HP, pH, reactants and temperature. Normally, a 50% HP solution is stabilized to maintain a pH between 1,6-2,2. Higher pH levels makes the solution more prone to decomposition. HP solutions at these pH levels are normally very stable if pure and it is normal that when stored in suitable tanks in cool temperatures the concentration in the solution decreases with no more than 1% annually.

[0014] Controlling temperature in the HP solution is imperative to safety as a rising temperature destabilizes the peroxide. As the decomposition is exothermic, an increasing temperature could be sign of contamination which may in a worst-case scenario lead to an explosive type event. Therefore, it is important to maintain storage temperature ranges for HP from -20° C to +25° C.

[0015] Reactivity makes HP based explosives, in particular water gel type compositions, challenging to handle, use safely, and store. Water gels with high HP concentrations (over 40%) can react aggressively with alkaline, sulfuric or mineral rock types commonly found in blast holes. The risks from the reactive behaviour of the HP itself in combination with catalytic fuels is the main reason why HP based explosives have been discarded as an unsafe alternative and not used in the industry.

[0016] Ammonium nitrate-based emulsions (ANE) contain high concentrations of salt dissolved in the discontinuous aqueous phase. AN is highly hygroscopic which allows for high solubility in water. The solubility in water is an endothermic process and proportional to the solution's temperature where a higher temperature increases solubility and possible concentrations (saturation maximum). The potency and performance of the explosive is directly proportional to the concentration of oxidizer available in the aqueous phase. It is therefore desirable to dissolve as much AN as possible to partly allow for a higher oxygen concentration, partly to minimize water content and also to increase density of the emulsion. Therefore, nitrate-based emulsions use hot AN solution as aqueous oxidizer phase where temperatures of the solution ranges from 60° C to 85° C. In some aspects, other nitrate salts such as sodium or calcium nitrate salts or alkaline salts are added.

[0017] It is important in this context to note that the solution is saturated at or close to this temperature. This implies that if the temperature of the solution drops under the saturation temperature, crystallization occurs where solid AN salt crystals are formed inside the solution in an amount relative to the change in temperature. The aqueous oxidizer phase must therefore be kept at or above the saturation temperature in the solution storage tank and during the emulsification process, else the emulsion will crystallize which affects quality and performance. Moreover, crystallization inside process equipment causes clogging in pipes etc. and is a well-known process problem.

[0018] To ensure temperature control in the ANE process, hot water or steam from boilers are traditionally used in a heating system which runs parallel or coaxial to the emulsification process equipment piping and functions. This makes ANE plants large, expensive and complicated to construct and design.

[0019] Heating nitrate solutions and ensuring temperature consistency is complex, expensive and requires high amounts of energy and is in general an operational risk and manufacturing challenge. Therefore, it is desirable to design emulsion explosives compositions which do not exhibit similar crystallization tendencies and which are able to form stable emulsions in a cold process not requiring strict temperature control and heating.

[0020] Modern bulk emulsion explosives used in the mining and civil industries today are made insensitive to detonation to allow for greater safety during production, transport and storing. The sensitisation process is normally conducted by mechanical agitation of gassing chemicals and emulsion just before the explosive is pumped into the drill hole where the sensitisation (gassing) process evolves and sensitizes the explosive. The emulsions need an addition of a sensitizer to reach detonability. This sensitizer commonly comprises small gas filled voids/bubbles distributed evenly throughout the explosive composition. Upon detonation, these gas voids are compressed and thereby generate high temperatures forming so called "hot-spots" in the explosive.

Definitions

[0021] Without wishing to be bound by any theory, the terms employed in the present invention should have the following meaning;

Adsorption - Shall mean the ability and tendency of a solid particle to cling to the dissimilar particles or surfaces formed by the liquids in the peroxide-based composition.

[0022] *Coalescence* - Shall mean the process by which the droplets of the two immiscible liquids in an emulsion pulls together to form larger droplets which destabilizes the emulsion and eventually separates the two liquids.

[0023] *Emulsion* - Shall mean a liquid dispersed and suspended in another liquid in the form of finely divided droplets and is a mixture between two immiscible liquids. An emulsion has higher viscosity than any of the immiscible liquids.

