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# (54) Water/melt-in-oil emulsion explosive composition.

(57) A detonator sensitive, stable water-in-oil or melt-in-oil emulsion explosive comprises an oxidiser containing discontinuous phase, a fuel containing continuous phase, and an emulsifier. To increase the safety of the explosive in flammable atmospheres, such as in coal mines, from 7% to 15% w/w of at least one of the following cooling agents is dissolved in the discontnuous phase: sulphonate, phosphonate, ammonium halide, alkali metal halide, alkaline earth metal halide, or a soluble phosphate salt. Preferably at least 20% of cooling agent is distributed between the continuous and discontinuous phases, with at least about 7% preferably about 12% present in the discontinuous phase.

# Water/Melt-in-oil Emulsion Explosive Composition

## Description

This invention relates to a water/melt-in-oil emulsion explosive composition suitable for use in a flammable environment, particularly underground,and especially in a coal mine. The invention particularly also relates to an emulsion which would qualify as P1 or P5 permitted explosives as set out by the UK regulatory authority.

Commercially available emulsion explosive compositions generally comprise an external or continuous organic fuel phase in which discrete droplets of an aqueous solution of an oxygen-supplying salt are dispersed as an internal or discontinuous phase and are stabilised by an emulsifier, which is believed to exist as a molecular coating layer on the surface of the droplets to reduce incipient agglomeration thereof. Such compositions are conventionally described as water-in-oil (w/o) emulsion explosive compositions; and examples thereof have been described, inter alia, in US patents 3 447 978, 3 674 578, 3 770 522, 4 104 092, 4 111 727, 4 149 916, 4 149 717, 4 490 194.

For certain applications the water content of the oxidiser phase of the emulsion explosive may be completely eliminated or at least reduced to a low level - for example, to less than 5% by weight of the total emulsion composition. Such compositions are conventionally referred to as melt-in-oil (m/o) or melt-in-fuel emulsion explosive and have been described, inter alia, in US patent 4 248 644.

Often density reducing agents such as entrained gas, either introduced mechanically or formed in situ by chemical reagents, or microballoons, perlites, polyurethene, or expanded polystyrene are added to control the density of the emulsion and ensure adequate detonator sensitivity.

Emulsion explosives, however, have a high weight strength (explosive power expressed as a percentage of that of blasting gelatine % BG) and a high velocity of detonation (VOD), which although ideal for most blasting applications, presents a problem with underground work such as in coal mines where there is a flammable atmosphere.

In many countries safety criteria are applied to test the suitability of an explosive before it can be used in a flammable atmosphere, such as coal mines.

To obtain a safe or permitted type of emulsion explosive, it is desirable therefore, to reduce its explosive strength and VOD, while still retaining an acceptable level of stability and detonator sensitivity, and desirably also minimising the amount of partially combusted toxic gases such as carbon monoxide.

There are a number of publications which have suggested ways of reducing the VOD of an emulsion. For example in European patent application nos. 0136081 and 0142271, the inventors teach controlling the size and nature of the density reducing agents which in this instance, were gas microballons or bubble agglomerates.

It is also known that the VOD and explosive strength can be reduced by adding inert or semi-inert solids, which act as cooling agents, to either the continuous or discontinuous phase. These cooling agents, however, can destablise the emulsion. The aforementioned European application nos. 0136081 and 0142271 acknowledged this problem and sought a solution in the strict control of the density reducing agents. US patent no. 4 566 920, however, teaches that a high weight percent of cooling agent such as NaC1 (as much as 45% w/w) having a strictly controlled particle size of between 250 and 500 microns can be dispersed as a dry solid in the continuous oil phase.

On the. other hand, the authors of Japanese early disclosure no. 81-155087 incorporate NaC1 and KC1 into both the continuous as well as the discontinuous phase. They recognise however that the dissolved oxidising salts in the discontinuous phase are quickly destablised by the cooling salts and suggests using higher amounts of emulsifier to overcome this in the region of 2.5 to 7.0 w/w. A known consequence of using too much emulsifier (greater than about 4% w/w) in the fuel phase is to produce an explosive which is deficient in oxygen, and which will in turn lead to the production of partially combusted toxic gases, such as carbon monoxide, in the after detonation fumes. In poorly ventilated mines this is unacceptable. Furthermore too much emulsifier can also affect the detonator sensitivity of the emulsion.

