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(54) **Emulsion blasting agent containing urea perchlorate.**

(57) Emulsion blasting agents comprising a discontinuous oxidiser component and an aqueous disperse phase, contain urea perchlorate as oxidiser. Such compositions require no or little gas sensitisation.

Emulsion Blasting Agent Containing Urea Perchlorate

This invention relates to emulsion type blasting agents having a discontinuous phase and a carbonaceous fuel component forming a continuous phase.

Emulsion type blasting agents (EBA's) are well known commercial explosive compositions but they are generally detonable only with difficulty and it is usual, therefore, to incorporate in them a sensitizing agent in the form of a gas, for example air, either in the form of bubbles or in microspheres of glass or plastic. Thus, conventional EBA's commonly comprise a discontinuous aqueous phase consisting of a solution of oxidiser salts, often also containing oxidiser salts suspended as fine particles, in a continuous oil phase and containing also a third, gaseous, phase dispersed in the emulsion as gas bubbles. The emulsion is stabilised against liquid separation by a lipophilic emulsifying agent. Such emulsions can also served as detonable matrices to carry solid fuels such as aluminium or inorganic oxidising agents of low solubility. EBA's typically can be made in a variety of forms from stiff plastic creams to almost fluid pumpable compositions and a stiff cream consistency is usually preferred.

Such compositions have been described for example

in US patents 3,447,978, 3,674,578, 3,770,522,
4,149,916, 4,149,917, 4,111,727 and 4,104,092.

EBA's commonly have an intrinsic density in the
region of 1.45 gm/cc, the occluded gas reducing this to
5 1.2 gm/cc or less, and the sensitivity of the gas con-
taining EBA is inversely related to its density for a
given chemical composition. However, where gas bubbles
are included in the emulsion they tend to coalesce,
reducing the detonability of the composition, and this
10 is sometimes overcome by incorporating the gas enclosed
in microspheres of glass or other material. The use of
such additional components, though, increases the cost
of the composition significantly.

We have now found that it is possible to prepare
15 an emulsion type blasting agent which does not depend
for its detonation upon the presence of a gaseous com-
ponent as a sensitizing agent, or, if a gaseous
sensitiser is needed, which requires less than would be
needed using conventional oxidisers.

20 The present invention provides an emulsion type
blasting agent comprising a discontinuous phase and a
carbonaceous fuel component forming a continuous phase,
in which the discontinuous phase comprises an aqueous
solution of urea perchlorate.

25 In addition to the solution of urea perchlorate
in water the aqueous phase optionally may comprise other
compatible water-soluble materials, particularly
inorganic oxidising materials, for example ammonium salts,
alkali metal and alkaline earth metal salts, in par-
30 ticular the nitrate, chlorate and perchlorate salts,
such as are mentioned for example in US Patent No.
3,447,978 and other literature, and hydrazine nitrate.
The nature and proportion of the various ingredients
will be chosen particularly with regard to the solubility
35 effect of the mixture of such ingredients. For example,
urea nitrate is only sparingly soluble in water and it

is preferred therefore that if a soluble nitrate is included in the composition it will only be present in such amount that the emulsification of the composition is not unduly impaired by formation of solid urea nitrate.

5 The aqueous component of the emulsion is usually formed by heating the water and dissolving in it the desired water soluble components. The mixture is usually heated to 50°C, or such other temperature as is appropriate, until complete solution occurs and heating
10 may be effected prior to or during formation of the emulsion. It is preferred that the proportions of solvent and solute are so chosen that in the final emulsion, after it has been cooled to ambient temperature, the aqueous component is supersaturated, although some
15 crystallisation, resulting in the presence of crystals in the aqueous component, may not adversely affect the properties of the blasting agent unduly.

 In addition to the urea perchlorate and, where present, any other oxidising agents, the aqueous phase
20 may comprise also water soluble fuel components to serve as supplemental fuels. As examples of such we may mention soluble carbohydrate materials, e.g. glucose, sucrose, fructose, maltose, molasses, lower glycols, formamide, urea, methylamine nitrate, hexa-
25 methylene tetramine, hexamethylene tetramine nitrate, and other organic nitrates, etc.

 The urea perchlorate conveniently is present in the discontinuous phase of the EBA of the invention in an amount forming from about 20 to about 95%, preferably at least 30% and more preferably at least 50% of
30 the discontinuous phase, although usually it will exceed 70% and more usually 80% or even 90% or 95% by weight of the discontinuous phase. The use of relatively low levels of urea perchlorate, for example below 60%
35 may require the presence of auxiliary oxidiser components to provide the required detonation characteristics.