[0024] *Emulsifier*- Shall mean a chemical molecule with at least one lipophilic moiety and at least one hydrophilic moiety which may form a multi molecular film around the dispersed particles and may stabilize the two immiscible liquids by increasing the kinetic stability of the composition.

[0025] *Wetting* - Shall mean the ability of a liquid to establish and maintain contact with a solid surface as a result of an intermolecular interaction between the solid and liquid through Adsorption.

[0026] *Solid adsorbent*- Shall mean solid particles, or mixture of solid particles which cannot be solved into HP, water or oil. The particles may however be dispersed or suspended in a liquid medium.

[0027] *Finely divided* - shall mean a material in a powder or pellets form, including particles suspended or dispersed in a liquid medium.

[0028] *Surfactant*- Shall mean compounds that lower the surface tension between two liquids. Surfactant shall in this context have the same meaning as *Emulsifier*.

Summary of the invention

[0029] An object of the invention is to offer an explosive composition which significantly improves on the environmental aspects of blasting compared to nitrate based explosives and minimizes or avoids the generation of toxic NO_x gas in the post detonation fumes and does not leach any nitrates. Another objective is to offer an emulsion type explosive composition which is easy to manufacture and achieves high stability using cold ingredients. A further object of the invention is to offer an emulsion explosive composition which can be manufactured in a process not requiring heating.

[0030] The present invention relates to explosives for use in the mining and civil construction industries and similar fields. These examples should not be considered limiting as it can be expected that other fields might be applicable such as underwater blasting, agriculture or oil well blasting.

[0031] According to one aspect of the invention, there is provided a composition for forming a hydrogen peroxide based emulsion explosive as set out in appended claim 1. The composition comprises a oxidizer-phase comprising at least 15% by weight of hydrogen peroxide and at least 15% by weight of water, a fuel-phase comprising at least one oil type fuel, at least one emulsifier and at least one finely divided solid adsorbent. The oxidizer-phase is discontinuously dispersed throughout the continuous fuel-phase.

[0032] Work has been conducted to investigate properties of emulsion type HP based explosives which are able to reliably detonate using lower concentrations of HP (50% or less) combined with improvements in stability and non-reactivity. It has been found that emulsion type HP explosives are significantly less reactive compared to HP based water gel formulations.

[0033] It has been discovered that a water-in-oil type emulsion HP composition significantly prohibits mass transfer or movement of HP inside the explosive, therefore, emulsions should be considered significantly more stable compared to water gels from a reactivity perspective. This assumes stable consistency of the composition which must stay in an emulsified state to ensure the bond between the HP and the fuel oil droplets over the storage and use period. HP emulsion explosives have also been proven to deliver blast results comparable to AN based emulsion and offer an attractive, nitrate-free and more environmentally friendly alternative.

[0034] HP emulsions made from the teachings of the prior art have been proven to be difficult to emulsify in lower temperatures. One reason for this is the very high viscosities of commercially available emulsifiers. Conventionally, the emulsifier must be heated and solved in a low viscous oil to enable solubility and by extension allow for high contact surface between emulsifier and oil once added to the continuous oil phase. This implies the need to use low viscosity oils which in turn lead to a relatively low viscosity in the emulsion itself.

[0035] A relationship between emulsion viscosity and reactivity exists where a low viscous emulsion allows for a higher degree of movement of potential impurities as well as a larger contact surface between the HP droplets and potential impurity particles which may catalyse HP decomposition. Hence, from a stability perspective, it is desirable to achieve high emulsion viscosities which requires the use of more viscous oils.

[0036] It has been seen that it is possible to produce Hydrogen peroxide water-in-oil emulsions in a cold production process using a hydrogen peroxide solution as discontinuous oxidizer phase dispersed in a combination of oil and emulsifiers as continuous fuel phase. However, test show that the stability and ability to form consistent emulsions are challenging. In particular, this is the case if the oxidizer and fuel phases are cold and if the oil phase are of higher viscosity (> 25 000 cP). Cold temperatures in this context should be understood as temperatures below 25° C.

