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Applicant: **IMPERIAL CHEMICAL INDUSTRIES LIMITED**  
Imperial Chemical House Millbank  
London SW1P 3JF(GB)

(72)

Inventor: **Cooper, John**  
4 Parkthorn View  
Dundonald Ayrshire Scotland(GB)

(72)

Inventor: **Sujansky, Vladimir**  
2 Neward Crescent  
Prestwick Ayrshire Scotland(GB)

(74)

Representative: **Bate, Bernard James et al,**  
Imperial Chemical Industries Limited Legal Department:  
Patents Thames House North Millbank  
London SW1P 4QG(GB)

(54)

**Emulsion type blasting agent containing hydrazine mononitrate.**

(57)

Emulsion blasting agents comprising a discontinuous oxidiser component and an aqueous disperse phase, contain hydrazine mononitrate as oxidiser. Such compositions require no or little gas sensitisation.

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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 comprising a solution of oxidiser salts, often also containing oxidiser salt suspended as microscopically fine particles, in a continuous oil phase and containing also a third, gaseous, phase dispersed in the emulsion as fine gas cells. The emulsion is stabilised against liquid separation by a lipophilic emulsifying agent. Such emulsions can also serve 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. A stiff cream consistency is usually preferred.

EBA's commonly have an intrinsic density in the region of 1.45 gm/cc, the occluded gas reducing this to 1.2 gm/cc or less, and the sensitivity of the gas sensitised 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 is sometimes overcome by incorporating the gas in the form of micro spheres of glass or other material. The  
5 use of such additional components, though, increases the cost of the composition significantly.

We have now found that it is possible to prepare an improved emulsion type blasting agent which does not depend for its detonation upon the presence of a gaseous  
10 component or, if a gaseous component is included as detonating sensitiser in the composition, in which coalescence of the gas does not seriously impair the detonability of the composition.

The present invention, therefore, provides an  
15 emulsion type blasting agent comprising a discontinuous phase and a carbonaceous fuel component forming a continuous phase, in which the discontinuous phase comprises hydrazine mononitrate.

The discontinuous phase is usually an aqueous  
20 phase, present as a solution of hydrazine mononitrate (and optionally solid hydrazine mononitrate) in water and also optionally may comprise other compatible water-soluble materials, particularly inorganic oxidising materials, for example ammonium salts, alkali metal and  
25 alkaline earth metal salts, in particular the nitrate, chlorate and perchlorate salts, such as are mentioned for example in US Patent No 3447978.

The discontinuous phase usually forms from 20 to 97%, preferably 40% to 97%, more preferably 60% to 97%  
30 and particularly 70 to 97% by weight of the composition, though the precise composition will, of course, be influenced by the proportion of other components present to the total of 100%.

The aqueous component of the emulsion is usually formed by heating the water and dissolving in it the  
35 desired water soluble components, the mixture usually being heated to about 80°C until complete solution occurs.

Heating may be effected prior to or during formation of the emulsion. It is preferred that the proportions of solvent and solute are chosen so that in the final emulsion, after it has been cooled to ambient temperature, the aqueous component is supersaturated, although some crystallisation, resulting in the presence of crystals in the aqueous component, might not adversely affect the properties of the EBA unduly.

In addition to the hydrazine nitrate and, where present, other oxidising agents, the aqueous phase 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, etc. Other possible components include for example, lower glycols, formamide, urea, methyl/amine nitrate, hexamethylene tetramine, hexamethylene tetramine nitrate, other organic nitrates, etc.