Contrary to this belief, the inventor has now surprisingly found that a significant amount of certain cooling agents can be dissolved in the discontinuous phase of the emulsion and yet still obtain a stable and detonator sensitive explosive.

Emulsions of the invention are regarded as stable if they have a shelf life of at least 3 months, preferably 6 months; and detonator sensitivity is a well known term in the art.

According to a first aspect of the invention there is provided a detonator sensitive, stable, water-in-oil or melt-in-oil emulsion explosive comprising an oxidiser containing discontinuous phase, a fuel containing continuous phase, and an emulsifier, characterised in that there is from 7% to 15% w/w of a cooling agent dissolved in the oxidiser containing discontinuous phase and selected from a soluble phosphate salt, sulphonate, sulphate, phosphonate, ammonium halide, alkali metal halide, and an alkaline earth metal halide.

As a result of having such a significant amount of cooling agent dissolved in the discontinuous phase, the VOD and weight strength of the emulsion are significantly reduced and the emulsion can therefore confer improved safety in a flammable atmosphere. Furthermore the introduction of the cooling agents in the manufacture of such an emulsion is easily controllable and cost effective. Therefore the invention has the advantage of emulsion explosives, but differs from standard emulsions in that it can be detonated more safely in a flammable atmosphere.

A major advantage of the invention is that emulsion explosives can now be formulated in a more cost effective and controllable manner and which will pass at least United Kingdom permitted tests. For example a P1 (approved explosive of the UK regulatory authorities) emulsion explosive can be obtained having a VOD of about 4200 m/s to 4500 m/s and a weight strength of about 55 to 60% BG, for about 7% w/w of dissolved cooling agents. On addition of about 10% of dissolved cooling agents in the discontinuous phase, the resulting emulsion explosive would have a VOD of about 4000 m/s and a weight strength of about 50 to 55% BG. In fact, even more surprisingly, as much as about 15% w/w of a sufficiently soluble cooling agent could be dissolved with an advantageous further reduction in the resulting VOD and weight strength. Most preferably there is about 12% w/w of dissolved cooling agent present.

Although a P1 explosive can be achieved by only dissolving the cooling agents in the discontinuous phase of the emulsion explosive, for stricter tests such as the P5 (explosive approved by the UK regulatory authorities) emulsion explosive some cooling agent must also be added to the continuous phase to a value allowing for at least 20% w/w of cooling salts to be distributed throughout the emulsion. Therefore in accordance with the invention, an amount of from 7% to 15% W/W, preferably 10% to 15% w/w. and particularly about 12% to 13% w/w, of cooling agent is dissolved in the discontinuous phase, and the desired extra quantity added as solids to the continuous phase.

As will thus be appreciate, the invention is very flexible in that it is possible to modify the explosive properties, such as the weight strength and VOD to suit the particular blasting environment. For example in underground rock blasting it may be preferred to have P1 explosive with a higher VOD, whereas in coal mines where a P5 explosive is required, a lower VOD may be desired.

A further advantage of the invention is that only a reasonably low level of emulsifier at most about 3% w/w and preferably 1.0 to 1.5% w/w of the emulsion explosive, is required. The explosive can therefore be substantially oxygen balanced and will not produce what would be regarded as an unsafe amount of uncombusted toxic gas in the after detonated fumes, which is important for underground or similarly poorly ventilated work. For open cast blasting this consideration is less significant.

What is meant by an oxygen balanced emulsion will be readily understood by those skilled in the art and typically would be about plus or minus 2 units.

Furthermore, the resultant emulsion explosives have a shelf life of at least 3 months and preferably at least 6 months, and can still retain detonator sensitivity without recourse to adding self-explosive materials such as methylamine mononitrate, ethylene diamine dinitrate, nitroglycerine, or sodium perchlorate.

It will of course be appreciated that such sensitisers and in fact high levels of emulsifier could be added if desired, but they are not necessary to achieve the stable, detonator sensitive emulsion explosive of the invention. For example an excess of emulsifier could substitute for some or all of the conventionally used fuel, but this may not be desirable.

As with standard emulsions, the invention can be pumped, loaded or poured to be used, for example, in blasting operations in oil shale or underground mining where regulations permit, or preferably can be packaged into standard cartridges.

