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71 Applicant: **ICI AUSTRALIA OPERATIONS PROPRIETARY LIMITED**

**1 Nicholson Street
Melbourne Victoria 3001 (AU)**

72 Inventor: **Ballard, Mathew
10/95, Victoria Street Flemington
Victoria 3031 (AU)**

**Curtin, David
32 O'Halloran Avenue Singleton Heights
New South Wales 2330 (AU)**

**Sujansky, Vladimir
29 Winton Street Burwood
Victoria 3125 (AU)**

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 **Explosive composition.**

57 An explosive composition comprising a blend of 45 to 95% by weight of the composition of a water-in-oil emulsion comprising a discontinuous aqueous phase comprising at least one oxygen-releasing salt, a continuous water immiscible organic phase and a water-in-oil emulsifying agent; and 5 to 55% by weight of the composition of solid particulate ammonium nitrate and wherein the Brookfield Viscosity of the water-in-oil emulsion is in the range of from 25,000 to 60,000 cps. The composition has the advantage of being collar loadable into water-containing bore-holes.

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Description

EXPLOSIVE COMPOSITION

The present invention relates to an explosive composition and in particular to such a composition comprising a blend of an emulsion explosive and solid ammonium nitrate particles.

Emulsion explosive compositions have been widely accepted in the explosives industry because of their excellent explosive properties and ease of handling. The emulsion explosive compositions now in common use in the industry were first disclosed by Bluhm in United States Patent No. 3 447 978 and comprise as components: (a) a discontinuous aqueous phase comprising discrete droplets of an aqueous solution of inorganic oxygen-releasing salts; (b) a continuous water-immiscible organic phase throughout which the droplets are dispersed; (c) an emulsifier which forms an emulsion of the droplets of oxidizer salt solution throughout the continuous organic phase; and (d) a discontinuous gaseous phase.

More recently explosive compositions which comprise a blend of a water-in-oil emulsion and a solid particulate ammonium nitrate (AN) such as ammonium nitrate prills or ammonium nitrate prills coated with fuel oil (referred to as ANFO) have become popular because of the reductions in cost due to the inclusion of a significant proportion, for example, 5 to 50% of AN.

Compositions comprising blends of a water-in-oil emulsion and AN (or ANFO) are described, for example, in Australian Patent Application No. 29408/71 (Butterworth) and US Patents 3 161 551 (Egley et al), and 4 357 184 (Binet et al). A serious problem of prior art blends is evident when loading the compositions into wet bore holes.

Although the tendency of the solid AN prill to break up or dissolve in water is reduced somewhat by the presence of the emulsion component, collar loading of prior art emulsion/prill blends into water-containing bore holes results in a significant reduction in blast performance.

As a result it has hitherto been necessary when loading emulsion/AN blends into water-containing bore-holes to pump the product to the bottom of the holes using a long delivery hose and to fill the hole by displacing water above the rising explosive column.

This pumping technique however does not allow the rapid loading rates that can be achieved when loading the blends from the top of bore-holes using techniques such as augering. Consequently as well as having to accept a slower loading rate in wet bore-holes frequent users of such explosives have been forced to maintain two sets of equipment for loading bore-holes according to the prevailing weather conditions.

We have now found that by selecting a water-in-oil emulsion having a viscosity in the range of from 25,000 to 60,000 cps the water resistance of a blend of water-in-oil emulsion and solid particulate ammonium nitrate is significantly increased while the blend retains a consistency suitable for collar-loading.

Accordingly we provide an explosive composition comprising a blend of 45 to 95% by weight of the composition of a water-in-oil emulsion comprising a discontinuous aqueous phase comprising at least one oxygen-releasing salt, a continuous water-immiscible organic phase and a water-in-oil emulsifying agent; and 5 to 55% by weight of the composition of solid particulate ammonium nitrate and wherein the Brookfield Viscosity of the water-in-oil emulsion is in the range of from 25,000 to 60,000 cps.

