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Water-in-Oil Emulsion Blasting Agents Containing
Unrefined or Partly Refined Petroleum Product as
Fuel Component.

The present invention relates to water-in-oil
5 emulsion explosive compositions which consist of a
continuous carbonaceous fuel phase which is external,
and a discontinuous aqueous oxidising salt solution
phase which is internal. In particular, the invention
relates to such emulsion explosive compositions con-
10 taining a carbonaceous fuel phase which is advantageous
over those disclosed in the prior art.

Water-in-oil emulsion explosives are now well
known in the explosives art and have been demonstrated
to be safe, economic and simple to manufacture and to
15 yield excellent blasting results. Bluhm, in United
States Patent No. 3 447 978, disclosed an emulsion
explosives composition comprising an aqueous
discontinuous phase containing dissolved oxygen-supplying
salts, a carbonaceous fuel continuous phase, an occluded
20 gas and an emulsifier. Since Bluhm, further disclosures
have described improvements and variations in water-in-oil
explosives compositions. These include United States
Patent No. 3 674 578, Cattermole et al; United States
Patent No. 3 770 522, Tomic; United States Patent No.
25 3 715 247, Wade; United States Patent No. 3 765 964,
Wade; United States Patent No. 4 110 134, Wade; United
States Patent No. 4 149 916, Wade; United States Patent
No. 4 141 817, Wade; United States Patent No. 4 141 767,
Sudweeks & Jessup; Canadian Patent No. 1 096 173, Binet
30 and Seto; United States Patent No. 4 111 727, Clay;
United States Patent No. 4 104 092, Mullay; United
States Patent No. 4 231 821, Sudweeks & Lawrence;
United States Patent No. 4 218 272, Brockington;

United States Patent No. 4 138 281, Olney & Wade; United States Patent No. 4 216 040, Sudweeks & Jessup and United States Patent No. 4 287 010, Owen. In Canadian Patent No. 1 106 835, Bent et al and in United States Patent Nos. 4 259 977 Brockington and 4 273 147, Olney, methods are disclosed for the preparation and placement of emulsion explosive compositions.

All of the aforementioned emulsion type explosive compositions contain an essential emulsifier ingredient. Without the presence of such an emulsifier, the mixed phases of the composition soon separate to form a layered mixture having no utility as an explosive. Additionally, all of the aforementioned compositions contain as the carbonaceous fuel fluidizable carbonaceous ingredients in a substantially highly refined or purified state. For example, United States Patent No. 4 231 821 discloses the use of materials selected from mineral oil, waxes, paraffin oils, benzene, toluene, xylenes and mixtures of liquid hydrocarbons generally referred to as gasoline, kerosene and diesel fuels. United States Patent No. 4 218 272 discloses the use of highly refined micro-crystalline waxes, for example, WITCO (Reg. TM) X145-A and ARISTO (Reg. TM) 143. In United States Patent No. 4 110 134, the use is proposed of INDRA (Reg. TM) 2119, a substantially refined blend of petrolatum, wax and oil and ATREOL (Reg. TM), a white mineral oil. The use of such refined or purified carbonaceous material as the continuous fuel phase of an emulsion explosive composition has heretofore been deemed essential.

According to the present invention a water-in-oil emulsion explosive composition is provided wherein the continuous carbonaceous fuel phase comprises an unrefined or partly refined petroleum product, the said petroleum product being characterised in that

(a) the component molecules have between 20 and 80 carbon atoms and less than 50% of the said molecules have a number of carbon atoms within the same five carbon atom range, and,

(b) wherein the said unrefined or partly refined petroleum product comprises at least 10% by weight of flowable oil if the said petroleum product is in the form of a petroleum wax or comprises at least 10% by weight of a distillation residue if the said petroleum product is in the form of a petroleum oil or tar.