Accordingly to a second aspect of the invention, there is provided a method of preparing a borehole for blasting in a flammable environment comprising pumping, pouring, loading an emulsion explosive into the borehole, or inserting a cartridge of emulsion explosive into the borehole, wherein the emulsion explosive is as defined in the first aspect of the invention.

The density of the invention emulsions can be controlled by known methods such as by the use of density reducing agents discussed heretofore, the density preferably varying between 0.8 to 1.2 g/cm$^3$.

Although both a w/o emulsion and m/o emulsion (having a water content of less than 5% w/w) can be prepared by the invention, a w/o emulsion is preferred having a water content of from 5% to 20% w/w, and more preferably from 10% to 15% w/w.

As regards the cooling agents, chlorides are preferred, as are also the alkali or alkaline earth metal cooling agents especially the chlorides thereof. A very high amount of KC1 and $CaCl_2$ can be loaded into the discontinuous phase to achieve very desirable VOD values suitable for permitted explosives. These (KC1 and $CaCl_2$) especially preferred cooling agents can of course be distributed along throughout the continuous or noncontinuous phase alone or in combination with any other known cooling salt, for example NaCl or $MgCl_2$.

The fuel used, which is preferably present at up to 10% w/w of the emulsion explosive, is typical for an emulsion explosive and would comprise, for example of the following: mineral oils, fuel oils, lubricating oils, liquid paraffin, micro crystalline waxes, paraffin waxes, petroleum, and slack wax.

Likewise, typical oxidisers for the discontinuous phase, preferably at around 30% w/w of the emulsion explosive would be $NH_4NO_3$, $NaHO_3$, $Ca(NO_3)_2$, and $KNO_3$, either in the melt or in an aqueous medium. Such salts could also be added as particulate solid to the formed emulsion.

Suitable emulsifiers for given emulsion systems are known in the art, but preferred emulsifiers for emulsion explosive compositions are sorbitan esters (mono- and sesquioleates; SMO and SSO resp.) and the reaction product of coupling a polyisobutenyl chain (functionalised with, for example succinic anhydride) with a hydrophilic head group such as an ethanolamine or substituted ethanolamine e.g. mono- and diethanolamines such as those disclosed in EP-A-0 155 800. Mixtures of a PIBSA-type emulsifier (which provides for long term storage stability), and a more conventional emulsifier such as a sorbitan ester (which provides rapid droplet stabilisation and so resists any tendency for droplet coalescence) are especially preferred in this invention.

A brief introduction to permitted tests in the United Kingdom may be helpful before proceeding with the examples.

The practical conditions under which explosives ignite a flammable atmosphere such as coal dust or methane/air mixture are difficult to establish with any degree of certainty. The normal way of assessing the safety of an explosive intended for use in a coal mine in the U.K. is by a series of gallery tests, details of which are contained in Testing Memorandum No. 2(TM 2) published by the U.K. Health and Safety Executive, Buxton. The testing gallery consists of a steel cylinder. The first part is sealed with a polythene diaphragm to contain the flammable atmosphere and the remaining part is left open. At the end opposite of the diaphragm there is a hole against which a heaby steel cannon containing the explosive is placed. The joint is sealed by a rubber ring. After the cannon has been placed in this position, methane for example is introduced into the enclosed chamber and thoroughly mixed with air. The explosive is then fired and the ignition, or otherwise, is observed from a safe distance. There are four type of test, P1, P3, P4 and P5, which simulate different explosive environments; and each test comprises a series ((i) to (iii)) in which shots are fired under different conditions. Although a test pass is achieved when a specific number of cartridges detonate in each series without igniting the explosive atmosphere, a reliable indication of a pass can be obtained by selective firing on the P1 and more strict P5 series of tests. In the examples, the VOD was measured using a series of standard reference detonators with a 35mm diameter unconfined tube and all values of the unconfined VOD in this specification should be understood in relation thereto.

The invention will now be described by way of illustration only, with reference to the accompanying examples.

## Example 1

A water-in-oil emulsion explosive with the following composition was prepared:-

| Component | Percentage by weight |
|---|---|
| Ammonium Nitrate | 65.97 |
| Potassium Chloride | 12.57 |
| Water | 13.41 |
| Emulsifier | 1.26 |
| Oil/Wax blend | 3.18 |
| Glass microspheres | 3.60 |

The potassium chloride was dissolved completely at about 90-95° C in a hot solution of the nitrate salts. The resulting solution was then combined with the emulsifier and oil/wax blend to form a w/o emulsion with an average droplet size of less than 5 microns, typically about 1 to 3 microns, in the conventional manner.