[0037] Selection of oils and emulsifiers affects the ability to form a stable emulsion at cold temperatures and often,

inconsistent stability over time is noted. It is also to be noted that emulsions might exhibit apparent stability but once gassing (chemical or mechanical addition of gas voids or micro balloons) is preformed these emulsions tend to separate and destabilize rapidly.

[0038] Tests also show that even if emulsifiers are pre-heated and combined with viscous oils, emulsification is still difficult once the temperature decreases to sub 25 degrees, this is especially true if oxygen balance must be kept in a reasonable interval between +1 to -4%.

[0039] Another problematic aspect of the known emulsion compositions is the process of sensitization. Test show that addition of hollow spheres (gas filled hollow micro balloons) commonly used as sensitizer for emulsion explosives, tend to quickly destabilize and separate these emulsions. If hydrogen peroxide decomposition catalysts are used as sensitizer, it has been found that controlling the gassed density is very difficult due to the movement capabilities of the catalyst particles inside the emulsion. In practice, such emulsions are not practically applicable due to their inherent instability and sensitization incompatibility.

[0040] Surprisingly, it has been found that combining traditional emulsifiers with finely divided solids having adsorbing characteristics in the continuous oil phase significantly increases the stability of HP based emulsions and prevents droplet coalescence. This improves the stability in general and particularly during incorporation of a sensitizer. By adding a certain amount of a finely divided solid adsorbent into the oil phase, it has been found that effective and rapid emulsification can be achieved using emulsifiers and oils in temperature ranges from 0 °C and upwards.

[0041] At least a portion of the solid adsorbent particles may be wetted by both the oxidizer and the fuel phase. Emulsions are mixtures of two or more liquids which are normally immiscible. Water insoluble fuel (oil) and water-soluble aqueous oxidizer (HP solution) droplets are bonded by a thin film of emulsifier molecules. The emulsifier molecule's lipophilic moiety bonds to the surface of an oil droplet and the hydrophilic moiety bonds to the surface of a proximate aqueous droplet forming a film between the droplets and bonding them through a polar/non-polar bonding force. Such bonding films are normally only a few molecules thick and the de-facto thickness is defined by the molecular structure of the emulsifier. For all technical purposes, the thickness of the emulsifier bonding film can be assessed to be in the range of molecules thick.

[0042] By adding finely divided solid adsorbents with the ability to be wetted by both the oxidizer and oil phase another barrier (film) between the HP and oil droplets may be formed. This barrier which comprises solid particles, are magnitudes thicker than the barrier formed by the emulsifier molecules.

[0043] The wetting binding of the solid particles between the oil and HP phases are weaker compared to the polar/non-polar binding of the colloidal emulsifier but physically adds a stronger protective film around the droplets. This implies that even if the solid particles add a stronger film, in absence of an emulsifier, they do not offer any improvement in stability as the droplets would not bond effectively and coalescence would occur. However, the combination of conventional colloidal emulsifiers together with at least one finely divided solid adsorbent significantly increases stability as the droplets are more protected from penetration of possible impurities, additives or reactants such as sharp edges found in glass micro balloons or from the pressure formed by expanding gas in the case of using chemical gassing agents or from edges in the blast hole rock wall.

[0044] The ability of the solid particles to be wetted by both the oil- and HP phases also allows the particles to homogenize even in cold and highly viscous oil phases and emulsifiers during high shear mixing. It has been seen that such solid adsorbent particles significantly improve the solubility of emulsifiers into oil, even at cold temperatures and as an extension the particles allows for a larger surface area during cold emulsification ensuring effective droplet bonding

[0045] According to an embodiment, the composition may further comprise a sensitizer, whereby the composition forms a sensitized emulsion explosive. Such sensitized explosive may be formulated to become detonation enabled (explosive) i.e. to be ready to be detonated with traditional initiation means such as a detonator of conventional strength with or without an amplification charge (booster or primer) such as normally used in blasting.

[0046] To reach detonability and to control performance factors such as density, critical diameter and velocity of detonation the emulsion explosive composition described herein must be sensitized. The preferred method of sensitization for the current invention is the use of gas filled voids by either in-situ generation of bubbles using chemical gassing agents or by adding hollow microspheres (commonly known as glass, plastic or cellulose micro balloons) or by injection of gas. In this context, the use of "sensitizer" refers to small bubbles of gas or compressible materials.