Particularly, the water-in-oil emulsion explosive composition of the invention preferably comprises a continuous phase of from 1-10% by weight of an unrefined or partly refined petroleum product as hereinabove defined containing from 0.5 - 3% by weight of an emulsifying agent, a discontinuous phase comprising from 10% to 25% by weight of water and from 65% to 85% by weight of water-soluble inorganic oxygen-supplying salts, and a sufficient amount of a density lowering ingredient to maintain the composition at a density between 0.9 and 1.4g/cc.

Exemplary of the unrefined or partly refined petroleum products suitable for use as the continuous fuel phase of the emulsion explosive compositions of the invention are slackwaxes, commercial wax/oils, residual fuel oils, asphalt, bunker oil, topped crude petroleum, petroleum tars, crude petroleum, bitumens, weathered crude petroleum and blended fuel oil.

By slackwax is meant the wax which results from the incomplete pressing of settlings from petroleum distillates and which contains at least 10% by weight and usually 10% to 25% of oil.

By commercial wax/oils is meant semi-solid mixtures of hydrocarbon oil and soft petroleum waxes and containing at least 10% by weight and usually over 25% of oil.

By residual fuel oil is meant topped crude petroleum or viscous residuals obtained in refinery operations or combinations of these materials with distilled petroleum.

By asphalt is meant a black to dark-brown solid or semi-solid cementitious material which liquefies when heated, in which the predominant constituents are

bitumens or combinations of bitumens with petroleum or petroleum derivatives.

By bunker oil is meant heavy residual fuel oil.

By topped crude petroleum is meant a residual
5 product remaining after separation by distillation or other means from crude petroleum of a substantial quantity of the more volatile components.

By petroleum tars is meant viscous black or dark-brown products obtained in petroleum refining which when
10 partially evaporated or fractionally distilled yield a substantial quantity of solid residue.

By bitumens is meant solid or semi-solid mixtures consisting predominantly of hydrocarbons which occur in nature or are obtained in petroleum refining
15 operations.

By weathered crude petroleum is meant products resulting from crude petroleum through loss due to natural causes during storage and handling of an appreciable quantity of the more volatile components.

By crude petroleum is meant a naturally occurring
20 mixture comprising predominantly hydrocarbons together with some or all of sulfur, nitrogen or oxygen derivatives of hydrocarbons which is capable of being removed from the earth in a liquid state.

Petroleum wax is a product separated from petroleum which is solid or semi-solid at 25°C and consists essentially of a mixture of saturated hydrocarbons. Distillation residues are the bottoms or residuals remaining after commercial distillation of petroleum
25 whose dominant components have boiling points in excess of 593°C at atmospheric pressure.
30

It has been found, contrary to all expectations, that the use of crude or unrefined petroleum products as the continuous fuel phase in an emulsion explosive
35 composition has no deleterious effect on the properties of the resultant explosive composition; that is, the strength, the detonation velocity, the stability and

storage properties are generally undiminished when compared to compositions comprising refined hydrocarbons, and in some cases are markedly improved. Indeed, it has been surprisingly found that the use of unpurified petroleum fuels provide emulsion explosives which are cap-sensitive even in small diameter charges. An additional and obvious advantage in the use of unrefined petroleum fuels is the substantial economic advantage enjoyed over the previously used, high cost, refined oils and waxes. Furthermore, in the prior art compositions, careful blending of the refined oils and waxes is typically required in order to provide emulsions having suitable rheology for practical cartridging. By employing unrefined petroleum fuels, an explosive product of high viscosity having good cartridging characteristics results without the need for fuel blending.

A particular advantage of the present invention lies in the property of explosive compositions containing unrefined fuels to tenaciously retain void spaces such as are provided by chemically generated or physically entrained gas bubbles. This unexpected property is of significant economic advantage since it eliminates the need for the incorporation into the composition of expensive void-containing material such as hollow glass or resin microspheres.