The hydrazine nitrate conveniently is present in the discontinuous phase of the EBA of the invention in an amount forming at least 10%, preferably at least 30% and more preferably at least 50%, although usually it will exceed 70% and more usually exceed 80% or even 90% by weight. Broadly, therefore, it will form 10% to 100% of the discontinuous phase. Where the hydrazine mononitrate forms a very high proportion of the phase it will usually be in the presence of little or no water, for example such as may occur when molten hydrazine mononitrate is emulsified into the continuous phase. The discontinuous phase may comprise, alternatively, a mixture of oxidising materials, including hydrazine mononitrate, emulsified in the continuous phase for example as a eutectic mixture. Where hydrazine mononitrate is the only oxidising material in the discontinuous phase it will preferably form at least 60% and more preferably at least 70% of the phase by weight.

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  
5 the discontinuous 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. Although for some purposes it may be desirable for the emulsion as  
10 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.

15 The carbonaceous fuel component preferably includes a wax and an oil component e.g. as an intimate wax/oil mixture, or a wax polymeric modified oil component. The fuel component may thus include hydrocarbons, whether paraffinic or olefinic, naphthenic,  
20 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  
25 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 oils  
30 for this purpose may have Brookfield viscosities at 30°C in the range 2 to 5000, preferably 10 to 1000 centipoises.

Non-volatile, water insoluble polymeric or elastomeric materials such as natural rubber, synthetic rubber and polyisobutylene may be included in the fuel  
35 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% by weight of the EBA, although higher proportions for example up to 10, 15 or  
5 even 20% may be acceptable.

The range and types of fuels are well exemplified in the literature.

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

15 Although EBA's of the invention containing at least 40%, and particularly containing 50% <sup>w</sup>/<sub>w</sub> of hydrazine mononitrate in the discontinuous phase are usually detonable without the inclusion of an occluded gas component we do not exclude the possibility that it may  
20 be preferred, particularly where the proportion of hydrazine mononitrate is less than the above, to include gas in some form, either a gas micro bubble or as gas in microspheres, in which case it will be convenient to include the gas, usually air, by any suitable known  
25 means.

Preferably, at least 50% of such gas will be in the form of microbubbles or spheres of diameter between 20 and 90  $\mu\text{m}$ , preferably 40 to 70  $\mu\text{m}$ .

The gas component is usually added during  
30 cooling such that the prepared emulsion comprises from about 0.05 to 50% by volume of gas at ambient temperature and pressure. However, because of improved detonability of the EBA's of the invention, low proportions of gas are preferred, since this leads to higher density com-  
35 positions. Typically the air will form less than 10%, preferably less than 7%, more preferably less than 5%

and particularly less than 3% by volume.

At gas volumes of 0 to 5% and particularly at 0 to 3% by volume of the composition, the detonation velocities of the EBA of the invention are superior to those of more conventional voidage, which typically are of the order of 30% and rarely less than 15%, gas.

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 included by bubbling the gas through the emulsion or by chemical generation of the gas in situ.

The EBA of the invention also comprises means for effecting stable emulsification of the components. 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 part to 5 parts by weight per 100 parts by weight of 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, 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 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 to, say, 10% by weight, may also be present.

The pH of the emulsion is usually between 2 and 8.

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  
5 may be prepared typically by mixing water with the hydrazine nitrate 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  
10 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  
15 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.

20 The invention is illustrated by the following examples, in which the emulsions were prepared by conventional techniques. Examples 3 and 25 to 30 provide controls to demonstrate the advantage of the presence of hydrazine mononitrate.