Where used herein the term Brookfield Viscosity refers to the viscosity measured at 60°C using a Brookfield RVT Viscometer No. 7 spindle at 50 rpm. It preferred that the Brookfield Viscosity of the water-in-oil emulsion be in the range of 28,000 to 40,000 cps.

A variety of factors influence the viscosity of the emulsion component. For example, the nature of the oil and the water-in-oil emulsifier as well as their interaction. These features may be balanced without undue experimentation to provide a Brookfield Viscosity within the characterising range of from 25,000 to 60,000 cps.

The emulsion explosive component of the composition may contain adjuvants, for example, void agents such as gas bubbles, porous particles or balloons to reduce the density agent which stabilize void agents and solid particulate material such as carbon or aluminium.

Such materials influence the viscosity of the composition as does the solid particulate ammonium nitrate and the Brookfield Viscosity of the water-in-oil emulsion is therefore determined on the water-in-oil emulsion devoid of adjuvants.

The water-immiscible organic phase component of the water-in-oil emulsion of the composition of the invention comprises the continuous "oil" phase of the water-in-oil emulsion and is the fuel. Examples of 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, furnace oils, distillate, kerosene, naphtha, waxes (eg. 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, 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, furnace oils, and paraffin oils.

Typically, the organic fuel of the continuous phase of the water-in-oil emulsion component comprises from 2 to 15% by weight and preferably 3 to 10% by weight of the water-in-oil emulsion component of the explosive composition of the invention.

Typically we have found that oils having a viscosity in the range of from 4 to 1000 and preferably 6 to 200 centi-stokes are particularly suited to providing a water-in-oil emulsion having the characteristic vis-

cosity range of from 25,000 to 60,000 cps.

It is particularly preferred that the organic fuel of the emulsion component of the compositions of the invention comprise at least one paraffinic oil.

Generally it has been the practice in the art to use diesel oil or No. 2 fuel oil in the emulsion phase of emulsion/AN blends. However we have found that the use of paraffinic oils is particularly suited to producing blends having high resistance to water absorption.

The emulsifying agent of the water-in-oil emulsion may be selected from the wide range of emulsifying agents known in the art. Examples of emulsifying agents include 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. 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), poly[alk(en)yl]succinic acid and derivatives thereof, and mixtures thereof.

Although a range of emulsifying agents may be used in preparing compositions of the invention we have found that a particularly high water resistance is provided where the water-in-oil emulsion component has a viscosity in the range of 25,000 to 60,000 cps and the emulsifying agent component comprises a condensation product of an amine and a poly[alk(en)yl]succinic acid and/or anhydride.

Typical examples of condensation products of an amine and poly[alk(en)yl]succinic acid and/or anhydride may include esters, imides amides, and mixtures thereof. Preferably, said emulsifier has an average molecular weight in the range 400 to 5000.

In said poly[alk(en)yl]succinic acid-based emulsifier it is preferred that the hydrocarbon chain is derived from polymerization of a mono-olefin and generally the polymer chain will contain from 40 to 500 carbon atoms.

Preferably the poly[alk(en)yl] moiety is derived from olefins containing from 2 to 6 carbon atoms and in particular from ethylene, propylene, 1-butene and isobutene. The emulsifier may be derived from poly[alk(en)yl]succinic anhydride. Such emulsifiers derivatives are disclosed in Australian Patent, Patent Application No. 40006/85.

Such derivatives are commercially-available materials which are made by an addition reaction between a polyolefin containing a terminal unsatu-

rated group and maleic anhydride, optionally in the presence of a halogen containing catalyst. The succinic acid or anhydride residue in the above compounds may be reacted to introduce a polar group. Generally the said polar group is monomeric although oligomeric groupings containing not more than about 10 repeat units may be employed. Examples of suitable polar groups may include polar groups derived from polyols such as glycerol, pentaerythritol, and sorbitol or an internal anhydride thereof (e.g. sorbitan); from amines such as ethylene diamine, tetraethylene triamine and dimethylaminopropylamine; and from heterocyclics such as oxazoline or imidazoline. Suitable oligomeric groupings include short-chain poly(oxyethylene) groups (i.e. those containing up to 10 ethylene oxide units).