The discontinuous aqueous component or phase of the emulsified explosive will have a dissolved inorganic oxygen-supplying salt therein. Such an oxidiser salt will generally be ammonium nitrate but a portion of the ammonium nitrate can be replaced by one or more other inorganic salts such as, for example, the alkali or alkaline earth metal nitrates or perchlorates.

Typical of emulsifiers suitable for use in the composition are the monomeric emulsifiers such as the saturated fatty acids and fatty acid salts, glycerol stearates, esters of polyethylene oxide, fatty amines and esters, polyvinyl alcohol, sorbitan esters, phosphate

esters, polyethylene glycol esters, alkyl-aromatic
sulphonic acids, amides, triethanolamine oleate, amine
acetate, imidazolines, unsaturated fatty chain oxazo-
lines and mercaptans. Among the polymeric emulsifiers
5 which may be employed are the alkyds, ethylene oxide/
propylene oxide copolymers and hydrophobe/hydrophil block
copolymers. Also suitable is an emulsifier which is the
reaction product of glycerol and a dimer acid. In some
cases, mixtures or blends of emulsifiers are used. The
10 emulsifier chosen will be the one which functions most
expeditiously in the environment of the emulsion
explosive being formulated.

Additionally, the emulsion explosive of the
invention may contain optional additional fuel,
15 sensitizer or filler ingredients, such as, for example,
hollow glass or resin microspheres, particulate light
metal, void-containing material such as styrofoam beads
or vermiculite, particulate carbonaceous material, for
example, gilsonite or coal, vegetable matter such as
20 ground nut hulls or grainhulls, sulfur and the like.

Air or gas bubbles, for density modification and
sensitization purposes, may be injected or mixed into
the emulsion composition or may be generated in situ from
a gas generating material such as a peroxide or sodium
25 nitrite.

The emulsion explosives of the present invention
are, preferably, made by preparing a first premix of
water and inorganic oxidizer salt and a second premix of
crude fuel and emulsifying agent. The aqueous premix is
30 heated to ensure dissolution of the salts and the fuel
premix is heated to provide liquidity. The premixes are
blended together and emulsified in a mechanical blade
mixer, rotating drum mixer or by passage through an
in-line static mixer. Thereafter, the density lowering
35 material, for example, hollow glass microspheres, are
added along with any auxiliary fuel and the final product
packaged into suitable cartridges or containers.

In general, the water-in-oil emulsion explosive compositions of the present invention are sensitive to initiation by blasting cap in small diameter (2.5cm) charges at ambient temperatures. The compositions display excellent storage properties and show no signs of demulsification, retaining cap sensitivity in most cases after being subjected to 10 temperature cycles of -17°C to +35°C or after being stored over a two-month period at 35°C.

The following Examples and Tables provide a more complete understanding of the present invention. Examples 1,3 and 6 are comparative Examples not in accordance with the invention. In the Examples all percentages are expressed as percentages by weight.

Examples 1-16

A water-in-oil emulsion explosive composition was prepared according to the following formula:

Ammonium nitrate	61.5%
Sodium nitrate	14.9%
Calcium nitrate	4.6%
Water	13.0%
Emulsifier	1.7%
Fuel	4.3%

The emulsifier consisted of a blend of 0.3% of a polymeric emulsifier, 0.7% of sorbitan sesquioleate and 0.7% of soya lecithin. A variety of refined and crude fuels were employed in separate batches and the resultant compositions were packaged in 2.54 cm diameter plastic tubular containers. The cartridges were tested for minimum primer detonation and velocity of detonation as made and after two months storage at 35°C and after 10 temperature cycles of +35°C and -17°C. The various fuels employed are shown in Table I below and the comparative performance results are shown in Table II.