[0047] The sensitizer may be added as a part of a pumping and charging process where the sensitizer is added and dispersed throughout the composition just before the sensitized composition is pumped into a blast hole, or, the sensitizer may be added in a process where the sensitized composition is loaded into a package to be used at a later stage.

[0048] Keeping the sensitizer and emulsion composition separate just until the moment of charging ensures that the risk of accidental initiation during production, transporting or handling is minimized. It further allows the operator to control the exact sensitivity or density of the explosive needed for each particular application at the point of use.

[0049] Preferably, chemical sensitization should be used where an agent is incorporated into the emulsion explosive close to point of insertion into the drill hole. The agent chemically generates bubbles of gas as a result of a chemical reaction. In one embodiment, the bubbles are generated by peroxide decomposition. In another embodiment the gen-

eration of gas bubbles are delayed and only generated in-situ of the drill hole.

[0050] Preferably, the sensitizer comprises enclosed gas bubbles or voids which are generated inside the explosive composition through a chemical reaction. Such voids are generated by a chemical decomposition process which may be delayed to achieve sensitization of the composition in-situ.

[0051] Alternatively, the sensitizer comprises enclosed gas bubbles or voids which are mechanically added into the explosive composition.

[0052] In preferred embodiments, a minimum of sensitizer must be added into the composition to achieve the desired detonability. Preferably, gas bubbles should be added until the sensitized emulsion explosive reaches a density between 0,4-1,25 grams / cm³. If secondary fuels or oxidizers are incorporated it is to be appreciated that the density range may be increased. This density could be higher depending on the base density of the unsensitized emulsion explosive and also based on the density of potential additives such as other oxidizers or secondary fuels.

[0053] By this means, 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. The skilled person will appreciate that a mathematical conversion may be used to convert the required weight of mechanical sensitizers for yielding a certain density into volume, correspondingly, the required amount of the chemical gassing agent to be decomposed into bubbles for yielding a certain density may be converted into volume by a mathematical conversion. Furthermore, the density of the unsensitized composition shall normally always be higher than the sensitized density of the same.

[0054] In preferred embodiments, the size of the gas bubbles should be between 10-200 micrometre (microns) and preferably larger than the dispersed droplets of the oxidizer phase. Larger bubbles may join forming instabilities in the emulsion matrix.

[0055] Preferably the particle size of the finely divided solid should be less than 10 micrometres, and more preferably less than 2 micrometres in average particle size which has been seen to be close to the oxidizer droplet mean size distribution. The size of the solid adsorbent particles should be in the same range as the range of sizes for the oxidizer droplets. Too large adsorbent particles may hinder the emulsifier's ability to bonding the oil and aqueous droplets. Too small particles may cause full adsorption into an oxidizer droplet which may destabilize the droplet.

[0056] Preferably, the finely divided solid adsorbent is included and dispersed in the continuous fuel-phase. This creates a better dispersion of the adsorbent particles. It has been seen that adsorbent particles exhibit clumping behaviour if added to the oxidizer phase. If added into the fuel-phase it has been found that the adsorbent improves emulsification due to the continuous wetting of the oxidizer phase upon emulsification.

[0057] The solid adsorbent may be added in a concentration between 0.1 to 10% by weight and dispersed into the oil phase together with fuel oils and emulsifiers prior to adding the discontinuous phase.

[0058] The finely divided solid adsorbent may comprise at least one solid selected from the group consisting of acrylic polymer powders, wheat, potato, rice or corn starch powders, organic gum powders, alginate cross linking powders, fumed silica powder, colloidal silica, silica powder, polymer zein powder, gluten powder, and clay particles.

[0059] The composition may further comprise a continuous fuel phase and a discontinuous aqueous oxidizer phase having a hydrogen peroxide concentration between 15-85% by weight, preferably between 30-60% by weight, a water content between 15-50% by weight.

[0060] Preferably, the oxygen balance between the fuel and oxidizer phases are between -10 and +3% where oxygen balance denotes the selected fuels ability to fully oxidize.

