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(54) **Titre :** EXPLOSIF EN EMULSION
(54) **Title:** EMULSION EXPLOSIVE

(57) **Abrégé/Abstract:**

An emulsion explosive composition comprising an emulsion explosive and a heave agent. In the context of the present invention, the heave agent is a compound, or mixture of compounds, which is capable of reducing the overall relative effective energy of the emulsion explosive but which, on combustion/detonation, yields gaseous products. Examples of suitable heave agents include inorganic ammonium compounds, organic ammonium compounds, amino acids and non-ammonium containing amides, carbonates and nitrates.

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(54) Title: EMULSION EXPLOSIVE

(57) **Abstract:** An emulsion explosive composition comprising an emulsion explosive and a heave agent. In the context of the present invention, the heave agent is a compound, or mixture of compounds, which is capable of reducing the overall relative effective energy of the emulsion explosive but which, on combustion/detonation, yields gaseous products. Examples of suitable heave agents include inorganic ammonium compounds, organic ammonium compounds, amino acids and non-ammonium containing amides, carbonates and nitrates.

EMULSION EXPLOSIVE

The present invention relates to an explosive composition, in particular to an emulsion explosive composition, to its preparation and to a method of blasting using the composition.

The detonation of explosives compositions releases energy in a number of forms. Two of these types of energy release are particularly important in providing control over the blast to ensure that the size distribution and scatter of the burden is as desired. These are fragmentation energy and heave energy. Fragmentation energy (often referred to as shock energy) determines the ability of an explosive composition to shatter the surrounding media. Blasting hard media, such as rock, requires explosive compositions with relatively high fragmentation energy. Heave energy (often referred to as bubble energy) determines the ability of an explosive composition to move its surrounds.

The desired energy characteristics of an explosive composition will depend on a number of factors, including the geological nature of the medium being blasted. For instance, when blasting soft media, such as overburden or coal, the use of explosive compositions with low fragmentation energy and relatively high heave energy is preferred. If the relative proportion of fragmentation energy is too high, energy will be wasted in creating excessive fines close to the blasthole. This particular problem may not be addressed simply by reducing the fragmentation energy associated with an explosive composition since, in conventional explosives, such a reduction would also involve reduction in heave energy. The concomminant local reduction in heave energy results in less spread of the burden and increases the difficulty and cost of its collection.

With this background in mind it would be desirable to provide an explosive composition in which it is possible to control the partitioning of fragmentation and heave energies. For instance, with blasting of relatively soft media in mind, it would be desirable to provide an explosive composition in which it is possible to reduce the fragmentation energy with negligible or minimal detriment to the heave energy.

In other words, it would be desirable to reduce the overall total energy of an explosive composition without undue effect on the associated heave energy. Whilst this could possibly be achieved by diluting the explosive composition by addition of an inert diluent or filler, this would also be expected to reduce significantly the volume of gas generated by the composition when detonated. A reduction in the volume of gas generated will lead to a reduced spread of the burden and would increase the difficulty and cost of collection.

The present invention seeks to provide an explosive composition in which it is possible to control the partitioning of fragmentation and heave energies. More particularly, the present invention seeks to provide an explosive composition in which the fragmentation energy may be reduced without significant effect on the associated heave energy and volume of gas generated on detonation. Thus, the explosive composition of the present invention may be tailored to provide the desired balance of fragmentation energy and heave energy and this balance can be readily varied within and between geological formations and blastholes in order to provide optimum blast performance.

The invention provides an explosive composition that on detonation produces relatively large gas volumes regardless of the relative effective energy of the explosive composition. This is achieved by incorporation into the composition of a specific type of additive/chemical agent. In turn, this enables retention of a relatively high level of heave energy in the explosive composition.

Furthermore, the invention enables effective control of the heave energy of the explosive composition by slowing down of chemical reactions at the detonation front. The rate of energy release in explosives is governed by their detonation velocity which is further dependent on completion of chemical reactions within the reaction zone of the explosive. Incomplete reactions behind the detonation front of the shock wave of an explosion causes the shock wave to slow down. The present invention affects a slowing down of the velocity of detonation through retardation of chemical interactions of the specially selected additives with the energy producing, decomposition reactions which take place on detonation of the explosive composition. This retardation between the detonation front and the end of the reaction zone allows more energy to be available for the residual gas expansion behind the C-J plane, that is situated at the end of the reaction zone. This in turn allows more energy to be available in the expanding gases and the practical consequence of this is more efficient medium (e.g. rock) breaking and heaving processes.