TABLE I

	<u>Fuel</u>	<u>Supplier</u>	<u>Description</u>
	<u>A. Refined Fuels</u>		
	Paraflex* HT-22	Gulf Oil Canada	Paraffin Oil
5	Refined Paraffin Wax 1230	International Waxes Ltd.	Refined paraffin wax
	Flexowax* C	Glyco Chemical	Refined micro- crystalline wax
	Multiwax 445	Glyco Chemical	Refined micro- crystalline wax
	<u>B. Crude Fuels</u>		
10	Slackwax 428	International Waxes Ltd.	Medium melt-point paraffin slackwax
	Slackwax 430	International Waxes Ltd.	Crude micro- crystalline wax
	Slackwax 431	International Waxes Ltd.	Paraffin slackwax
15	Petrofibe* 206	International Waxes Ltd.	Low pour-point wax oil
	Petrofibe* 225	International Waxes Ltd.	Mixture of soft waxes and oils
	Bunker Oil 6C	Gulf Oil Canada	Heavy residual oil
20	Asphalt 85-100	Gulf Oil Canada	Petroleum residue

*Reg. TM.

TABLE II

Example No.	Fuel	Voids Type	Density (g.cc)
1	0.9% Multiwax 3.3% Flexowax	gas	1.19
2	Slackwax	gas	1.13 1.06
3	1.0% Paraflex 3.3% Paraffin 1230	gas	1.14
4	Slackwax 430	gas	1.12
5	Slackwax 431	m.s.	1.13
6	2.7% Paraflex 1.5% Paraffin 1230	m.s.	1.15
7	Slackwax 431	plastic spheres	1.13
8	Slackwax 431	perlite	1.16
9	Bunker Oil	m.s.	1.13
10	Bunker Oil	gas	1.32
11	Asphalt	m.s.	1.11
12	Asphalt	gas	1.27
13	Petrofibe 206	gas	1.25
14	Petrofibe 206	m.s.	1.13
15	Petrofibe 225	gas	1.17
16	Petrofibe 225	m.s.	1.14

m.s. = microspheres (glass)

...contd.

TABLE II (cont.)

Example No.	Properties as made		Properties after storage	
	Minimum primer (m.p.)	V.O.D. (km/sec)	m.p. (V.O.D.) 10 cycles	m.p. (V.O.D.) 2 mo + 35°
1	* R-7	3.4	R-10 (2.9) (8 cycles)	
2	R-6 R-7	4.4 4.3	- R-7 (4.1)	R-7 (4.0) R-5 (4.0)
3	R-10	2.9	-	F E.B.
4	R-7	3.7	R-7 (3.9)	R-8 (3.6)
5	R-7	4.5	R-8 (4.4)	R-9 (4.3)
6	R-9	4.6	F E.B. -	-
7	R-8	5.4	E.B. (5.0)	E.B. (5.0)
8	R-7	2.9	E.B. (2.6)	E.B. (2.5)
9	R-6	4.2	E.B. (3.9)	R-10 (4.1)
10	R-9	3.6	R-9 (2.3)	R-9 (2.4)
11	R-6	4.2	E.B. (3.8)	R-15 (3.8)
12	R-6	3.3	R-9 (3.0)	R-9 (2.6)
13	R-8	3.0	R-11 (2.4)	F E.B.
14	R-6	4.3	R-15 (4.3) 5 cycles	F E.B.
15	R-7	3.4	R-11 (2.3)	F E.B.
16	R-7	4.4	R-9 (4.1)	R-10 (4.1)

*Caps designated R-n contain 0.1 g initiating composition and $(n-3) \times 0.05$ g PEIN $13 \geq n \geq 4$ or $(n-13) \times 0.1 + 0.5$ g. PEIN $16 \geq n \geq 14$ base charge. E.B. indicates electric blasting caps containing .08 g initiating composition and .78 g PEIN. F indicates a failure to detonate. All properties were measured at 5°C.

