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71 Applicant: **AECI LIMITED**
16th Floor Office Tower Carlton Centre
Commissioner Street P.O. Box 1122
Johannesburg 2000 Transvaal(ZA)

72 Inventor: **Halliday, Pieter Stephanus Jacobus**
85 Market Street
Johannesburg North Randburg
Transvaal(ZA)
Inventor: **Swartz, Lynette**
28 Milner Avenue
St Andrews Bedfordview Transvaal(ZA)

74 Representative: **Reid, Thomas James et al**
Imperial Chemical Industries PLC Legal
Department: Patents PO Box 6 Bessemer
Road
Welwyn Garden City Herts, AL7 1HD(GB)

54 **Low water content emulsion.**

57 The invention provides an emulsion explosive of the so-called water-in-oil type. An aqueous oxidizing salt-containing component forms the discontinuous phase of the emulsion. A fuel-containing component forms its continuous phase and is immiscible with the discontinuous phase. The explosive comprises at most 9% by mass water and the discontinuous phase has a crystallization point of at least 80°C.

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THIS INVENTION relates to an emulsion explosive. More particularly it relates to an emulsion explosive of the so-called water-in-oil or melt-in-oil type.

According to the invention there is provided an emulsion explosive which comprises an emulsion in which an aqueous oxidizing salt-containing component forms a discontinuous phase and a fuel-containing component forms a continuous phase which is immiscible with the discontinuous phase, the explosive comprising at most 9% by mass water and the discontinuous phase having a crystallization temperature of at least 80°C.

The explosive may comprise 3 - 9% by mass water, eg 7 - 8% by mass, the discontinuous phase having a crystallization temperature of 80 - 90°C, eg about 85°C. This crystallization temperature is also known in the art as the so-called crystallization point or fudge point of the discontinuous phase and in fact represents the melting point of the discontinuous phase.

The explosive may be cap-sensitive, being sensitized with gas bubbles to have a density of at most 1,26 g/cm³ at 25°C. The explosive may be chemically gassed with nitrogen bubbles, having a density in the range 1,15 - 1,20 g/cm³ at 25°C.

When the explosive is chemically gassed it should preferably have a continuous phase with a softening point above the maximum anticipated ambient temperatures to which it will be exposed before use, eg during storage. By suitable selection of the constituents of the continuous phase, eg by formulating a blend of oils and waxes such as microcrystalline waxes and/or paraffin waxes, a softening point above eg 40°C with a safety margin of say 5 - 15°C, can be obtained for the continuous phase. Suitable blending of the continuous phase constituents can also provide a sufficiently low viscosity in the continuous phase at those temperatures, eg about 75 - 95°C, typically encountered in the art, during formation of the emulsion, for introduction and dispersion in the emulsion of gas bubbles or a suitable chemical gassing agent, such as sodium nitrite, which forms nitrogen bubbles in the emulsion.

Typically the discontinuous phase may comprise at least one oxidizing salt selected from the group comprising:

- ammonium nitrate
- alkali metal nitrates
- alkaline earth metal nitrates
- ammonium perchlorate
- alkali metal perchlorates and
- alkaline earth metal perchlorates.

The oxidizing salt will be present in the form of an aqueous solution or water-containing melt in the discontinuous phase.

In the case of melt-in-oil emulsions or emulsions in which the discontinuous phase, like the continuous phase, contains very little if any water, the discontinuous phase can solidify at ambient temperatures, but the explosive is still regarded as an emulsion for the purpose of the present invention.