Accordingly, the present invention provides an emulsion explosive composition comprising an emulsion explosive and a heave agent. In the context of the present invention, the heave agent is a compound, or mixture of compounds, which is capable of reducing the overall relative effective energy of the emulsion explosive but which, on combustion/detonation, yields gaseous products. In having these characteristics, the heave agent allows the production of relatively large gas volumes on detonation of the explosive composition, regardless of the relative effective energy of the composition. In other words, addition of the heave agent results in a reduction in the relative effective energy with negligible or minimal detriment to the volume of gas produced.

The heave agent may be an oxygen carrier with a negative heat of complete combustion, for instance from –100 to –500kcal/kg (H_2O_{liq} at 0°C). Alternatively, the heave agent may be a relatively weak fuel when compared with the fuel component(s) of the emulsion explosive. Preferably, combustion of the heave agent generates the minimum amount of solid residues on combustion. More preferably still, the heave agent produces only gaseous products on combustion so that no explosive energy is wasted due to retention of heat in solid combustion by-products. As a relatively weak fuel, the heave agent typically has a low heat of complete combustion, typically from a few hundred to a few thousand kcal/kg, for instance from 400 to 5000 kcal/kg (H_2O_{liq} at 0°C).

Numerous compounds may satisfy the requirements described above and so would function as a heave agent in accordance with the present invention. As examples of such, mention may be made of inorganic ammonium compounds, organic ammonium compounds, amides, amino acids, carbonates and nitrates. Mixtures of any two or more of such compounds may be used provided the mixture satisfies the requirements called for above. Useful compounds are commercially available or may be made by the application and adaptation of known techniques.

Useful inorganic ammonium compounds include ammonium salts, ammonium double salts and mixtures thereof. Preferred inorganic ammonium compounds include ammonium sulphate, ammonium chloride, ammonium carbonate, ammonium bicarbonate, ammonium thiosulphate, ammonium thiocyanate, ammonium sulphonate, and ammonium phosphate. Preferred double salts include ammonium sulphate nitrate, ammonium phosphate nitrate and ammonium calcium nitrate. The preferred inorganic ammonium containing double salt is ammonium sulphate nitrate. We have found that fertilizer grade ammonium sulphate nitrate is particularly suited for use in the present invention.

It is possible to use ammonium nitrate as the heave agent but this will depend upon the characteristics of the emulsion explosive. The latter must be such that the ammonium nitrate satisfies the requirements called for above for functioning as a heave agent. Thus, it would not be appropriate to include ammonium nitrate in an emulsion explosive where the effect of adding the ammonium nitrate was to increase the relative effective energy of the emulsion explosive.

Solid ammonium nitrate may be used together with any of the other specified heave agents in the form of a blend of solids. In this case ammonium nitrate-fuel in the emulsion explosive may be replaced by solid ammonium nitrate heave agent. The combination of solid ammonium nitrate and (other) heave agent is very beneficial in some blasting applications. In the case that oxygen negative emulsion explosives are used, it is advantageous to add solid ammonium nitrate in combination with the heave agent. For instance, where the heave agent is very oxygen negative and there is a need to use larger amounts of it, then it is desirable to use this combination.

Organic ammonium compounds suitable for use in the present invention include ammonium acetate, ammonium oxalate, ammonium tartrate and ammonium citrate.

Useful carbonates include alkali metal and alkaline earth metal carbonates such as sodium carbonate, barium carbonate and calcium carbonate.

Nitrates suitable for use in the present invention include alkali metal and alkaline earth metal nitrates such as sodium nitrate and calcium nitrate.

Urea and dicyandiamide may be mentioned as suitable amides. When urea is used, the amount thereof is usually from 10% to 30% by weight based on the total weight of the composition. The use of such quantities of urea is particularly effective in reducing the velocity of detonation of the explosive composition whilst generating significant volumes of gas. Also, urea is a desired heave agent due to its cost effectiveness. Acid amides, such as organic compounds containing the structural moiety – $CONH_2$, or their derivatives, are included as useful amides suitable for use as the heave agent.

Amino acids may be used as the heave agent. As examples of such, mention may be made of glycine, methionine, alanine and lysine. Animal feed grade methionine is preferable due to its relatively low cost.

The heave agent used in the explosive compositions of the present invention is typically present in an amount of greater than 5% by weight. The heave agent may be readily used in amounts up to about 60% by weight. It is preferred however that the heave agent be present in the explosive composition in amount of from 20 to 40% by weight.