An examination of the results shown in Table II demonstrate that the use of crude or unrefined fuels as the continuous phase in an emulsion explosive provide compositions which have no less utility than those using more refined or pure fuels. A gassed slackwax formulation, for example (Ex. 2), has an initial V.O.D. equivalent to that of a refined wax/glass microsphere formulation (Ex. 6) and higher than that of gassed refined wax formulations (Ex. 1 and 3). The storage properties of slackwax formulae, gassed (Ex. 2) or with microspheres (Ex. 5) are superior to refined wax formulations (Ex. 3 and 6). Compositions formulated with crude fuels using enclosed voids (Ex. 5, 7 and 8) or unenclosed voids (Ex. 2), remain cap-sensitive for up to two months at +35°C or through 10 temperature cycles of from -17°C to +35°C. Compositions which are cap-sensitive (Ex. 9-16) can be made using a variety of crude petroleum products and can be formulated with either gassing agents or void-containing material. The velocity of detonation of crude fuel-containing compositions varies with the type of void, from low (Ex. 8) to high (Ex. 7).



Claims

1. A water-in-oil emulsion explosive composition comprising a continuous carbonaceous fuel phase and a discontinuous aqueous oxidiser salt solution phase,
5 the said continuous carbonaceous fuel phase comprising an unrefined or partly refined petroleum product, the said petroleum product being characterised in that,

(a) the component molecules have between 20 and 80 carbon atoms and less than 50% of the said
10 molecules have a number of carbon atoms within the same five carbon atom range, and

(b) wherein the said unrefined or partly refined petroleum product comprises at least 10% by weight of flowable oil if the said petroleum product is in the form of a petroleum wax or comprises at least 10% by weight of
15 a distillation residue if the said petroleum product is in the form of a petroleum oil or tar.

2. A composition as claimed in Claim 1 wherein the said unrefined or partly refined petroleum product is selected from the group consisting of slackwax, commercial
20 wax/oils, residual fuel oil, asphalt, bunker oil, topped crude petroleum, petroleum tars, crude petroleum, weathered crude petroleum, blended fuel oil, bitumens and mixtures of these.

25 3. A composition as claimed in Claim 1 wherein the said carbonaceous fuel phase comprises up to 10% by weight of the total composition.

4. A composition as claimed in Claim 1 containing an amount of density lowering ingredient to provide a
30 composition density of from 0.9 to 1.4 grams per cubic centimeter.

5. A composition as claimed in Claim 4 wherein the said density lowering ingredient is selected from solid particulate void-containing material, chemically
35 generated gas bubbles, and entrained air bubbles or mixtures of these.



6. A composition as claimed in any one of Claims 1 to 5 inclusive comprising an emulsifying agent selected from the group consisting of the monomeric emulsifiers comprising the saturated fatty acids and fatty acid salts, glycerol stearates, esters of polyethylene oxide, fatty amines and esters, polyvinyl alcohol, sorbitan esters, phosphate esters, polyethylene glycol esters, alkyl-aromatic sulphonic acids, amides, triethanolamine oleate, amine acetate, imidazolines, unsaturated fatty chain oxazolines, and mercaptans, polymeric emulsifiers comprising the alkyds, ethylene oxide/propylene oxide copolymers and hydrophobe/hydrophil block copolymers, the reaction product of glycerol and a dimer acid, and mixtures or blends of these.

7. A composition as claimed in any one of Claims 1 to 6 inclusive wherein the said oxidiser salt comprises ammonium nitrate, alkali or alkaline earth metal nitrates and perchlorates or mixtures of these.

8. A water-in-oil emulsion explosive composition as claimed in one of Claims 1 to 7 inclusive comprising,

(a) a continuous phase comprising from 1% to 10% by weight of the said unrefined or partly refined petroleum product and from 0.5% to 3% by weight of an emulsifying agent,

(b) a discontinuous phase of from 10% to 25% by weight of water and from 65% to 85% by weight of water-soluble inorganic oxidiser salt, and,

(c) an amount of density lowering ingredient to achieve a composition density of from 0.9 to 1.4 grams per cubic centimeter.

9. A water-in-oil emulsion explosive composition substantially as described herein with reference to any one of Examples 2,4,5 and 7 to 16 inclusive.