The discontinuous phase may form from about 20 to about 97%, although usually it will form more than 40%; preferably more than 60% and more preferably more than 80% by weight of the EBA. The precise proportion will, of course, depend upon the amount of other ingredient present, to 100%.

The second component of the EBA of the invention is a carbonaceous fuel component forming a continuous phase. Such a component must be non-water soluble and must be capable of forming a water-in-oil emulsion with the aqueous component when an appropriate emulsifying agent is present in suitable quantity. The fuel component must be capable of being rendered fluid to permit formation of the emulsion. Thus, although for some purposes it may be desirable for the emulsion as finally prepared to have a solid or near solid continuous phase it will usually be necessary for it to be capable of being rendered sufficiently liquid by raising its temperature to an appropriate level to enable emulsification to occur.

The carbonaceous fuel component preferably includes a wax and an oil component e.g. an intimate oil/wax mixture, or a wax polymeric modified oil component. The fuel component may thus include hydrocarbons whether paraffinic or olefinic, naphthenic, aromatic saturated or unsaturated.

Waxes which may form part of the carbonaceous fuel component include waxes derived from petroleum, mineral waxes, animal waxes, and insect waxes. The preferred waxes are those which have melting points of at least 30°C and which are readily compatible with the formed emulsion. Preferably the waxes have a melting point in the range 40°C to 75°C.

A petroleum of a suitable viscosity may be used as a component of the carbonaceous fuel and typical materials for this purpose may have Brookfield

viscosities at 30°C in the range 160 to 5000 centipoises.

Non-volatile, water insoluble polymeric or elastomeric materials such as natural rubber, synthetic rubber and polyisobutylene may be included in the fuel component, as may also be copolymers, for example of butadiene-styrene, of isopren-isobutylene, or of isobutylene-ethylene.

The carbonaceous fuel component is generally present in an amount from 2 to 8 parts by weight per 100 parts by weight of the EBA, although higher proportions for example up to 10, 15 or even 20% may be employed.

Supplementary fuels which may be included in the carbonaceous fuel component include fatty acids, higher alcohols, vegetable oils, nitro organic compounds, both aliphatic and aromatic, e.g. dinitrotoluene, nitrate esters, solid particulate materials for example coal, graphite, carbon, sulphur, aluminium, magnesium, etc.

It will often be necessary to include gas in some form, either as gas micro-bubbles or as gas in microspheres of glass or other material e.g. Perlite, in which case it will be usual to include the gas, usually air, by any suitable known means. The gas component is usually added during cooling such that the prepared emulsion comprises from about 0.05 to 50% by volume of gas at ambient temperature and pressure. We usually employ gas of bubble diameter below 200 μm , preferably below 100 μm , more preferably between 20 and 90 μm and particularly between 40 to 70 μm , in proportions less than 10%, preferably less than 7%, more preferably less than 5%, and particularly less than 3% or even 1% by volume. Preferably at least 50% of the occluded gas will be in the form of bubbles of microspheres of 20 to 90 μm , preferably 40 to 70 μm internal diameter.

Where gas is included in the composition in the free state, as distinct from enclosed within microspheres it will usually be introduced simply by mixing the emulsion in an open vessel, although it may also be
5 included by bubbling the gas through the emulsion or by chemical generation of the gas in situ. Suitable techniques are described in the literature.

The EBA of the invention also comprises means for effecting stable emulsification of the components.
10 Conveniently a water-in-oil type surfactant or emulsifying agent is used in a proportion appropriate to the requirement to produce a sufficiently permanent emulsion. Typically the surfactant is used in an amount of 0.5 parts to 5 parts by weight per 100 parts by weight of
15 the EBA though the proportion for any particular composition can easily be determined by experiment. Many suitable surfactants have been described in the literature and include for example those derived from sorbitol by esterification, the glycerides of fat-forming fatty acids,
20 the polyoxyethylene sorbitol esters, the isopropyl esters of lanolin fatty acids, mixtures of higher molecular weight fatty alcohols and wax esters, polyoxyethylene(4) lauryl ether, polyoxyethylene(2) oleyl ether, polyoxyethylene(2) stearyl ether, polyoxyalkylene oleyl/
25 laurate, oleyl acid phosphate, substituted oxazolines and phosphate esters etc. Mixtures of such surfactants may also be used.