[0061] Fuel additives may be added to modify the oxygen balance, energy, and detonation temperature and detonation pressure.

[0062] The oil type fuel may comprise at least one oil selected from the group consisting of mineral oils, aromatic oils, bio-oils, synthetic fuel oils, diesel oils, lubrication oils, kerosene oils, naphtha oils, paraffin oils, chlorinated paraffin oils, , benzene, toluene, polymeric oils, rapeseed oils, coconut oils and fish oils or mixtures thereof.

[0063] The composition may further comprise a density modifying additive fuel comprising at least one of metal powders such as non-reactive metal powders such as aluminium powder, silica powder, sugars, glycerol, cellulose and alcohols. Such an additive fuel may be used to change the energy of the fuel component.

[0064] Preferably, the density of the unsensitized explosive composition s in the range of 0,8-1,4 grams per cm³. Unsensitized Compositions using secondary oxidizers or secondary fuels may have an unsensitized density up to 1,8.

[0065] The emulsifier may comprise at least one Polyisobutylene succinic anhydride (PIBSA), PIBSA amine derivatives, PIB-lactone and its amino derivatives, Sorbitan monooleate (SMO), sorbitan sesquioleate, lecithin, alkoxylates, esters combinations, fatty amines, alkylloxazolines, alkenyloxazolines, imidazolines, alkyl-sulfonates, alkylarylsulfonates, alkyl-sulfosuccinates, alkylphosphates, alkenylphosphates, phosphate esters and mixtures thereof. Such emulsifiers efficiently stabilize the emulsion and fix the two immiscible phases to thereby prevent phase separation.

[0066] The concentration of emulsifier in the explosive composition may range from 0,8 - 5% by weight, preferably from 1,1 to 3% by weight.

[0067] Preferably, the composition contains less than 1.5% nitrates by weight. More preferably it contains less than

0.5% nitrates by weight. Commonly available emulsifiers often comprise nitrate bearing molecules. When such emulsifiers are used in the composition, they should preferably be selected to minimize the nitrate content in the overall emulsion such that nitrate content may be kept below the preferred or the more preferred limit.

[0068] The viscosity of the HP emulsion composition and its components will be discussed in terms of apparent viscosity. Where used herein the term "apparent viscosity" refers to the viscosity measured by using a Brookfield RVT viscometer, #7 spindle at 20 r.p.m.

[0069] The viscosity of the oil phase during emulsification is relevant for effective droplet bonding, it is therefore preferred that oils, emulsifiers and solid adsorbents are selected and pre-mixed so that the oil phase has an apparent viscosity lower than 25 000 centipoise (cP).

[0070] Another embodiment of the invention the explosive composition of the water-in-oil emulsion explosive have an apparent viscosity greater than 35 000 centipoise (cP) at 25 °C prior to the introduction of the sensitizing gas bubbles. Apparent viscosity is more preferably in the range 60 000 to 120 000 cP. Preferably the explosive composition of the invention can be pumped.

[0071] In another embodiment the viscosity of the unsensitised, emulsion is greater than 60 000 centipoises [cP] to ensure stability in the drill hole and to avoid mass transfer of HP and resulting reactivity. Preferably, the oxidizer phase should be free of nitrogen, and in one embodiment the oxidizer phase may consist only of hydrogen peroxide and water where the concentration of hydrogen peroxide in the oxidizer phase is no less than 35%.

[0072] In another embodiment, secondary oxidizers such as other peroxide oxidizers such as sodium or potassium peroxide or perchlorates such as potassium perchlorate may be added to the oxidizer phase in combination with the hydrogen peroxide and water solution. The concentration of hydrogen peroxide in this embodiment should be no less than 15%.

[0073] According to a second aspect there is provided a method of preparing an emulsion type explosive composition. The method comprises

- providing an oxidizer-phase comprising at least 15% by weight of hydrogen peroxide and at least 15% by weight of water,
- providing a fuel-phase comprising at least one oil type,
- providing at least one emulsifier,
- providing at least one finely divided solid adsorbent,
- forming an emulsion comprising the oxidiser phase, the fuel-phase, the emulsifier and the solid adsorbent, and
- sensitizing the emulsion by adding gas filled compressible solid micro-balloons, and/or by generating gas bubbles by means of a gassing agent and/or by adding gas bubbles to the emulsion.