Formation of emulsifiers for use in accordance with the invention may be effected by conventional procedures depending upon their chemical nature.

In order to prepare a derivative of poly(alk(en)yl)succinic acid comprising a polar group derived from an alcohol or amine, the acid group or anhydride thereof can be caused to react with the hydroxyl or amino group by heating the two components together in a suitable solvent, in the presence of a catalyst if desired.

The emulsifiers may be of a non-ionic character, but they may alternatively be anionic or cationic in nature, as, for example, where the hydrophilic moiety incorporates the residue of a polyamine or a heterocyclic compound.

Preferred emulsifiers are poly(isobutylene) succinic anhydride derivatives and most preferably condensates thereof with amines such as ethanolamine.

Typically, the emulsifying agent component of the composition of the present invention comprises up to 5% by weight of the emulsion component of the 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.

In particular we have found that the use of a poly(isobutylene)succinic anhydride/amine condensation product in combination with a paraffinic oil in the composition of the invention provides particularly good water resistance and is well suited for collar loading into significant volumes of water.

It is preferred that the composition of the invention further comprises voiding agents which may, for example, be in the form of fine gas bubbles dispersed through the composition, hollow particles (often referred to as microballoons), porous particles or mixtures thereof.

Techniques for preparing gassed emulsion explosives are well known in the art and include mechanical agitation, injection or bubbling the gas through the composition, or chemical generation of the gas in situ.

The preferred process for introducing a gaseous phase is by in situ chemical gassing. Suitable chemicals for the in situ generation of gas bubbles include peroxides, such as hydrogen peroxide,

peroxide nitrates, such as sodium nitrite, nitro-samines, such as N, N'-dinitrosopentamethylene tetramine, alkali metal borohydrides, such as sodium carbonate. Catalytic agents such as thiocyanate or thiourea may be used to accelerate the decomposition of a nitrite gassing agent.

Where used the voiding agent may be added before or after the emulsion is blended with the ammonium nitrate particles however it is generally preferred that the voiding agent is added to a blend of the emulsion and particles.

Typically the voiding agent comprises 0.05 to 50% by volume of the emulsion explosive component at ambient temperature and pressure. More preferably, where used, the voiding agent is present in the range 10 to 30% by volume of the emulsion explosive component and preferably the preferred bubble size of occluded gas is below 200 μm . More preferably, at least 50% of the gas component will be in the form of bubbles or microspheres of 20 to 200 μm internal diameter.

We have found that the presence of a dispersed gaseous phase significantly improves the water resistance of the composition of the invention when a gas bubble stabilising agent is also present. Such agents are described in our copending Australian patent application No. 40968/65.

Accordingly we further provide an explosive composition comprising from 45 to 95 percent by weight of the total composition of a water-in-oil emulsion comprising a discontinuous aqueous phase comprising at least one oxygen-releasing salt, a continuous water immiscible organic phase, a water-in-oil emulsifying agent and at least one agent capable of facilitating the production of gas bubbles in the presence of said water immiscible organic phase; and 5 to 55% by weight of the total composition of solid particulate ammonium nitrate; and wherein said water-in-oil emulsifying agent is selected from the group consisting of condensation products of an amine and a poly[alk(en)yl]succinic acid and/or anhydride and mixtures thereof.

The ability of various agents to facilitate the production of small gas bubbles in compositions of the invention may be determined by a foam stabilization test.

Accordingly in another aspect of the invention there is provided an explosive composition as hereinbefore described wherein the agent referred to therein is characterized further in that it has properties which provide a suitable stabilizing effect and which are established by means of a foam stabilization test as hereinafter described.