In particular the discontinuous phase may comprise ammonium nitrate and at least one compound selected from the group comprising oxidizing salts or organic materials which, together with the ammonium nitrate, forms a melt which has a melting point which is lower than that of ammonium nitrate, the oxidizing salt content of the explosive being 70-90% by mass and the relative proportions between the ammonium nitrate and said compound or compounds in the discontinuous phase being such as to form, when mixed together, a melt having a melting point in the range 75-130°C. Such further compound may be an inorganic salt such as lithium nitrate, silver nitrate, lead nitrate, sodium nitrate, calcium nitrate, potassium nitrate, or mixtures thereof. Instead or in addition, the compound which together with the ammonium nitrate on heating forms a melt having a melting point which is lower than the melting point of ammonium nitrate may be an alcohol such as methyl alcohol, ethylene glycol, glycerol, mannitol, sorbitol, pentaerythritol, or mixtures thereof. Other compounds which can instead or in addition be used to form said melts together with ammonium nitrate may be used carbohydrates such as sugars, starches and dextrans, and aliphatic carboxylic acids and their salts such as formic acid, acetic acid, ammonium formate, sodium formate, sodium acetate, and ammonium acetate. Yet further compounds which can instead or in addition be used to form said melts with ammonium nitrate include glycine, chloroacetic acid, glycolic acid, succinic acid, tartaric acid, adipic acid, and lower aliphatic amides such as formamide, acetamide and urea. Urea nitrate can also be used as can certain nitrogenous substances such as nitroguanidine, guanidine nitrate, methylamine, methylamine nitrate, and ethylene diamine dinitrate. Each of these substances may be used alone with the ammonium nitrate, or mixtures thereof can be used to form said melt with the ammonium nitrate, the mixtures being selected to form melts with the ammonium nitrate which have suitably low melting points and are substantially insoluble in the continuous phase.

The oxidizing salt or salts may be present in a proportion, as mentioned above, of from 70 - 92% by

mass of the explosive, preferably 80 - 86%.

In general, the substance[s] chosen to form melts with the ammonium nitrate are selected according to the criterion, in addition to cost, that they form melts with acceptably safe and low melting points, for example, as indicated above, within the range 75°C - 130°C, although melts with melting points above
5 130°C can in principle be used.

The fuel component of the emulsion may comprise at least one water-in-oil emulsifier selected from the group comprising sorbitan sesquioleate, sorbitan monooleate, sorbitan monopalmitate, sodium monostearate, sodium tristearate, the mono- and diglycerides of fat-forming fatty acids, soya bean lecithin, derivatives of lanolin, alkyl benzene sulphonates, oleyl acid phosphate, laurylamine acetate, degaglycerol
10 decaoleate, decaglycerol decaatearate, 2-oleyl-4-4'-bis[hydroxymethyl]-2-oxazoline, polymeric emulsifiers containing polyethylene glycol backbones with fatty acid side chains and polyisobutylene succinic anhydride derivatives.

The emulsifiers act as surfactants and stabilizers to promote the formation of the emulsion and to resist crystallization and/or coalescence of the discontinuous phase.

15 The explosive may comprise 1-2% by mass of said water-in-oil emulsifier, preferably from 1,3 - 1,5%.

The explosive may contain, in addition, a solid fuel such as aluminium, which may be paint fine or atomized aluminium. When aluminium is used, the explosive may comprise from 3 - 8% by mass aluminium solid fuel, preferably 3,5 - 6%.

The fuel of the continuous phase will be immiscible with and insoluble in water. In particular the fuel
20 may be an organic fuel which is non-self-explosive and comprises at least one member of the group comprising hydrocarbons, halogenated hydrocarbons and nitrated hydrocarbons, the fuel comprising a wax constituent and having a softening point temperature in the range 45- 65°C, the fuel-containing component forming 2-25% by mass of the explosive. The fuel in general may form 2-25% by mass of the explosive, preferably 3 - 12%. As mentioned above, the fuel typically contains one or more waxes, such as paraffin
25 waxes, microcrystalline waxes and/or slack waxes, whereby its softening point and viscosity are controlled, and it may also include one or more members of the group comprising mineral oils, fuel oils, lubricating oils, liquid paraffin, xylene, toluene, petrolatum and dinitrotoluene.

In general, water in the discontinuous phase will be kept to a minimum consistent with formulating the discontinuous phase and with formulating the emulsion at an elevated temperature which is acceptably low,
30 so as to avoid unnecessarily wasted energy arising from steam production upon eventual detonation.

The density of the base emulsion will be such as to form a suitable explosives composition after incorporation of the bubbles. The base emulsion may thus have a density of eg 1,30-1,56 g/cm³ at 25°C. The density of the eventual explosive should, as mentioned above, after bubble introduction be less than 1,26 g/cm³, preferably in the range 1,15 - 1,20 g/cm³ at 25°C.