The heave agent is included in the compositions of the invention as a solid and usually takes the form of granules/particles. The particle size of the heave agent is usually from 1 to 10 mm diameter. The optimum particle size is dependent upon the size (diameter) of the charge. It is preferable to use larger diameter particles of heave agents in large diameter boreholes such as those used for blasting overburden or coal (150 to 320 mm blastholes). This said, the most commonly used particle size is about 1 to 2 mm. Ammonium sulphate nitrate (fertilizer grade) is commercially available in a particle size of 85% in the range of 2 to 5 mm and a mean particle size from 2.8 to 3.5mm.

The explosives emulsion suitable for use in the present invention may be a water-in-oil, melt-in-oil emulsion or melt-in-fuel emulsion. Water-in-oil emulsion explosive compositions were first disclosed by Bluhm in United States Patent 3,447,978 and comprise (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 and (c) an emulsifier which forms an emulsion of the droplets of oxidiser salt solution throughout the continuous organic phase. Where these types of emulsions comprise very little water or adventitious water only in the discontinuous phase they are more correctly referred to as melt-in-fuel emulsion explosives.

Suitable oxygen releasing salts for use in the aqueous phase of the emulsion include 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 comprises ammonium nitrate or a mixture of ammonium nitrate and sodium or calcium nitrates. These salts are dissolved in and form part of the aqueous phase of the emulsion.

Typically the oxygen releasing salt component of the compositions of the present invention comprise from 45 to 95 % w/w and preferably from 60 to 90 % w/w of the total emulsion 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 composition the oxygen releasing salt component comprises from 45 to 90 % w/w (of the total emulsion composition), ammonium nitrate or mixtures of from 0 to 40 % w/w, sodium or calcium nitrates and from 50 to 90 % w/w ammonium nitrate.

Typically the amount of water employed in the compositions of the present invention is in the range of from 0 to 30 % w/w of the total emulsion composition. Preferably the amount employed is from 4 to 25 % w/w and more preferably from 6 to 20 % w/w.

The water immiscible organic phase of the emulsion composition of the present invention comprises the continuous "oil" phase of the emulsion composition and is the fuel. Suitable organic fuels include aliphatic, alicyclic and aromatic compounds and mixtures b thereof which are in the liquid state at the formulation temperature. Suitable organic fuels may be chosen from fuel oil, diesel oil, distillate, furnace oil, kerosene, naphtha, waxes such as microcrystalline wax, paraffin wax and slack wax, paraffin oils, benzene, toluene, xylenes, asphaltic materials, polymeric oils such as the low molecular weight polymers of olefines, animal oils, vegetable 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 and paraffin oils.

Typically the organic fuel or continuous phase of the emulsion comprises from 2 to 15 % w/w and preferably 3 to 10 % w/w of the total composition.

The emulsifier of the emulsion composition of the present invention may comprise emulsifiers chosen from the wide range of emulsifiers known in the art from the preparation of emulsion explosive compositions. It is particularly preferred that the emulsifier used in the emulsion composition of the present invention is one of the well known emulsifiers based on the reaction products of poly[alk(en)yl] succinic anhydrides and alkylamines, including the polyisobutylene succinic anhydride (PiBSA) derivatives of alkanolamines. Other suitable emulsifiers for use in the emulsion of the present invention include alcohol alkoxylates phenol 5 alkoxylates, poly(olyalkylene)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 amines, fatty acid amide alkoxylates, fatty amines, quaternary amines, alkyloxazolines, alkenyloxazolines, imidazolines, alkylsulphonates, alkylarylsulphonates, alkylsulphosuccinates, alkylarylsulpnonates, alkylsulphosuccinates, alkylphosphates, alkenylphosphates, phosphate esters, lecithin, copolymers of poly(oxyalkylene)glycols and poly(12-hydroxystearic)acid and mixtures thereof.

Typically the emulsifier of the emulsion comprises up to 5 % w/w of the emulsion. Higher proportions of the emulsifying agent may be used and may serve as supplemental fuel for the composition but in general it is not necessary to add more than 5 % w/w of emulsifying agent to achieve the desired effect. Stable emulsions can be formed using relatively low levels of emulsifier and for reasons of economy it is preferable to keep the amount of emulsifying agent used to the minimum required to form the emulsion. The preferred level of emulsifying agent used is in the range of from 0.1 to 3.0 % w/w of the water-in-oil emulsion.

Generally emulsions themselves are not detonable and in order to form an explosive composition, the emulsion must be mixed with sensitising agents such as a self explosive (e.g. trinitrotoluene or nitroglycerine) or a discontinuous phase of void agents. Suitable void agents include glass microballoons, plastic microballoons, expanded polystyrene beads and gas bubbles, including bubbles of nitrogen generated in-situ by chemical gassing agents and entrained air.