In the said foam stabilization test 0.2 part by weight of active ingredient of the candidate agent or mixture of agents to be tested is added to and mixed with 100 part by weight of diesel fuel. 5 ml of the mixture is placed in a graduated cylindrical vessel of 15 mm internal diameter. The mixture is shaken for 15 seconds. A foam forms on the surface of the mixture. The volume (V_5) of the foam is measured 5 minutes after the mixture has ceased to be shaken using the graduations on the vessel. The foam volume (V_{60}) is measured again 60 minutes after the mixture has ceased to be shaken, the vessel and the

mixture being kept at a temperature of 18 to 22°C during this period of time. A foam stability parameter $\phi^{60/5}$ is calculated from the foam volumes by means of the formula

$$\phi^{60/5} = \frac{V_{60}}{V_5}$$

It has been found that those agents or mixtures of agents in which the V_5 value was equal to or greater than 1 cubic centimetre and had a $\phi^{60/5}$ equal to or greater than 0.3 impart the desired gas bubble stabilization effect of this embodiment of the invention. Hence the foam stabilizing agents preferred for use in the compositions of the invention are those having a V_5 value equal to or greater than 1 cubic centimetre and a $\phi^{60/5}$ value equal to or greater than 0.3 as determined by the foam stabilization test hereinbefore described.

The most preferred gas bubble stabilising agents are non-ionic fluoroalkyl esters such as are available under the trade name "FLUORAD".

Typically when used in the gas bubble stabilising agent will be present in the range of 0.0001 to 5.0% by weight of the emulsion component of the composition and preferably in the range 0.001 to 1%.

Suitable oxygen-releasing salts for use in the aqueous phase component of the composition of the present invention include the alkali and alkaline earth metal nitrates, chlorates and perchlorates, ammonium nitrate, ammonium chlorate, ammonium perchlorate and mixtures thereof. The preferred oxygen-releasing salts include ammonium nitrate, sodium nitrate and calcium nitrate. More preferably the oxygen-releasing salt comprising ammonium nitrate or a mixture of ammonium nitrate and sodium or calcium nitrates.

Typically, the oxygen-releasing salt of the emulsion component of the compositions of the present invention comprises from 45 to 95% and preferably from 60 to 90% by weight of the total emulsion component of the composition. In compositions wherein the oxygen-releasing salt comprises a mixture of ammonium nitrate and sodium nitrate the preferred composition range for such a blend is from 5 to 80 parts of sodium nitrate for every 100 parts of ammonium nitrate. Therefore, in the preferred compositions of the present invention the oxygen-releasing salt component comprises from 45 to 90% by weight (of the emulsion component) ammonium nitrate or mixtures of from 0 to 40% by weight (of the emulsion component) ammonium nitrate.

Typically, the amount of water employed in the composition of the present invention is in the range of from 1 to 30% by weight of the emulsion component. Preferably the amount employed is from 5 to 25%, and more preferably from 6 to 20% by weight of the emulsion component.

Preferably the ratio of water-in-oil emulsion:solid particulate ammonium nitrate is in the range 45:55 to 70:30 and more preferably 45:55 to 60:40.

The term ammonium nitrate particulates is used herein to encompass compositions of prilled ammonium nitrate which may optionally be coated with a fuel component such as in the case of the well known ANFO compositions.

Typically the solid particulate ammonium nitrate will comprise up to 10% w/w of fuel oil with about 6% being preferred. At about 6% the solid particulate ammonium nitrate is essentially oxygen-balanced.

In a further embodiment of the invention there is provided a process for preparing the composition hereinbefore described, the process comprises blending from 45 to 95 parts by weight of a water-in-oil emulsion and from 5 to 55 parts by weight of a solid particulate ammonium nitrate.

The water-in-oil emulsion may be prepared in a preliminary procedure comprising : dissolving the oxygen-releasing salt in water at a temperature above the fudge point of the salt solution, preferably at a temperature in the range from 25 to 110°, to give an aqueous salt solution; combining the aqueous salt solution, the water-immiscible organic phase and the water-in-oil emulsifying agent with rapid mixing to form a water-in-oil emulsion; and mixing until the emulsion is uniform.

In a preferred embodiment of this process the process further comprises mixing with the emulsion component or one or more constituents thereof a gas bubble stabilising agent and an agent capable of in situ generation of gas bubbles.