35 In a particular embodiment of the invention, the oxidizing salt-containing component preferably comprises, at least in part, ammonium nitrate, in which case a chemical gassing agent comprising nitrite ions, eg sodium nitrite, may be employed, conveniently in the form of an aqueous solution of say 5-30% m/m concentration, eg 20% m/m, which is blended into the emulsion at said elevated temperature.

As soon as blending is initiated, nitrite ions start to react with ammonium ions in accordance with the
40 equation



to produce nitrogen bubbles.

45 It is desirable for the explosive to contain evenly distributed gas bubbles in the emulsion of an average size [diameter] in the range 20 - 40, eg 25, microns, and to have bubbles of a relatively uniform size, ie a relatively narrow bubble size distribution. The desired bubble size and bubble size distribution can be promoted by selecting an appropriate reaction speed [pH and catalyst content] and appropriate mixing characteristics in formulating the explosive.

50 The amount of sodium nitrite used will depend on the proportion or number of bubbles required, ie on the eventual density required for the explosive, and, if desired, one or more catalysts such as thiourea, thiocyanate or urea may be dissolved into the discontinuous phase prior to said blending, to accelerate the nitrite ion/ammonium ion reaction.

When a wax-based formulation is used for the continuous phase, the material of the continuous phase
55 conveniently has a hardness according to the Stanhope Penetrometer method of 6-16 mm, preferably 13,5 mm, at the maximum anticipated ambient temperature, eg at 40°C, and a setting point at 5 - 25°C, eg 10°C, above said anticipated temperature.

The explosive may be cap-sensitive being cartridgeed in cartridges of 22 mm - 32 mm diameter, eg as

22 mm, 25 mm or 32 mm cartridges.

The invention will now be described, by way of illustration, with reference to the following non-limiting Examples.

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EXAMPLES 1 - 3

Three emulsion explosive formulations were prepared in accordance with the present invention, as set out hereunder, in which compositions are expressed as percentages on a mass basis:

<u>Constituent</u>	<u>EXAMPLE 1</u> <u>% m/m</u>	<u>EXAMPLE 2</u> <u>% m/m</u>	<u>EXAMPLE 3</u> <u>% m/m</u>
15 Ammonium Nitrate	70,00	68,21	67,04
Sodium Nitrate	15,45	14,80	14,28
Water	7,86	7,86	7,86
20 Sorbitan Monooleate	1,47	1,42	1,37
Mineral Oil	0,99	0,80	0,66
Paraffin Wax	2,02	1,61	1,30
25 Microcrystalline Wax	2,02	1,61	1,30
Thiourea	0,10	0,10	0,10
Sodium Nitrite	0,09	0,09	0,09
30 Atomized Aluminium	Nil	3,50	6,00

With regard to the foregoing, it should be noted that the ammonium nitrate and sodium nitrate, together with the water, formed the discontinuous phase; the sorbitan monooleate was the emulsifier and was Crill 4 sorbitan monooleate obtained from Croda Chemicals [South Africa] [Proprietary] Limited; the mineral oil was 35 P95 oil obtained from BP South Africa [Proprietary] Limited; the paraffin wax was Sasolwaks obtained from Sasol Chemicals [Proprietary] Limited; the microcrystalline wax was BE SQUARE AMBER 175 wax obtained from Bareco Inc, USA; and the atomized aluminium was Supramex 2022 aluminium obtained from Hulett Aluminium Limited.

The sodium nitrate was used as a chemical gassing agent to produce nitrogen bubbles in the explosive 40 to reduce its density to 1,15 g/cm³, and the thiourea acted as a catalyst for the chemical gassing reaction.

The above formulations were cartridged into standard 32 mm paper shells and, after hot storage at 40°C [three months and continuing] were found to be capsensitive to detonation by a No. 2D detonator cap containing 0,022 g of pentaerythritol tetranitrate [PETN]. In each case an unconfined velocity of detonation 45 of about 4 km/sec was obtained.