|                                      | 1    | 2    | 3                 | 4    | 5    | 6    | 7    |
|--------------------------------------|------|------|-------------------|------|------|------|------|
| Hydrazine mono-nitrate aq 80% w/w    | 94   | 93   |                   | 95   | 94   | 95.7 | 95.6 |
| Ammonium nitrate                     |      |      | 94                |      |      |      |      |
| Calcium nitrate tetrahydrate         |      |      |                   |      |      |      |      |
| Sodium nitrate                       |      |      |                   |      |      |      |      |
| Methylamine nitrate                  |      |      |                   |      |      |      |      |
| Hexamethylene tetra-mine mononitrate |      |      |                   |      |      |      |      |
| Ethanolamine nitrate                 |      |      |                   |      |      |      |      |
| Kaycol oil                           | 3    | 3    | 3                 |      |      |      |      |
| Liquid paraffin                      |      |      |                   | 2    | 2    | 2    | 2    |
| Paraffin wax (49-51°C)               |      |      |                   |      |      |      |      |
| Water                                |      |      |                   |      |      |      |      |
| Sorbitan monooleate                  |      |      |                   |      |      |      |      |
| Sorbitan sesquioleate                | 3    | 3    | 3                 | 2.7  | 2    |      |      |
| Glycerol mono/dioleate mixture       |      |      |                   |      |      | 2    |      |
| Polyglycerol polyoleate              |      |      |                   |      |      |      | 2    |
| Oleic ethanolamide                   |      |      |                   |      |      |      |      |
| Urea                                 |      |      |                   |      |      |      |      |
| Micro-balloons                       |      | 1    |                   | 0.3  | 2    | 0.3  | .4   |
| Soya lecithin                        |      |      |                   |      |      |      |      |
| Perlite                              |      |      |                   |      |      |      |      |
| Size (mm)                            | (i)  | (i)  | (i)               | (ii) | (ii) | (ii) | (ii) |
| Density g/cm <sup>3</sup>            | 1.38 | 1.28 | 1.37              | 1.35 |      | 1.35 | 1.33 |
| Detonation Velocity m/s              | 4100 | 5700 | Did not           | 3521 | 5900 | 3200 | 3436 |
| Initiation                           | (a)  | (b)  | Detonate with (a) | (b)  | (b)  | (b)  | (b)  |

In all cases the Microballoons were Glass air-filled microballoons of average diameter 50 microns

|                                     | 8    | 9    | 10   | 11    | 12   | 13    |
|-------------------------------------|------|------|------|-------|------|-------|
| Hydrazine mono-nitrate aq 80% w/w   | 75   | 95   | 75.5 | 15    | 40.8 | 40.55 |
| Ammonium nitrate                    |      |      | 20   | 66.75 | 40   | 40    |
| Calcium nitrate tetrahydrate        | 20   |      |      |       |      |       |
| Sodium nitrate                      |      |      |      |       |      |       |
| Methylamine nitrate                 |      |      |      |       |      |       |
| Hexamethylene tetramine mononitrate |      |      |      |       |      |       |
| Ethanolamine nitrate                |      |      |      |       | 12.2 | 12.2  |
| Kaydol oil                          |      |      |      |       |      |       |
| Liquid paraffin                     | 2    | 1    | 2    | 3.75  | 2.5  | 2.5   |
| Paraffin wax (49-51°C)              |      | 1    |      |       |      |       |
| Water                               |      |      |      | 13    | 3.0  | 3.0   |
| Sorbitan monooleate                 |      |      |      |       |      |       |
| Sorbitan sesquioleate               | 2    | 2    | 2    | 1.5   | 1.5  | 1.5   |
| Glycerol mono/dioleate mixture      |      |      |      |       |      |       |
| Polyglycerol polyoleate             |      |      |      |       |      |       |
| Oleic ethanolamide                  |      |      |      |       |      |       |
| Urea                                |      |      |      |       |      |       |
| Micro-balloons                      | 1    | 1    | .5   |       |      | .25   |
| Soya lecithin                       |      |      |      |       |      |       |
| Perlite                             |      |      |      |       |      |       |
| Size (mm)                           | (ii) | (ii) | (ii) | (i)   | (i)  | (i)   |
| Density g/cm <sup>3</sup>           | 1.30 | 1.30 | 1.40 | 1.4   | 1.5  | 1.4   |
| Detonation Velocity m/s             | 4785 | 5882 | 2830 | 2762  | 1600 | 3155  |
| Initiation                          | (b)  | (b)  | (b)  | (b)   | (b)  | (b)   |