[0074] The emulsifier and/or the solid adsorbent may be added to the fuel-phase prior to forming the emulsion or during the formation of the emulsion.

[0075] Further objects and advantages of the invention will be apparent from the following detailed description of examples and from the appended claims

Detailed description of examples

[0076] According to one aspect there is provided a composition for forming a hydrogen peroxide based emulsion explosive. The composition comprises an oxidizer-phase comprising at least 15% by weight of hydrogen peroxide and at least 15% by weight of water which oxidizer-phase is discontinuously dispersed throughout a continuous fuel-phase comprising at least one oil type fuel. The composition further comprises an emulsifier and at least one finely divided solid adsorbent.

[0077] In practice, the composition may be formed by mixing the hydrogen peroxide water solution forming the oxidiser-phase with the fuel-phase in a mixer to thereby create an emulsion with the oxidiser phase being dispersed in the fuel phase. Preferably the emulsifier and the solid adsorbent should be added to the fuel phase prior to mixing. Alternatively, the emulsifier and/or the solid adsorbent may be added during the mixing process for forming the emulsion. Typically, the temperature of the oxidiser-phase may be kept at approx. 10-20° C when added to the mixer. During preparation of the fuel-phase, which may comprise mixing an oil-based fuel with the emulsifier and the finely divided solid adsorbent, the temperature of the fuel-phase may be kept at room temperature. However, when oil fuels having lower viscosity are used it may be preferable to add heat during the formation of the fuel phase. Correspondingly, the fuel phase may be supplied to the emulsification mixer at room temperature or it may be somewhat pre-heated before being supplied to the mixer.

[0078] By adding a sensitizer, the so formed composition becomes detonation enabled and explosive though initiation with conventional means, such a detonator with or without an amplification charge (known as a primer or booster). The sensitizer may be chemically generated though a chemical reaction between a gassing agent added as a part of a

pumping process whereby gas bubbles are formed slowly in-situ of the composition once placed in a blast hole. An example of gassing agents which may be used is carbon powder suspended in water. Another example is a mixture of vinegar (CH_3COOH) and bicarbonate solved in water. When carbon powder suspended in water is used, the suspension will react with the hydrogen peroxide to form oxygen bubbles which act as hot spots in the composition. When vinegar and bicarbonate is used, these two substances react with each other to form hot carbon dioxide bubbles acting as hot spots.

[0079] In another embodiment, the sensitizer in the form of solid compressible gas filled micro-balloons is added mechanically and mixed into the composition making the composition detonation enabled immediately.

[0080] It will be appreciated that the composition can be used for many purposes, but in particular to break and move rock in mining operations.

[0081] According to different embodiments of the composition it may comprise the types of functional components listed in Table 1;

Table 1: Typical types of functional components and ratios of exemplifying compositions

Type of functional component	Ratios in % by weight of the total composition
HP (primary oxidizer)	From 15 to 85
Water	From 15 to 55
Fuels	From 2 to 15
Emulsifiers	From 0.5 to 5
Solid adsorbents	From 0.01 to 2
Secondary fuels	From 0 to 15
Secondary oxidizers	From 0 to 50
Additives	From 0 to 5

[0082] Such compositions may have the properties listed in Table 2:

Table 2: Properties of the exemplifying compositions

Properties	Value
Oxygen balance	From -10 to +5
Un-sensitized density	From 0.8 to 1,8
Sensitized density	From 0.3 to 1,5
Viscosity	From 35000 to 120 000 cP
Preparation temperature	From 5 to 25° C
Velocity of detonation	2800-5500 m/s

[0083] Exemplifying typical substances for each type of functional component are listed in Table 3:

Table 3: Exemplifying substances comprised in the compositions

Functional component	Substance
Oxidizers(s)	At least 15% Hydrogen peroxide by weight, optionally potassium peroxide/and, or sodium peroxide/ and, or perchlorate salts/and, or chlorate salts.
Fuel(s)	Water immiscible fuels and optionally water miscible fuels
Emulsifiers	Emulsifiers containing simultaneously lipophilic and hydrophilic moieties (PIBSA, SMO or the like)
Solid adsorbents	Finley divided solids which can be adsorbed and wetted at the interface between the two liquid phases to form a film of particles around the dispersed phases. No limiting examples are