If desired, other optional fuel materials, hereinafter referred to as secondary fuels may be incorporated into the emulsion in addition to the water immiscible organic fuel phase. Examples of such secondary fuels include finely divided solids and water miscible organic liquids which can be used to partially replace water as a solvent for the oxygen releasing salts or to extend the aqueous solvent for the oxygen releasing salts. Examples of such secondary fuels include finely divided solids and water miscible organic liquids which can be used to partially replace water as a solvent for the oxygen releasing salts or to extend the aqueous solvent for the oxygen releasing salts. Examples of solid secondary fuels include finely divided materials such as sulphur and carbonaceous materials such as gilsonite, comminuted coke or charcoal, carbon black, sugars such as glucose or dextrose and vegetable products such as starch, nut meal, grain meal and wood pulp. Examples of water miscible organic liquids include alcohols such as methanol and glycols such as ethylene glycol. Typically the optional secondary fuel component of the composition of the present invention comprises from 0 to 30 % w/w of the total composition.

The water-in-oil emulsion composition may be prepared by a number of different methods. One preferred method of manufacture includes: dissolving said oxygen releasing salts in water at a temperature above the fudge point of the salt solution, preferably at a temperature in the range from 20 to 110 °C to give an aqueous salt solution; combining an aqueous salt solution, a water immiscible organic phase, and an emulsifier with rapid mixing to form a water-in-oil emulsion; and mixing until the emulsion is uniform.

It lies within the invention that there may also be incorporated into the emulsion other substances or mixtures of substances which are oxygen releasing salts or which are themselves suitable as explosive materials.

It is believed that the heave agent used in practice of the present invention plays an important part in the decomposition process of emulsion explosives. In the following, by way of illustration only, reference is made to compositions in which the oxygen-releasing salt is ammonium nitrate.

The rate determining step in the combustion of emulsion explosives is believed to be the dissociation reaction of ammonium nitrate into ammonia and nitric acid;

$NH_4\,NO_3 > NH_3 + HNO_3$ endothermic (1)

$<$

It is believed that the heave agent inhibits or retards the process of above reaction (1) by:

(i) Generation of excess ammonia through decomposition with an associated substantial shift of the equilibrium of the dissociation to the left, for example

$(NH4)_2\,C_2O_4 > 2NH_3 + (COOH)_2$ (2)

Ammonium Oxalate > Ammonia + Oxalic Acid

(ii) Amides (e.g. urea, dicyandiamide), acid amides, amino acids or other reducing materials combining with nitric acid or the nitrogen oxides produced during ammonium nitrate decomposition in reaction (1). It is believed that the unoxidised ammonia accumulates in the reaction zone and the burning process in reaction (1) is inhibited or retarded. In the following reaction scheme urea is included by way of illustration.

$HNO_3 + CO\,(NH_2) > CO(NH_2)_2\,HNO_3$ (3)

Nitric Acid + Urea > Urea Nitrate

Thus, it is believed that the heave agent acts as a retarding agent in the ammonium nitrate decomposition reactions. The reactions (2) and (3) shift the equilibrium of reaction (1) to the left and therefore are believed to control the rate of energy release.

The interaction of the heave agent with the emulsion explosives allows the following reaction to proceed to completion:

$$NH_4\,NO_3 > 2H_2O + 0.5\,O_2 + N_2 \text{ exothermic (4)}$$

Driving of reaction (4) towards the release of exothermic heat is believed to be possibly due to elimination of the excess of oxygen through reaction with ammonia, which is generated from the decomposition of the retarding agent in reaction (2)

$$2\,NH_3 + 1.5\,O_2 > N_2 + 3\,H_2O \text{ exothermic (5)}$$

Even small amounts of combustible substances influence exothermic decomposition to proceed with the release of appreciable quantities of exothermic heat energies. Decomposition into gaseous constituents is believed to be facilitated by the use of weaker acid ammonium salts, ie ammonium salts with lower disassociation temperatures (viz 2).

