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# (54) W/O EMULSION EXPLOSIVE COMPOSITION.

(57) A W/O emulsion explosive composition having a high explosion energy especially in water, which comprises a continuous phase comprising a carbonaceous fuel component, a disperse phase comprising an aqueous solution of an inorganic oxoacid salt, an emulsifying agent, an organic foam retaining agent, and aluminum powder.

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## Technical Field

This invention relates to a water-in-oil emulsion explosive (hereinafter abbreviated as W/O explosive) composition having high underwater explosion energy, which can be used as an explosive for coal mining and in other mining industries.

## Background Art

When evaluating the power of explosives, studies have conventionally investigated the degree of sympathetic detonation, ballistic mortar value, and the detonation velocity. Recently, underwater explosion energy has also been studied.

Aluminum powder-containing W/O explosives are disclosed, for example, in the specifications of Japanese Patent Laid-open Application No. 110308/1979, U.S. Patent Nos. 3770522 and 3447978. These explosives each contain a glass microballoon (GMB) which acts as a gas retaining agent, and an aluminum powder.

One proposed technique of enhancing the underwater explosion energy of the W/O explosive compositions is to increase the content of inorganic oxidizer salt such as ammonium nitrate, sodium nitrate and potassium nitrate.

However, the W/O explosive compositions disclosed in the above three references may show enhanced power in the detonation velocity, sympathetic detonation and ballistic mortar value, but the amount of the aluminum powder to be added in combination with GMB is limited to about 20 % by weight in view of production limitations. These explosives suffer a problem in that they do not explode if the content of the aluminum powder is increased. Moreover, the content of the inorganic oxidizer salt cannot be increased so much because of production limitations. Therefore the effect of the inorganic oxidizer salt is small.

It is an object of this invention to provide a W/O explosive composition having excellent emulsion stability and a particularly high underwater explosion energy.

It is another object of this invention to provide a W/O explosive composition having high detonation reliability and improved low-temperature detonating properties.

## DISCLOSURE OF THE INVENTION

This invention provides a W/O explosive composition containing a continuous phase consisting of a carbonaceous fuel component; a disperse phase consisting of an aqueous solution of inorganic oxidizer salt; an emulsifier; and an organic gas-retaining agent having an average particle size of 10 to 4,000 $\mu$m, characterized in that the explosive contains 10 to 70 % by weight of an aluminum powder having an average particle size of not greater than 1 mm based on the total amount of the explosive composition (hereinafter referred to as a first aspect of this invention). Therefore, the W/O explosive composition according to the first aspect of this invention has high underwater explosion energy and also excellent emulsion stability.

This invention further provides a W/O explosive composition comprising a continuous phase consisting of a carbonaceous fuel component; a disperse phase consisting of an aqueous solution of an inorganic oxidizer salt; an emulsifier; a sensitizer; and a gas-retaining agent characterized in that the gas-retaining agent is of an organic material (hereinafter referred to as a second aspect of this invention) and that said explosive composition further contains an aluminum powder. Therefore, the W/O explosive composition according to the second aspect of this invention has high detonation reliability and excellent low-temperature detonating properties in addition to high underwater explosion energy.

The constitution of this invention will be discussed in detail below.

The carbonaceous fuel which forms a continuous phase includes those conventionally employed in the W/O explosives; for example, in the first aspect of this invention, hydrocarbons such as paraffinic hydrocarbons, olefinic hydrocarbons, naphthenic hydrocarbons, aromatic hydrocarbons, saturated or unsaturated hydrocarbons, petroleum purified mineral oils, lubricants and liquid paraffin; hydrocarbon derivatives such as nitrohydrocarbon; waxes including those derived from fuel oils and/or petroleum such as purified or unpurified microcrystalline wax, paraffin wax and petrolatum, mineral waxes such as montan wax, animal waxes such as whale wax and insect waxes such as beeswax. These carbonaceous fuels can be used alone or in admixture.

Preferred carbonaceous fuels include microcrystalline wax and petrolatum in view of storage stability, and particularly preferred is microcrystalline wax. At the same time, preferred carbonaceous fuels to be used in the second aspect of this invention include waxes such as microcrystalline wax, paraffin wax and polyethylene wax; and fuel oils such as light oils of classification No. 2, which are conventionally used in the W/O explosives. The waxes are particularly preferred in view of their texture such as hardness etc.

For the purpose of texture adjustment, a low-molecular weight hydrocarbon polymer such as a petroleum resin, a low-molecular weight polyethylene and a low-molecular weight polypropylene may be added in combination with the carbonaceous fuel component. The carbonaceous fuel is usually added in an amount of 1 to 10 % by weight based on the total amount of the W/O explosive.

The inorganic oxidizer salt, which forms the disperse phase in the form of aqueous solution, includes those conventionally used in the W/O explosive compositions; for example, nitrates of alkali or alkaline earth metals such as ammonium nitrate, sodium nitrate and potassium nitrate; and inorganic chlorates or perchlorates such as sodium chlorate, ammonium perchlorate and sodium perchlorate. Usually ammonium nitrate is used alone or in admixture with other inorganic oxidizer salt. The inorganic oxidizer salt is usually added in an amount of 5 to 90 % by weight, preferably 40 to 80 % by weight.