Other conventional components, for example compatible thickening agents in small proportions up
30 to, say, 10% by weight, may also be present.

The preparation of EBA emulsions has been described in the literature mentioned above and reference may be made thereto for further discussion of the various procedures. Thus, the EBA of the invention
35 may be prepared typically by mixing water with the

urea perchlorate and, where present, other oxidising agents to form a solution. Dissolution and preparation of a saturated solution may be facilitated by heating the water, though we do not exclude the possibility that
5 all or most of the ingredient of the emulsions may be mixed together and heated together. The emulsifier and fuel are then added at an appropriate temperature and the resulting mixture agitated to produce the required emulsion. Other ingredients, particularly solids, are
10 conveniently, though not essentially, added and further agitation applied.

The EBA's of the invention can be used as such, or they may be packaged into charges of convenient dimensions.

15 The invention is illustrated by the following Examples, for which the compositions were made by the conventional technique of preparing an aqueous solution of the urea perchlorate and any other water soluble components at a suitably elevated temperature. The emulsifier
20 and fuel were then mixed with the aqueous solution and the whole submitted to thorough agitation to produce the desired emulsion. Where appropriate air, in the form of Microballoons, was also incorporated and distributed thoroughly by further agitation.

25 In the following Table constituent quantities are on a weight/weight basis.

Notes on Table

Size (a) represents a charge 30 x 200 mm

30 Size (b) represents a charge 18 x 200 mm

Initiation

i) 4g Pentolite primer (50:50 PETN/TNT)

ii) No 8 Detonator

iii) No 6 Detonator

35 In Example 6 the temperature was 5°C; for the remaining Examples the temperature was 25°C.

EXAMPLE NO.	1	2	3	4	5	6	7	8	9	10	11
Urea Perchlorate	89.3	89.3	91.2	91.2	91.2	91.2	81.6	81.6	73.1	73.1	73.1
Sodium Perchlorate									10	10	
Nitromethane											10
Water	4.7	4.7	4.8	4.8	4.8	4.8	14.4	14.4	12.9	12.9	12.9
Kaydol Oil	3	3	2	2	2	2	2	2	2	2	2
Sorbitan Sesquioleate	3	3	2	2	2	2					2
Glycerol mono/dioleate							2	2	2	2	
Glass Micro-balloons B15/250		0.5		0.5	2.2	2.2		0.3		0.3	
Charge size	(a)	(a)	(a)	(a)	(b)	(a)	(a)	(a)	(a)	(a)	(a)
Density g/cm ² at 20°C	1.58	1.47	1.54	1.44	1.2	1.2					
Detonation Velocity	partial	4670	2000	3620	5400	5200	1900	3610	2000	3420	1900
Initiation	(1)	(11)	(11)	(11)	(11)	(111)	(11)	(11)	(11)	(11)	(11)

Kaydol Oil is a white mineral oil of high purity supplied by Witco Chemical Company.

"Microballoons" is a Registered Trade Mark

5 A No. 6 Detonator is an Instant Electric No. 6 detonator having a base charge of 0.24 gm PETN and initiating charge of 0.15 gm ASA.

A No. 8 detonator is an Instant Electric No. 8 detonator having a base charge of 0.45 gm PETN and initiating charge of 0.15 gm ASA.

1. An emulsion blasting agent comprising a discontinuous phase and a carbonaceous fuel component forming a continuous phase, in which the discontinuous phase comprises urea perchlorate.
2. An agent as described in claim 1, in which the discontinuous phase forms 20 to 97% by weight of the composition and the urea perchlorate forms from about 20 to about 95% by weight of the discontinuous phase.
3. An agent as described in claim 2 in which the discontinuous phase forms from 40 to 97% by weight of the composition.
4. An agent as described in claim 2 in which the discontinuous phase forms from 60 to 97% by weight of the composition.
5. An agent as described in any one of the previous claims in which the discontinuous phase comprises water soluble inorganic oxidising materials in addition to the urea perchlorate.
6. An agent as described in any of the preceding claims comprising a detonation sensitiser in the form of bubbles of gas, particularly air.
7. An agent as described in claim 6 in which the sensitiser is in the form of microbubbles of diameter smaller than about 200 microns.
8. An agent as described in claim 7 in which at least 50% by volume of the sensitiser is in the form of microbubbles of diameter between about 20 and 90 microns.
9. An explosive charge comprising an agent as described in any one of claims 1 to 8.

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