Ammonium nitrate is an oxygen positive molecule containing one atom of oxygen per molecule in excess what is required for the complete combustion of its hydrogen (viz 4). When heat is present, the excess oxygen is available for oxidation of the hydrogen of the ammonia group in the ammonium salt added (viz 5). The oxidation of ammonia (in the ammonium salt) generates heat, which is then further demanded for the conversion of the acid residues (in the ammonium salt) into gaseous products.

$$(COOH)_2 + \text{Heat} > H^{+}_2 + 2\,COO^{-} \text{ endothermic (6)}$$

In addition to the above, there is at the same time demand for thermal energy for the preceding disassociation of ammonium nitrate into ammonia and nitric acid.

$$NH_4NO_3 + \text{Heat} > NH_3 + HNO_3 \text{ endothermic (1)}$$

The addition of heave agent in accordance with the present invention appears to have a retarding and slightly desensitising effect on the explosive decomposition process. Furthermore, the heave agent appears to provide a thermal energy surplus due to oxidation of the ammonia group (shown in reaction (5) below) and a thermal energy deficit due to the disassociation reaction of the acid radical (6).

It is believed that the heave agent has significant impact on chemical reactions and thermochemistry. The rate of the chemical energy release is extremely important in performance of explosives to break media such as rock. The partition of the energy into fragmentation and heave energies determines the ability of the explosives to break and move its surrounds.

The heave agent used in practice of the invention effectively controls delivery of the heave energy through slowing down the chemical reactions in the detonation front as shown by reduction of velocity of detonation values and extension of the reaction zone length (critical diameter). The heave agent, through reactions with the emulsion explosive, produces large volumes of gas as a result of the detonation process. The delivery of large gas volumes provides efficient blasting. The direct oxidation of the fuel oil by the discontinuous oxygen releasing salt phase also produces large volumes of extremely hot gas and thus tends to have very high energy.

Advantageously, the present invention provides a readily variable explosive composition which permits the rate of energy release to be controlled whilst maintaining the generation of high volumes of gas. The composition of the present invention permits a predrilled pattern of boreholes to be loaded with explosive compositions having an energy release rate specifically selected for each borehole and even regions within each borehole. The use of variable energy explosives according to the present invention permits greater control in the placing of broken overburden and may reduce or eliminate back break.

The compositions of the present invention may be provided with variable energy profiles and rates of energy release by varying the proportion of heave agent incorporated into the explosive composition during manufacture and pumping and/or auguring of the explosive composition into the borehole. Emulsion explosive compositions are often manufactured by mixing the components with fuel oil on site using bulk trucks. The on site manufacture of emulsion explosive compositions may be readily adapted for the manufacture of the explosive compositions of the present invention.

An additional storage facility may be incorporated into a mobile explosive manufacturing unit, thereby allowing the control of the amount of heave agent to be readily varied by controlling the rate at which the heave agent is metered during the explosive manufacturing process. This will allow the composition of the explosive to be varied easily from blasthole to blasthole and also varied readily within any particular blasthole. Local variations in geology may thus be readily taken into account by providing appropriate energy releases even within a blasthole.

The compositions of the present invention permit a reduction in the generation of fines, reduce the back break, improve the formation and placement of rock overburden thereby providing increased drag line and shovel efficiency and may reduce or eliminate bullying of the ground.

While the emulsion explosive compositions of the instant invention may be used by themselves, these explosives may also be blended with ANFO-based explosives as is known in the art.

The compositions of the present invention may readily be made by blending a heave agent as described herein with an emulsion explosive. The emulsion may be a manufactured batch or, alternatively, the heave agent may be blended with the components of the emulsion explosive during preparation of the emulsion explosive. Blending may be achieved by conventional means.

The present invention also provides a method of blasting which comprises detonating an explosive composition of the present invention. The composition may be detonated by conventional means.

The present invention is now illustrated by the following examples and comparative examples.

Example 1

An explosive emulsion composition having the following formulation was prepared by blending components in the weight percentage proportions shown in the following table.

Oxidiser Solution:	
Ammonium nitrate (non-porous)	73.80
Water	18.40
Acetic acid (75%)	0.16
Soda ash	0.04
Fuel Blend:	
Emulsion	1.85
Paraffin oil	5.75

This emulsion was sensitised by use of a gassing agent (30% w/w sodium nitrite in water). To the sensitised emulsion was blended fertiliser grade ammonium sulphate nitrate (ASN) particles of mean diameter 2.8-3.5mm. The blending ration of ASN:emulsion is shown in the following table together with the density of each formulation. A number of theoretical calculations were performed in order to asses the likely performance of each composition. The results of these calculations using "Ideal Explosives Code" ("IDEX") to calculate ideal explosives properties are also shown in Table 1.