(continued)

Functional component	Substance
	gums, cross linkers, poly acrylic acids (tradenames Carbopol, carbomer, Utrez, Floset), starches (wheat, corn, rice, potato), polymer zein, fumed silica, colloidal silica, silica powder, titanium dioxide, clay particles.
Additives	pH adjusters, thickeners, rheology modifiers, phosphonic or tin based HP stabilizers.
Sensitizer	Gas filled voids or bubbles either chemically generated (delayed or instant) and/or gas entrapped compressible materials.

Examples

[0084] The present invention can be used for a variety of forms of emulsion type explosive compositions provided that the principles of the invention as described herein are observed. The invention is further illustrated with reference to the following examples.

Example 1

[0085] A hydrogen peroxide emulsion formulation containing an oil-based fuel phase was calculated and hand made at a preparation temperature of 14°C using a bench drill driven mixer. The oil phase combined one PIBSA type emulsifier and one SMO type emulsifier with a HP and water solution of 49.9% by weight concentration. A mineral oil with density of 0.83 g / cm³ was selected and combined with the two emulsifiers. 4 attempts to emulsify the above was conducted, 2 attempts without any solid adsorbent and 2 attempts with addition of approximately 0.8% by weight of a finely divided solid adsorbent in the form of powdery wheat starch (wheat flour) with an estimated particle size of 10-40 microns. Phase separation (ps) and pH was monitored over a 5-day period. The samples were stored in room temperature (21° C). Oxygen balance was calculated to -4%. If phase separation was detected, no further test where done. Density of the samples day 1 was approximately 1.15 g/cm³.

Table 3: Phase separation and pH change during 5 days using compositions with and without solid adsorbent.

Sample	Solid adsorbent	Ps/pH day 1	Ps/pH day 2	Ps/pH day 3	Ps/pH day 4	Ps/pH day 5
1	Yes	No/3.7	No/3.67	No/3.4	No/3.3	No/3.27
2	Yes	No/3.9	No/3.82	No/3.8	No/3.4	No/3.4
3	No	No/3.3	No/3.1	Yes/-	-	-
4	No	No/2.8	Yes/-	-	-	-

[0086] The formulations with adsorbent where significantly easier to emulsify. The pH levels stayed significantly more stable of multiple days indicating less separation between HP and fuel.

Example 2

[0087] Gassing stability tests were performed using a chemical gassing agent in combination with an emulsion composition similar to example 1 including a solid adsorbent. The composition emulsified readily at 15° C using a bench drill driven mixer resulting in a measured viscosity of 112 000 cP. The estimated oxygen balance was calculated to -5.4%. 1% of gassing agent was incorporated. 3 samples of the gassed emulsion were placed in a density cup. Once gassing had finished, the excess emulsion which had risen over the cup was cut and discarded, remaining gassed emulsion inside the cup was checked for density over the following 5 days. The sensitized emulsion was stored in room temperature.

Table 4: Density change in gassed HP emulsion

Sample	Un sensitized density	Gassed density	Day 1	Day 2	Day 3	Day 4	Day 5
1	1.15	0.98	0.97	0.94	0.94	0.93	0.93
2	1.15	1.03	1.01	1.00	0.98	0.97	0.97

(continued)

Sample	Un sensitized density	Gassed density	Day 1	Day 2	Day 3	Day 4	Day 5
3	1.15	1.05	1.05	1.03	1.03	1.02	1.00

[0088] Attempts to gas emulsions without adsorbents were made, however, the gassing in these instances caused the emulsion to separate and destabilized within a few hours.

Example 3

[0089] Detonation testing of the above compositions comprising a solid adsorbent were performed where the compositions were chemically gassed and pumped into drilled holes in boulders. The holes were drilled to a diameter of 48 mm and charges of about 1 kg were used. Initiation was done with an 8d electric detonator in combination with a 20 gram PETN primer. VOD was measured using the MREL microtrap copper probes. The charges were left to sleep in the holes for 48 hours at a temperature of 12-14°C. Detonation speeds from 4100 to 4300 m/s were measured and performance was deemed acceptable for mining applications.