In all cases the Microballoons were Glass air-filled microballoons of average diameter 50 microns

|                                     | 14   | 15    | 16    | 17    | 18   | 19    | 20   |
|-------------------------------------|------|-------|-------|-------|------|-------|------|
| Hydrazine mono-nitrate aq 80% w/w   | 95.6 | 25    | 41.8  | 40    | 15   | 15    | 15   |
| Ammonium nitrate                    |      | 58.75 | 31.2  | 45.75 | 56   | 55.75 | 55.5 |
| Calcium nitrate tetrahydrate        |      |       |       |       |      |       |      |
| Sodium nitrate                      |      |       |       |       |      |       |      |
| Methylamine nitrate                 |      |       | 22.73 |       | 14   | 14    | 14   |
| Hexamethylene tetramine mononitrate |      |       |       | 8     |      |       |      |
| Ethanolamine nitrate                |      |       |       |       |      |       |      |
| Kaydol oil                          |      |       |       |       | 2.5  | 2.5   | 2.5  |
| Liquid paraffin                     | 2    | 2.5   | 2.5   | 2.5   |      |       |      |
| Paraffin wax (49-51°C)              |      |       |       |       |      |       |      |
| Water                               |      | 6     |       | 2     | 11   | 11    | 11   |
| Sorbitan monooleate                 |      | 1.5   | 1.5   | 1.5   |      |       |      |
| Sorbitan sesquioleate               |      |       |       |       | .75  | .75   | .75  |
| Glycerol mono/dioleate mixture      |      |       |       |       |      |       |      |
| Polyglycerol polyoleate             |      |       |       |       |      |       |      |
| Oleic ethanolamide                  | 2    |       |       |       |      |       |      |
| Urea                                |      | 6     |       |       |      |       |      |
| Micro-balloons                      | .4   | .25   | .25   | .25   |      | .25   | .5   |
| Soya lecithin                       |      |       |       |       | .75  | .75   | .75  |
| Perlite                             |      |       |       |       |      |       |      |
| Size (mm)                           | (ii) | (i)   | (i)   | (i)   | (i)  | (i)   | (i)  |
| Density g/cm <sup>3</sup>           | 1.34 | 1.4   | 1.44  | 1.43  | 1.43 | 1.38  | 1.36 |
| Detonation Velocity m/s             | 3195 | 2857  | 3025  | 2920  | 1835 | 3096  | 4202 |
| Initiation                          | (b)  | (b)   | (b)   | (b)   | (b)  | (b)   | (b)  |

In all cases the Microballoons were Glass air-filled microballoons of average diameter 50 microns

|                                      | 21    | 22   | 23    | 24   | 25             |
|--------------------------------------|-------|------|-------|------|----------------|
| Hydrazine mono-nitrate aq 80% w/w    | 42.8  | 42.8 | 39.75 | 85.3 |                |
| Ammonium nitrate                     | 30.95 | 31.2 | 46    |      | 78             |
| Calcium nitrate tetrahydrate         |       |      |       |      |                |
| Sodium nitrate                       |       |      |       | 10   |                |
| Methylamine nitrate                  | 22    | 22   |       |      |                |
| Hexamethylene tetra-mine mononitrate |       |      | 8     |      |                |
| Ethanolamine nitrate                 |       |      |       |      |                |
| Kaydol oil                           |       |      |       |      |                |
| Liquid paraffin                      | 2.5   | 2.5  | 2.5   | 2    | 4              |
| Paraffin wax (49-51°C)               |       |      |       |      |                |
| Water                                |       |      | 2     |      | 16             |
| Sorbitan monooleate                  |       |      | 1.5   |      |                |
| Sorbitan sesquioleate                | 1.5   | 1.5  |       | 2    | 1.5            |
| Glycerol mono/dioleate mixture       |       |      |       |      |                |
| Polyglycerol polyoleate              |       |      |       |      |                |
| Oleic ethanolamide                   |       |      |       |      |                |
| Urea                                 |       |      |       |      |                |
| Micro-balloons                       | .25   |      | .25   |      | .5             |
| Soya lecithin                        |       |      |       |      |                |
| Perlite                              |       |      |       | 0.7  |                |
| Size (mm)                            | (i)   | (i)  | (i)   | (ii) | (i)            |
| Density g/cm <sup>3</sup>            | 1.44  | 1.49 | 1.43  | 1.34 | 1.33           |
| Detonation Velocity m/s              | 3025  | 1950 | 2920  | 2800 | No             |
| Initiation                           | (b)   | (b)  | (b)   | (b)  | Detonation (b) |