TABLE 1

EXPLOSIVE EMULSION

ASN: Explosive Emulsion – IDEX Calculations						
	0/100	**20/80**	**30/70**	**40/60**	**50/50**	**60/40**
Density (g/cc)	1.20	1.28	1.32	1.37	1.42	1.48
Gas Volume (l/kg)	1100	1080	1070	1060	1040	1020
REE (%)	95	88	85	82	78	73
RBS (%)	143	141	141	140	138	135

REE stands for Relative Effective Energy at a pressure of 100MPa and is standardised relative to ANFO. The REE for ANFO is taken to be 100%.

RBS stands for Relative Bulk Strength and is standardised relative to ANFO (which has RBS of 100%). The RBS includes a density weighting and may be calculated by multiplying the REE for a given composition by a factor d_c/d_{ANFO} where d_c is the density of the composition under consideration and d_{ANFO} is the density of ANFO.

As can be seen, addition of heave agent (ammonium sulphate nitrate) reduces the Relative Effective Energy of the composition. However, this reduction is associated only with a marginal reduction in volume of gas generated. Thus, the heave agent may be used to tailor the characteristics of the emulsion explosive composition. In practical terms, the Relative Bulk Strength is essentially unaffected due to an increase in density of the composition as heave agent is added.

Example 2

A sensitised water-in-oil emulsion was prepared by blending components in the weight percentages shown below.

Oxidiser Solution:	
Ammonium nitrate	72.80
Sodium perchlorate	9.00
Water	8.00
Fuel Blend:	
Emulsifier	1.60
Paraffin oil	4.60
Sensitising Agent:	4.00

The resulting emulsion was detonator sensitive.

With one exception, to this emulsion was added particles of fertiliser grade ASN (2.8-3.5mm mean diameter) in the weight proportions shown in the following table. The density of each formulation is also given in the table.

The compositions were tested to measure their velocities of detonation as follows. Two lengths of optical fibre with clean cut ends are inserted a known distance apart (typically 100mm) into the explosive under test in a cardboard tube. The other ends of the fibres are connected to the terminals of an electronic timer which is capable of timing the light pulses from a start and stop signal. The optical fibre which is located in the charge closest to the detonator is the start signal for the timer and should be connected to terminal 0. The second optical fibre stops the timer and should be connected to terminal 1. The timer times the light pulse from the detonation front as it passes the start and stop optical fibres and displays this time in milliseconds. The velocity of detonation is calculated from the time taken for the detonation front to pass from the first to the second fibre.

Charges of explosive in different diameter cardboard tubes were detonated. The critical diameter was determined by the smallest charge diameter at which 100% detonation of the charges was obtained. Available Relative Effective Energy, available Relative Bulk Strength and gas volume were also calculated.

The results of these tests are shown in Table 2 below.

TABLE 2

Formulation No.	**CE1**	**1**	**2**	**3**	**4**
Emulsion (wt %)	100	70	60	50	40
ASN (wt %)	-	30	40	50	60
Density (g/cc)	1.10	1.20	1.26	1.32	1.34
VOD(km/s)					
Unconfined charge diameter					
19mm	4.65	3.85	3.40	F	

25mm	4.95	4.30	3.95	3.60	F
32mm	5.05	4.50	4.20	3.80	3.10
45mm	5.25	4.65	4.45	4.25	3.70
100mm	5.40	4.90	4.80	4.50	4.00
Critical Diameter (mm)	>8	>12	>16	>18	>25
Available Energy:					
REE (%)	103	90	84	79	73
RBS (%)	142	139	135	133	130
Gas Volume (l/kg)	1010	987	982	977	973

F – Failure to detonate.

Example 3

An unsensitised water-in-oil emulsion having the composition shown above in Example 1 was prepared by blending of components. The emulsion was sensitised with a gassing solution as in Example 1 and the resultant sensitised emulsion had the density shown in Table 3 below. With one exception, to each formulation was added fertiliser grade ASN, as in Example 1. The compositions were tested and REE, RBS and gas volumes calculated. The results are given below.

TABLE 3

Formulation No.	**CE2**	**5**	**6**	**7**	**8**
Emulsion (wt %)	100	70	60	50	40
ASN (wt %)	-	30	40	50	60
Density (g/cc)	1.12	1.23	1.29	1.33	1.35
VOD(km/s)					
Unconfined charge diameter					
28mm	4.95	F			
40mm	5.15	4.20	F	F	F
70mm	5.40	4.80	4.60	3.80	/
100mm	5.50	5.00	4.80	4.40	4.40
152mm	5.65	5.10	5.00	4.60	/
Critical Diameter (mm)	>28	>40	>50	>60	>120

Available Energy:					
REE (%)	87	78	75	70	65
RBS (%)	121	120	121	117	110
Gas Volume (l/kg)	1100	1070	1060	1040	1020

F - Failure to detonate.