EXAMPLE 4

50 Thirty cases of the explosive of Example 1 were produced, in cartridged form, cartridged in 25 mm diameter plastics sleeves. This explosive was prepared in accordance with the present invention with the base emulsion at a temperature of 100°C.

The discontinuous phase of this emulsion explosive had a crystallization temperature or fudge point of 85,7°C, and a pH measured at 99,3°C of 4,60. The emulsion was chemically gassed with sodium nitrite to 55 a density of 1,15- 1,17 g/cm³. The appearance of the emulsion was satisfactory with no signs of free melt.

Tests were performed on velocity of detonation in the cartridges, and values of 4,3 4,6 km/sec were obtained. Cartridges could be fired with a No. 2D detonator cap. Bubble energies measured were between 2,00 and 2,10 MJ/kg. Confined velocities of detonation measured in a 1 m steel pipe were of the order of

5,06 km/sec.

Stopping trials were carried out with these cartridge explosives with satisfactory results. Acceptable advances and fragmentation were achieved.

A selection of these cartridges was stored for three months at 40°C and thereafter when detonated at ambient temperatures yielding velocities of detonation of 3,2-3,5 km/sec [for one test] and 3,8-4,2 km/sec [for another test]. In the first of these tests a No. 5D detonator cap containing 0,180 g of PETN was required for minimum initiation, and in the second of these tests a No. 4D detonator cap containing 0,090 g of PETN was required for minimum initiation.

It is an advantage of the invention, at least as illustrated by the Examples, that an emulsion explosive is provided with a low water content, leading to a powerful explosive with reduced energy loss on detonation arising from the steam production. In contrast with similar formations having similar low water contents but employing glass microballoons instead of gassing with gas bubbles, the explosives of the Examples were found to be substantially more stable and substantially more sensitive to detonation, particularly after extended storage at elevated [40°C] temperatures. Furthermore when microballoons are used instead of chemical gassing, unacceptable crystallization of the discontinuous phase is found to take place. It is also believed that, particularly on a mass production scale, the explosives of the present invention promise to be less expensive to produce than similar explosives sensitized with microballoons.

20 Claims

1. An emulsion explosive which comprises an emulsion in which an aqueous oxidizing salt-containing component forms a discontinuous phase and a fuel-containing component forms a continuous phase which is immiscible with the discontinuous phase, the explosive comprising at most 9% by mass water and the discontinuous phase having a crystallization temperature of at least 80°C.

2. An explosive as claimed in claim 1, which comprises 3 - 9% by mass water and has a crystallization temperature of 80 -90°C.

3. An explosive as claimed in claim 1 or claim 2, which is cap-sensitive, being sensitized with gas bubbles to have a density of at most 1,26 g/cm³ at 25°C.

4. An explosive as claimed in any one of the preceding claims, in which the discontinuous phase comprises ammonium nitrate and at least one compound selected from the group comprising oxidizing salts and organic materials which, together with ammonium nitrate, forms a melt which has a melting point lower than that of ammonium nitrate, the oxidizing salt content of the explosive being 70-92% by mass and the relative proportions between the ammonium nitrate and said compound or compounds in the discontinuous phase being such as to form, when mixed together, a melt having a melting point in the range 75-130°C.

5. An explosive as claimed in any one of the preceding claims, which comprises 1-2% by mass of a water-in-oil emulsifier.

6. An explosive as claimed in any one of the preceding claims, which comprises 3-8% by mass of aluminium solid fuel.

7. An explosive as claimed in any one of the preceding claims, in which the fuel of the fuel-containing component is an organic fuel which is non-self-explosive and comprises at least one member of the group comprising hydrocarbons, halogenated hydrocarbons and nitrated hydrocarbons, the fuel component comprising a wax constituent and having a softening point temperature in the range of 45-65°C, the fuel-containing component forming 2-25% by mass of the explosive.

8. An explosive as claimed in claim 7, in which the material of the continuous phase has a hardness according to the Stanhope Penetrometer method of 6-16 mm at 40°C.

9. An explosive as claimed in any one of the preceding claims, which is cap-sensitive and is cartridge in cartridges of 22-32 mm diameter.

10. An emulsion explosive substantially as described herein.