The microspheres were then dispersed into the material to give a resulting explosive composition with a density of 1.05 g/cm$^3$.

The unconfined velocity of detonation was 4,000 cm/s at a diameter of 35mm packaged in a plastic film. All other experiments were carried out in a similar 35mm tube. The weight strength was found to be 50%BG.

The incendivity of this explosive was tested in the P1 series (i) condition as specified in TM 2 at a test weight of 200g. In four tests, no ignitions were observed, indicating a P1 type explosive.

## Example 2

A water-in-oil emulsion explosive with the following composition was prepared.

| Component | Percentage by weight |
|---|---|
| Ammonium Nitrate | 58.01 |
| Sodium Nitrate | 9.86 |
| Potassium Chloride | 9.48 |
| Water | 11.60 |
| Emulsifier | 1.46 |
| Oil/Wax Blend | 4.59 |
| Glass Microsphere | 5.00 |

As in example 1, the potassium chloride was dissolved completely in the hot solution in oxidiser salts and then formed into an emulsion explosive in the conventional manner.

The resulting explosive had a density of 0.99 g/cm$^3$. The incendivity of this composition was tested in the P1 condition according to TM 2. In the series (i) test, seven shots were fired at a test weight of 200g. No ignition was observed. In the series (ii) test, five shots were fired at a test weight of 800g. The unconfined VOD was 4200 m/s. Since no ignitions again were observed, this indicated a P1 type explosive.

## Example 3

A water-in-oil emulsion explosive with the following composition was prepared:-

| Component | Percentage by weight |
|---|---|
| Ammonium | 46.09 |
| Sodium Nitrate | 7.68 |
| Water | 12.10 |
| Sodium Chloride | 12.69 |
| Potassium Chloride | 12.40 |
| Emulsifier | 1.04 |
| Oil/Wax blend | 2.63 |
| Glass microsphere | 5.37 |

The potassium chloride was dissolved completely in the hot solution of nitrate salts at about 90 to 95° C. The resulting solution was then combined with the emulsifier and oil/wax blend to form a w/o emulsion in the conventional manner. The solid crystalline sodium chloride was then dispersed into the preformed emulsion in a similar manner to that commonly used for the dispersion of glass microspheres. Finally, the said microspheres were themselves dispered into the material to give a resulting explosive composition with a density of 0.95 g/cm$^3$.

The unconfined VOD was 3500 m/s, and the weight strength was 38% BG.

The incendivity of this composition was tested in the P5 condition, according to TM2. The diameter of the explosive charge was 35mm. In the series (i), a testing weight 570g is specified in the Memorandum. The composition was tested at a variety of weights and the results are summarised below:-

| Test Weight | No. of Ignitions (for five shots) |
|---|---|
| 500g | 0/5 |
| 600g | 0/5 |
| 650g | 0/5 |
| 700g | 0/5 |
| 750g | 0/5 |

As can be seen from the above, no ignitions were observed at any of the test weights thus demonstrating the improved safety of this composition.

In the series (ii) test, where the specified testing weight is 1200g, a total of twenty shots were fired. Again, no ignitions were observed.

Another type of testing other than Gallery testing which is specified in TM 2 for P5 class explosives (but not for the P1 class) is the so called Deflagration test. The details of this test are described in TM 2. This explosive composition was subjected to the demands of this test and the results are summarised below.

| Explosive Diameter | Aperture | No. of Deflagrations |
|---|---|---|
| 37mm | 1/8 inch | 0/5 |
| 35mm | none | 0/5 |
| 35mm | 1/8 inch | 0/5 |
| 35mm | 2/8 | 0/5 |
| 35mm | 3/8 | 0/4 |

Thus in none of the conditions tested was there any deflagration observed. This emulsion composition is indicative of a P5 type explosive.