/ - Not determined.

Example 4

Example 3 was repeated with a variation in the exact formulation of the sensitised emulsion; the degree of gassing being adjusted. The results are shown in Table 4 below.

TABLE 4

Formulation No.	**CE3**	**9**	**10**
Emulsion (wt %)	100	80	60
ASN (wt %)	-	20	40
Density (g/cc)	1.26	1.31	1.39
VOD(km/s)			
Unconfined charge diameter			
70mm	F		
80mm	4.90	/	
90mm	5.40	F	
100mm	5.60	4.30	F
125mm	5.80	5.00	3.80
150mm	6.00	5.50	4.10
Critical Diameter (mm)	>70	>90	>100
Available Energy:			
REE (%)	100	91	84
RBS (%)	157	149	146
Gas Volume (l/kg)	1100	1080	1060

F – Failure to detonate

\ - Not determined.

Example 5

An (unsensitised) emulsion was prepared as in Example 1. With one exception the emulsions were blended to include particulate mix ammonium nitrate and urea or ASN (fertiliser grade;

mean diameter 2.8 – 3.5mm) as heave agent.

The formulated explosives were tested in accordance with the procedures described above and the results shown in Table 5.

TABLE 5

Formulation No.	**CE4**	**CE5**	**11**	**12**	**13**
Emulsion (wt %)	100	100	70	60	60
Ammonium Nitrate (wt %)	-	-	24	-	-
Urea (wt %)	-	-	6	-	-
ASN (wt %)	-	-	-	40	40
Density (g/cc)	1.12	1.26	1.18	1.29	1.39
VOD(km/s)					
Unconfined charge diameter					
50mm	/	/	4.50	4.60	/
70mm	5.40	/	4.60	4.80	/
100mm	5.50	5.60	5.00	5.00	/
150mm	5.65	6.00	5.00	/	4.10
180mm	/	/	/	/	/
Critical Diameter (mm)	>35	>70	>60	>50	>120
Available Energy:					
REE (%)	87	100	/	75	84
RBS (%)	121	157	/	121	146
Gas Volume (l/kg)	1100	1100	1090	1060	1060

/ - Not determined.

The results of Examples 2-5 may be summarised as follows.

Addition of heave agent to each composition leads to an increase in critical diameter. For instance, increasing the amount of heave agent from 30 wt % to 60 wt % in formulation nos. 1-4 results in the critical diameter increasing from about 12mm to about 25mm. This kind of effect is observed in the remaining examples. The critical diameter of the charges are a function of the reaction zone length. The reaction zone lengths are very short for fast detonating explosives (2-10mm) and very long for relatively slow detonating charges (35-70mm). It has been observed that an appreciable slowing down of the reactions within the detonation front allows more energy to be available for the residual gas expansion behind the C-J plane.

Significantly, addition of the heave agent causes a reduction in REE, the extent of the reduction increasing with increasing amount of heave agent. For instance, through formulation nos. 1-4 the REE falls from 90 to 73%. However, the volume of gas generated remains relatively constant, fluctuating only from 987 to 973 l/kg over these formulations. The volume of gas is certainly not adversely affected to a significant degree. This effect is also consistent over all of the examples where heave agent is employed. These results show that in accordance with the present invention the detonation characteristics of the composition may be controlled by introduction of heave agent. The RBS values remain unchanged with the exception of additions in excess of 60%. The RBS varies as a function of the density of the composition under test.

Comparative Example 1

A water-in-oil explosive emulsion was prepared as in Example 2. With one exception, sodium chloride (10-40% passing 36 mesh; British standard sieve, 10% passing 72 mesh; British standard sieve) was included in the emulsion in the weight % shown in the following table. The emulsions were tested and calculations performed as in earlier examples and the results shown below.

TABLE 6

Formulation No.	**CE5**	**CE6**	**CE7**	**CE8**
Emulsion (wt %)	100	80	70	50
Sodium Chloride (wt %)	-	20	30	50

Density (g/cc)	1.10	1.26	1.35	1.45
25mm	4.95	4.75	4.40	3.95
32mm	5.05	4.90	/	4.20
45mm	5.25	4.85	4.75	4.40
100mm	5.40	5.15	5.00	4.60
Critical Diameter(mm)	>19	>19	>19	>19
Available Energy:				
REE (%)	103	76	63	39
RBS (%)	142	116	102	71
Gas Volume (l/kg)	1010	808	707	506

/ - Not determined.