[0090] 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 within the scope of the appended claims. 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. A composition for forming a hydrogen peroxide-based emulsion explosive which composition comprises;

- an oxidizer-phase comprising at least 15% by weight of hydrogen peroxide and at least 15% by weight of water,
- a fuel-phase comprising at least one oil type fuel,
- an emulsifier,
- at least one finely divided solid adsorbent, wherein

the oxidizer-phase is discontinuously dispersed throughout the continuous fuel-phase.

2. An explosive composition according to claim 1, further comprising a sensitizer, whereby the composition forms a sensitized emulsion explosive.

3. A composition according to claim 2, wherein the sensitizer comprises enclosed gas bubbles or voids which are generated inside the explosive composition through a chemical reaction.

4. A composition according to claim 2 wherein the sensitizer comprises enclosed gas bubbles or voids which are mechanically added into the explosive composition.

5. A composition according to any of claims 1-4 wherein at least a portion of the finely divided solid adsorbent may be wetted by both the oxidizer and the fuel phase.

6. A composition according to any of claims 1-5 wherein the particles of the finely divided solid adsorbent are smaller than 10 micrometres in average size.

7. A composition according to any of claims 1-6 wherein the finely divided solid adsorbent is included and dispersed in the continuous fuel-phase.

8. A composition according to any of claims 1-7 wherein the finely divided solid adsorbent comprises at least one solid selected from the group consisting of acrylic polymer powders, wheat, potato, rice or corn starch powders, organic gum powders, alginate cross linking powders, fumed silica powder, colloidal silica, silica powder, polymer zein powder, gluten powder, and clay particles.

9. A composition according to any of claims 1-8 wherein the oil type fuel comprises at least one oil selected from the

group consisting of mineral oils, aromatic oils, bio-oils, synthetic fuel oils, diesel oils, lubrication oils, kerosene oils, naphtha oils, paraffin oils, chlorinated paraffin oils, benzene, toluene, polymeric oils, rapeseed oils, coconut oils and fish oils.

- 5 10. A composition according to any of claims 1-9 further comprising a density modifying additive fuel comprising at least one of aluminium powder, silica powder, sugars, glycerol, cellulose or alcohols.
- 10 11. A composition according to any of claims 1-10, wherein the emulsifier comprises at least one of Polyisobutylene succinic anhydride (PIBSA), PIBSA amine derivatives, PIB-lactone or its amino derivatives, Sorbitan monooleate (SMO), sorbitan sesquioleate, lecithin, alkoxylates, esters combinations, fatty amines, alkyloxazolines, alkenyloxazolines, imidazolines, alkyl-sulfonates, alkylarylsulfonates, alkylsulfosuccinates, alkylphosphates, alkenylphosphates or phosphate esters.
- 15 12. A composition according to any of claims 1-11, wherein the composition contains less than 1.5% nitrates by weight.
- 20 13. A composition according to any of claims 1-12 wherein the apparent viscosity of the unsensitized composition is greater than 35 000 centipoises [cP] at 25° C.
- 25 14. A composition according to any of claims 2-13 wherein the density of the sensitized explosive composition is between 0.4 to 1.25 g/cm³.
- 30 15. A method of preparing an emulsion type explosive composition, which method comprises;
 - providing -an oxidizer-phase comprising at least 15% by weight of hydrogen peroxide and at least 15% by weight of water,
 - providing a fuel-phase comprising at least one oil type,
 - providing at least one emulsifier,
 - providing at least one finely divided solid adsorbent,
 - forming an emulsion comprising the oxidiser phase, the fuel-phase, the emulsifier and the solid absorbent, and
 - 35 - sensitizing the emulsion by adding gas filled compressible solid micro-balloons, and/or by generating gas bubbles by means of a gassing agent and/or by adding gas bubbles to the emulsion.



EUROPEAN SEARCH REPORT

 Application Number
 EP 21 17 2313

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