As hereinbefore discussed the present invention provides significant advantages in loading of water containing bore-holes.

Accordingly we further provide a method of loading a water-containing bore-hole comprising pouring an explosive hereinbefore described into the water-containing borehole from a position adjacent the collar of the water-containing bore-hole.

By the term "pouring" it is meant that the explosive composition is released from its containment or transport means. It is preferred that the explosive composition is augered to the collar of the bore-hole and released from a position above the collar.

We also provide a method of blasting in a water-containing borehole comprising the steps of loading a water-containing bore-hole as hereinbefore described and detonating the explosive.

It is a particular advantage of our compositions that they detonate well even when poured from adjacent the collar of the borehole into significant depths of water.

Typically compositions of our invention may be detonated successfully even when the explosive/water weight ratio is less than 10 and preferably in the range of from 1/1 to 6/1.

We also provide a method of blasting comprising detonating an explosive composition as hereinabove described in water wherein the explosive/water

weight ratio is less than 10, preferably in the range of from 1/1 to 6/1.

The invention is now demonstrated by but in no way limited to the following examples in which the term Brookfield viscosity is used to refer to measurements carried out at 20°C using a Brookfield viscometer No 7 spindle at 50 rpm.

Example 1 and Comparative Example A

The Explosives of Example 1 and Comparative Example A having the compositions as shown in Table 1 were prepared according to the following procedure.

TABLE 1

	Example 1 Parts w/w	CE A Parts w/w
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Emulsion component

Ammonium nitrate	22.77	22.77
Calcium nitrate	20.32	20.32
Water	6.85	6.85
Acetic acid	0.48	0.48
Distillate (oil)	-	4.20
Sorbitan mono-oleate	-	0.84

Paraffin (oil)	4.2	-
* PIBSA emulsifier	0.84	-

Ammonium nitrate particles

ANFO	44.7	44.7
Gas bubble stabiliser		

"FLUORAD", 5% solution in distillate	0.3	0.3
Gasser agent (solution of 15% sodium nitrite and 30% sodium thiocyanate in water)	0.1	0.1

* The PIBSA emulsifier use was a 1:1 molar condensate of polyisobutylene succinic anhydride and ethanolamine.

An aqueous solution was prepared by mixing the ammonium nitrate, CN water and acetic acid. The composition was heated to about 80°C and was added to a rapidly stirred blend of the oil and emulsifier. When addition was complete stirring was continued until the emulsion was uniform (about 60 seconds).

The ANFO (which comprised particulate ammonium nitrate on which had been absorbed 6% by weight of fuel oil) was blended with the emulsion and

the gas stabilizing agent was then added with mixing, followed by the addition of the gasser solution.

The water-in-oil emulsion of the explosive composition of Example 1 prepared according to this process had a Brookfield Viscosity of 30,000 cps.

The water-in-oil emulsion of the explosive composition of Comparative Example A had a Brookfield Viscosity of 10,000 cps.

The compositions prepared according to the above process were tested as follows:-

The explosive (15 kg) is poured down a 4 m high (150 mm diameter) artificial borehole with a 200 mm diameter package at the bottom containing water (15 kg). The package was removed and the excess water poured from the top. The explosive was then primed with 400 g of "ANZOMEX" (trade mark) primer.

The composition of Example 1 successfully detonated on carrying out the above test but the composition of comparative Example A failed to detonate.

Examples 2 and 3

The Explosives of Example 2 and 3 having the compositions as shown in Table 2 were prepared according to the following procedure.

TABLE 2

	Example 2 Parts w/w	Example 3 Parts w/w
<u>Emulsion component</u>		
Ammonium nitrate (chemically pure)	40.66	40.66
Water	10.16	10.16
Paraffin (oil)	2.65	2.65
* PIBSA emulsifier	1.53	1.53
<u>Ammonium nitrate particles</u>		
ANFO	45.0	45.0
<u>VOIDING MATERIAL</u>		
"MICROBAL-LOONS"		4.0

* The PIBSA emulsifier was the condensation product of "MOBILAD C207" (MOBILAD is a trade mark) and ethanolamine in 1:1 molar ratio. MOBILAD C207 is polyisobutylene succinic anhydride in a paraffin diluent.