In the context of the present invention, sodium chloride is an inert diluent/filler. Addition of sodium chloride has no effect on critical diameter, this remaining constant at about 19mm. The sodium chloride causes a reduction in REE and results in significantly reduced volumes of gas being generated on combustion. For instance, addition of 50 wt % sodium chloride effectively halves the volume of gas generated when compared with the unadditised emulsion (formulation CE5). This reduction in gas volume is due to the fact that sodium chloride does not contribute to gas generation on detonation. This should be contrasted with the heave agent used in the present invention, which enables a reduction in REE but with little detriment to the volume of gas generated on combustion. This is because the heave agent contributes to improving the efficiency of the detonation process.

It has also been observed that the compositions which include heave agent provide a cleaner detonation in terms of the detonation fumes generated. This is illustrated by absence of brown/yellow fumes produced on detonation while firing of formulations 1-4 (Table 2). At a larger testing site range, comparative formulation CE2 produced some yellow coloured fumes, while formulations 5-8 produced white/pale grey after-detonation fumes. The comparative formulation (CE1) produced a slight tinge of yellow/brown colour on detonation. The yellow/brown coloured fumes are believed to be lower nitrogen oxides. The use of heave agents is believed to provide more complete combustion resulting in less partially oxidised species.

This is a further advantage associated with the present invention.

Those skilled in the art will appreciate that the invention described herein is susceptible to variations and modifications other than those specifically described. It is to be understood that the invention includes all such variations and modifications which fall within its spirit and scope. The invention also includes all of the steps, features, compositions and compounds referred to or indicated in this specification, individually or collectively, and any and all combinations of any two or more of said steps or features.

Throughout this specification and the claims which follow, unless the context requires otherwise, the word "comprise", and variations such as "comprises" and "comprising", will be understood to imply the inclusion of a stated integer or step or group of integers or steps but not the exclusion of any other integer or step or group of integers or steps.

CLAIMS:

1. An emulsion explosive composition comprising an emulsion explosive and a heave agent which is a compound or mixture of compounds capable of reducing the overall relative effective energy of the emulsion explosive but which, on combustion/detonation, yields gaseous products.

2. A composition according to claim 1, wherein the heave agent is a compound which is an oxygen carrier with a negative heat of complete combustion or a weak fuel when compared with fuel present in the emulsion explosive and which yields gaseous products on detonation of the explosive composition.

3. A composition according to claim 1 or claim 2, wherein the heave agent is present in an amount of at least 5% by weight based on the total weight of the composition.

4. A composition according to any one of the preceding claims, wherein the heave agent is selected from inorganic ammonium compounds, organic ammonium compounds, amino acids and non-ammonium containing amides, carbonates and nitrates.

5. A composition according to claim 4, wherein the heave agent is an inorganic compound selected from ammonium nitrate, ammonium sulphate, ammonium chloride, ammonium carbonate, ammonium bicarbonate, ammonium thiosulphate, ammonium thiocyanate, ammonium sulphonate, ammonium phosphate, ammonium sulphate nitrate, ammonium phosphate nitrate and ammonium calcium nitrate.

6. A composition according to claim 4, wherein the organic ammonium compound is selected from ammonium acetate, ammonium oxalate, ammonium tartrate and ammonium citrate.

7. A composition according to claim 4, wherein the carbonate is selected from sodium carbonate, barium carbonate and calcium carbonate.

8. A composition according to claim 4, wherein the nitrate is selected from sodium nitrate and calcium nitrate.

9. A composition according to claim 4, wherein the amide is selected from urea, dicyandiamide and acid amides containing the functional moiety -CONH$_2$, or derivatives thereof.

10. A composition according to claim 4, wherein the amino acid is selected from glycine, methionine, alanine and lysine.

11. A composition according to any one of the preceding claims, wherein the emulsion explosive is a water-in-oil emulsion comprising an aqueous phase including an oxygen-releasing salt and a water-immiscible organic phase including a fuel.

12. A method of manufacturing an emulsion explosive composition which comprises blending a heave agent into an emulsion explosive.

13. A method according to claim 12, wherein the heave agent is as defined in any one of claims 2 and 4 to 10.

14. A method according to claim 12 or 13, wherein the amount of heave agent blended into the emulsion explosive is at least 5% by weight based on the total weight of the composition.

15. A method according to any one of claims 12 to 14, wherein the emulsion explosive is as defined in claim 11.

16. A method of blasting which comprises detonating an emulsion explosive composition as defined in any one claims 1 to 11.