In all cases the Microballoons were Glass air-filled microballoons of average diameter 50 microns

Example No.

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|                                     | 26   | 27   | 28         | 29   | 30   |
|-------------------------------------|------|------|------------|------|------|
| Hydrazine mono-nitrate aq 80% w/w   |      |      |            |      |      |
| Ammonium nitrate                    | 78   | 78   | 76.8       | 76.4 | 75.6 |
| Calcium nitrate tetrahydrate        |      |      |            |      |      |
| Sodium nitrate                      |      |      |            |      |      |
| Methylamine nitrate                 |      |      |            |      |      |
| Hexamethylene tetramine mononitrate |      |      |            |      |      |
| Ethanolamine nitrate                |      |      |            |      |      |
| Kaydol oil                          |      |      | 2          | 2    | 2    |
| Liquid paraffin                     | 3.75 | 3.5  |            |      |      |
| Paraffin wax (49-51°C)              |      |      |            |      |      |
| Water                               | 16   | 16   | 18.7       | 18.6 | 18.4 |
| Sorbitan monooleate                 |      |      |            |      |      |
| Sorbitan sesquioleate               | 1.5  | 1.5  | 2          | 2    | 2    |
| Glycerol mono/dioleate mixture      | •    |      |            |      |      |
| Polyglycerol polyoleate             |      |      |            |      |      |
| Oleic ethanolamide                  |      |      |            |      |      |
| Urea                                |      |      |            |      |      |
| Micro-balloons                      | .75  | 1    | .5         | 1    | 2    |
| Soya lecithin                       |      |      |            |      |      |
| Perlite                             |      |      |            |      |      |
| Size (mm)                           | (i)  | (i)  | (i)        | (i)  | (i)  |
| Density g/cm <sup>3</sup>           | 1.29 | 1.27 | No         |      |      |
| Detonation Velocity m/s             | 2350 | 3775 | Detonation | 3640 | 4800 |
| Initiation                          | (b)  | (b)  | (b)        | (b)  | (b)  |

In all cases the Microballoons were Glass air-filled microballoons of average diameter 50 microns

Notes on Tables

Size (i) - represents 32 x 200 mm charge

(ii) - represents 20 x 200 mm charge

- 5 Initiation - (a) - No 6 + 4 gm Pentolite primer  
(50% PETN : 50% TNT)  
(b) - No 6 detonator

- 10 Kaydol oil is a white mineral oil of high purity  
supplied by Witco Chemical Company.  
"Microballoons" is a Registered Trade Mark  
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 mm ASA.

What we claim is:

1. An emulsion blasting agent comprising a discontinuous phase and a carbonaceous fuel component forming a continuous phase, in which the discontinuous phase comprises hydrazine mononitrate.
2. An agent as described in claim 1, in which the discontinuous phase forms 20 to 97% by weight of the composition and the hydrazine mononitrate forms from 10% to 100% 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 claim 1 or 2, in which the discontinuous phase comprises water soluble inorganic oxidising materials in addition to the hydrazine mononitrate.
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 at least 50% by volume of the sensitiser is in the form of microbubbles of diameter between 20 and 90 micron.
8. An explosive charge comprising an agent as described in any one of claims 1 to 7.

B J BATE  
AGENT FOR THE APPLICANTS