An aqueous solution was prepared by mixing the ammonium nitrate and water. The composition was heated to about 80°C and was added to a rapidly stirred blend of the oil and emulsifier. When addition was complete stirring was continued until the emulsion was uniform (about 60 seconds).

The ANFO (which comprised particulate ammonium nitrate on which had been absorbed 6% by weight of fuel oil) was blended with the emulsion and the MICROBALLOONS were then added with mixing.

The water-in-oil emulsion of the explosive composition of Examples 2 and 3 had a Brookfield Viscosity of 34,560 - 38560 cps.

The compositions of examples 2 and 3 showed little loss of AN from the ANFO when immersed in water.

The composition of example 2 gave 88% of shock when detonated in water-containing bore-holes.

Example 4

The composition of example 2 was prepared and chemically gassed to a density of 1.10 gcm⁻³.

The composition of example 4 gave 83% of full energy (shock and bubble) when detonated in water-containing bore-holes.

Example 5

The composition of example 2 was prepared except that the paraffin oil was replaced with Furnace oil.

The composition of example 5 gave 85-90% of full energy (shock and bubble) when detonated in water-containing bore-hole (200 mm diameter).

Example 6

The composition of example 5 was prepared except that the PIBSA emulsifier was replaced with sorbitan mono-oleate.

The composition of example 6 gave 81-86% of full energy (shock and bubble) when detonated in water-containing bore-holes (200mm diameter).

Claims

1. An explosive composition comprising a blend of 45 to 95% by weight of the composition of a water-in-oil emulsion comprising a discontinuous aqueous phase comprising at least one oxygen-releasing salt, a continuous water immiscible organic phase and a water-in-oil emulsifying agent; and 5 to 55% by weight of the composition of solid particulate ammonium nitrate and wherein the Brookfield Viscosity of the water-in-oil emulsion is in the range of from 25,000 to 60,000 cps.

2. An explosive composition according to claim 1 wherein the Brookfield Viscosity of the water-in-oil emulsion is in the range of 28,000 to 40,000 cps.

3. An explosive composition according to either of claims 1 or 2 wherein the water-in-oil emulsion comprises a discontinuous phase having a viscosity in the range of from 4 to 1000 centi-stokes.

4. An explosive composition according to any one of claims 1 to 3 wherein the water-in-oil emulsion comprises a discontinuous phase having a viscosity in the range of from 6 to 200 centi-stokes.

5. An explosive composition according to any one of claims 1 to 4 wherein the discontinuous phase comprises a paraffinic oil.

6. An explosive composition according to any one of claims 1 to 5 wherein the emulsifying agent comprises a condensation product of an amine and a poly[alk(en)yl]succinic acid and/or anhydride.

7. An explosive composition according to any one of claims 1 to 6 wherein the emulsifying agent comprises a condensation product of ethanolamine and polyisobutylene succinic anhydride.

8. An explosive composition according to any one of claims 1 to 7 wherein the emulsifying agent comprises a condensation product of ethanolamine and polyisobutylene succinic anhydride and wherein the discontinuous phase comprises a paraffinic oil.

9. An explosive composition according to any one of claims 1 to 8 wherein the explosive composition further comprises voiding agents selected from the group consisting of fine gas bubbles dispersed through the composition, hollow particles, porous particles or mixtures thereof.

10. An explosive composition according to any one of claims 1 to 9 wherein the explosive composition comprises: from 45 to 95% by weight of a water-in-oil emulsion comprising a discontinuous aqueous phase comprising at least one oxygen-releasing salt, a continuous water-immiscible organic phase, a water-in-oil emulsifying agent and at least one agent capable of facilitating the production of gas bubbles in the presence of said water immiscible organic phase; and from 5 to 55% by weight of the total composition of solid particulate ammonium nitrate; and wherein said water-in-oil emulsifying agent is selected from the group consisting of the condensation products of an amine and a poly[alk(en)yl]succinic acid and/or anhydride and mixtures thereof.