Example 4 (Comparative example)

A water-in-oil emulsion explosive with the following composition was prepared in the same manner as Example 1, but without the dissolved cooling salt:-

| Component | Percentage by Weight |
|---|---|
| Ammonium Nitrate | 62.2 |
| Sodium Nitrate | 12.4 |
| Water | 16.0 |
| Emulsifier | 1.35 |
| Paraffin Oil | 0.91 |
| Paraffin Wax | 1.91 |
| Microcrystalline Wax | 1.92 |
| Glass microsphere | 3.31 |

The density of this composition was 1.11 g/cm$^3$.

the incendivity of this composition was tested in the P1 Series (i) condition. Two shots were fired at a test weight of 200g. An unconfined VOD of 5000 m/s and a weight strength of 67% BG was found. Since ignitions were observed in both cases, the explosive is likely to have failed the P1 test.

Example 5 (Comparative example)

A water-in-oil emulsion explosive with the following composition was prepared:-

| Component | Percentage by Weight |
|---|---|
| Ammonium Nitrate | 30.57 |
| Norsk-Hydro Calcium Nitrate | 28.63 |
| Methylamine Mononitrate (70% solution) | 7.10 |
| Emulsifier | 1.25 |
| Oil | 3.95 |
| Potassium Sulphate | 22.50 |
| Glass microspheres | 6.00 |

A hot solution of the nitrate salts was prepared and added to the oil/emulsifier at about 90-95° C in the conventional manner to form a w/o emulsion. To this performed emulsion, the solid potassium sulphate and the microspheres were added to produce a explosive composition. The resulting density of this explosive composition was 0.98 g/cm$^3$.

The unconfined VOD was 3000 m/s and the weight strength was 40% BG.

The incendivity of this explosive was tested in the P5 (i) condition at the defined test weight of 570g. Two shots were fired with on ignition being observed. Since no ignitions are allowed in any of the test conditions this explosive composition would not pass the P5 requirements.

Although the emulsion explosive in examples 1, 2, and 3 hereabove used only potassium chloride as a cooling salt dissolved in the discontinuous phase, early results have shown that any alkali metal halide, alkaline earth metal halide or ammonium halide will be suitable, as in fact will any phosphonate, sulphonate, sulphate or sufficiently soluble phosphate salt.

## Claims

1. A detonator sensitive, stable water-in-oil or melt-in-oil emulsion explosive comprising an oxidiser containing discontinuous phase, a fuel containing continuous phase, an emulsifier, and an amount of cooling agent characterised in that the cooling agent is dissolved in the oxidiser containing continuous phase at from 7% to 15% w/w and in that it is at least one of a soluble phosphate salt, sulphonate, sulphate, phosphonate, ammonium halide, alkali metal halide, and an alkaline earth metal halide.

2. An emulsion explosive as claimed in claim 1, characterised in that the amount of dissolved cooling agent present in the discontinuous phase is 10% to 15% w/w.

3. An emulsion explosive as claimed in claim 2 characterised in that the amount of dissolved cooling agent present in the discontinuous phase is about 12% to 13% w/w.

4. An emulsion explosive as claimed in any one of claims 1 to 3 characterised in that the cooling agent in the discontinuous phase is an alkali metal halide or an alkaline earth metal halide.

5. An emulsion explosive as claimed in any one of the preceding claims characterised in that the halide cooling agents are chlorides.

6. An emulsion explosive as claimed in claims 4 or 5 characterised in that the cooling agent is potassium chloride or calcium chloride.

7. An emulsion explosive as claimed in any one of the preceding claims characterised in that there is at least 20% w/w cooling agent distributed between the continuous and discontinuous phases.

8. An emulsion explosive as claimed in any one of the preceding claims which is substantially oxygen balanced and which has up to 3% w/w emulsifier present.

9. An emulsion explosive as claimed in claim 8 characterised in that there is 1.0 to 1.5% w/w of emulsifier present.

10. An emulsion explosive as claimed in any one of the preceding claims which is a water-in-oil emulsion.

11. An emulsion explosive as claimed in any one of the preceding claims wherein there is up to 10% w/w fuel present.

12. An emulsion explosive as claimed in any one of the preceding claims which has density of between 0.8 and 1.2 g/cm$^3$.

13. A cartridge explosive including an emulsion explosive as claimed in any one of the preceding claims.

14. A method of preparing a borehole for blasting in a flammable environment comprising pumping, pouring or loading an emulsion explosive into the borehole, or inserting a cartridge of emulsion explosive into the borehole, characterised in that the emulsion explosive is as defined in any one of the claims 1 to 12 and in that the cartridge explosive is as defined in claim 13.