11. An explosive composition according to any one of claims 1 to 10 wherein the explosive composition comprises a water-in-oil emulsion and a solid particulate ammonium nitrate in the ratio, water-in-oil emulsion:solid particulate ammonium nitrate, in the range 45:55 to 70:30.

12. An explosive composition according to any one of claims 1 to 11 wherein the explosive composition comprises a water-in-oil emulsion and a solid particulate ammonium nitrate in the ratio, water-in-oil emulsion:solid particulate ammonium nitrate, in the range 45:55 to 60:40.

13. An explosive composition according to any one of claims 1 to 12 wherein the solid particulate ammonium nitrate comprises fuel oil constituting less than 10% by weight of the solid particulate ammonium nitrate.

14. An explosive composition according to any one of claims 1 to 13 wherein the solid particulate ammonium nitrate comprises fuel oil constituting 6% by weight of the solid particulate ammonium nitrate.

15. A process for preparing a composition according to any one of claims 1 to 14, which process comprises blending from 45 to 95 parts by weight of a water-in-oil emulsion with from 5 to 55 parts by weight of a solid particulate ammonium nitrate.

16. A process according to claim 15 wherein the water-in-oil emulsion is prepared in a preliminary procedure comprising:

dissolving the oxygen-releasing salt in water at a temperature above the fudge point of the salt solution, preferably at a temperature in the range from 25 to 110°, to give an aqueous salt solution;

combining the aqueous salt solution, the water-immiscible organic phase and the water-in-oil emulsifying agent with rapid mixing to form a water-in-oil emulsion; and mixing until the emulsion is uniform.

17. A process according to either of claims 15 or 16 wherein said process further comprises mixing with the emulsion component, or one or more constituents thereof, a gas bubble stabilising agent and an agent capable of in situ generation of gas bubbles.

18. A method of loading an explosive composition according to any one of claims 1 to 14 into a water-containing bore-hole comprising pouring said explosive composition into the water-containing bore-hole from a position adjacent the collar of the water-containing bore-hole.

19. A method of blasting in a water-containing bore-hole comprising the steps of loading an explosive composition according to any one of claims 1 to 14 into a water-containing bore-hole and detonating the explosive.

20. A method of blasting in a water-containing bore-hole according to claim 19 wherein the explosive composition/water weight ratio is less than 10.

21. A method of blasting in a water-containing bore-hole according to claim 19 wherein the explosive composition/water weight ratio is in the range of from 1/1 to 6/1.

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EP 89 30 1976

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
A	EP-A-0 213 786 (ICI AUSTRALIA LTD) * Claims; example 1; column 9, lines 24-36 *	1,6-8	C 06 B 47/00
Y	EP-A-0 161 821 (ICI AUSTRALIA LTD) * Claims *	3,5,17	
X	EP-A-0 131 355 (E.J. DU PONT DE NEMOURS AND CO.) * Claims; page 8, lines 3-12; page 17, lines 17-32; page 20, line 18 - page 21, line 5; page 22, lines 16-35 *	1,9,11-16	
Y		3,5-8, 10,18, 19	
Y	US-A-4 181 546 (R.B. CLAY) * Claims; column 6, lines 21-35 *	18,19	
P,Y	GB-A-2 194 527 (ICI AUSTRALIA OPERATIONS PROPRIETARY LTD) * Claims; page 8, lines 25-30 *	3,5-8, 10	TECHNICAL FIELDS SEARCHED (Int. Cl.4)
A	EP-A-0 152 184 (AECJ LTD) * Claims *	1,15,18	C 06 B F 42 D
A	GB-A-2 055 358 (E.J. DU PONT DE NEMOURS AND CO.) & US-A-4 287 010		
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 02-06-1989	Examiner SCHUT, R.J.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			