The water content in the W/O explosive composition according to this invention is preferably in the range of 3 to 30 % by weight, more preferably 7 to 30 % by weight.

Now, as the emulsifier, which plays a role to stabilize the emulsion, any of those conventionally used in the W/O explosives can be used; for example, fatty acid esters of sorbitan such as sorbitan monolaurate, sorbitan monooleate, sorbitan monopalmitate, sorbitan monostearate, sorbitan sesquioleate, sorbitan dioleate and sorbitan trioleate; mono or diglycerides of fatty acids such as stearic acid monoglyceride; fatty acid esters of polyoxyethylene sorbitan, oxazoline derivatives, imidazoline derivatives, phosphoric acid esters, alkali or alkaline earth metal salts of fatty acids and primary, secondary or tertiary amine salts. These emulsifiers may be used alone or in admixture. Preferred of these emulsifiers are fatty acid esters of sorbitan. The emulsifier is preferably added in an amount of 0.1 to 10 % by weight, more preferably 1 to 5 % by weight.

As the sensitizer, which enhances detonation reliability and improves low-temperature detonating properties, those conventionally used in the W/O explosives such as monomethylamine nitrate, hydrazine nitrate and ethylenediamine nitrate can be used. However, hydrazine nitrate is preferred since it can improve solubility of ammonium nitrate and has high explosion energy. When such sensitizer is used, it is preferably added in an mount of 1 to 40 % by weight, more preferably not more than 30 % by weight, most preferably not more than 20 % by weight in the W/O explosive composition. If the percentage of the sensitizer exceeds 40 % by weight, danger in handling the explosive composition will sometimes be increased.

Particularly when hydrazine nitrate and the like is used as the sensitizer, it is advantageous to use a chelating agent such as sodium ethylenediaminetetraacetate so as to prevent decomposition of the hydrazine nitrate. The chelating agent is preferably added in an amount of 0.1 to 10 % by weight based on the amount of the sensitizer.

The gas-retaining agent is an organic material. The organic gas-retaining agent may be selected from various types of single hollow microspheres or bubble assemblies containing a plurality of cells; for example, carbonaceous hollow microspheres obtained from pitch, coal, etc.; synthetic resin hollow microspheres obtained from phenol resins, polyvinylidene chloride, epoxy resins, urea resins, etc. The bubble assemblies containing a plurality of cells include milled powder and grains prepared by incorporating air into a raw material synthetic high polymer, for example, olefins such as ethylene, propylene and styrene; polymers of vinyl compounds such as vinylidene chloride, vinyl alcohols, vinyl acetate, and acrylic acid, methacrylic acid or esters thereof, or copolymers, modified polymers or mixed polymers thereof; synthetic polymers such as polyurethane, polyester, polyamide, urea resin, epoxy resin and phenol resin, by means of various techniques such as mechanical foaming, chemical foaming, micro-encapsulation, incorporation of an easily volatile material, etc., followed by milling.

Preferred of these organic gas-retaining agents are those made from polystyrene, polyethylene or polyvinylidene chloride. These organic gas-retaining agents, unlike the inorganic gas-retaining agents such as glass, silica, etc., do not damage the emulsion membrane and can maintain the emulsion stable. These organic gas-retaining agents are superior to the inorganic ones, since they have low specific gravity, they do not assume a form of inactive additive, and they are easily available at low costs.

When an organic gas-retaining agent is used, it never happens that the emulsion is partly damaged by pumping during the process of manufacturing unlike the inorganic gas-retaining agents. Accordingly, an explosive which can exhibit the designed detonation performance and has good storage stability can be provided.

Further, the organic gas-retaining agent may be of single bubbles or assemblies of single bubbles, and the diameter of which is not critical. However, in the first aspect of this invention, one having an average particle size in the range of 10 to 4,000 $\mu$m is particularly used. If one having an average particle size of less than 10 µm is used, it comes to have a greater specific gravity and must be added in an increased amount; whereas if one having an average size of greater than 4,000 µm is used, the underwater explosion energy will be lowered. Incidentally, the particle shape of the gas-retaining agent may be any spherical, cylindrical, polyhedral, etc.

A suitable organic gas-retaining agent is selected depending on the application of the W/O explosive. The organic gas-retaining agent is preferably added in an amount of 1 to 50 % by volume in the W/O explosive. If the content of the organic gas-retaining agent is less than 1 % by volume, cap-sensitivity of the resulting explosive composition will be lowered or the detonation will be interrupted; whereas if the content of the organic gas-retaining agent exceeds 50 % by volume, the underwater explosion energy tends to be lowered.

The aluminum powder is used as a fuel and also to improve underwater explosion energy. While ordinary aluminum powders can be used, those having a particle size of not more than 1 mm, preferably in the range of 0.01 to 1 mm, more preferably in the range of 0.03 to 0.1 mm, are particularly used in the first aspect of this invention. If an aluminum powder having a particle size of more than 1 mm is used, the underwater explosion energy will be lowered. The particle shape of the aluminum powder may be any spherical, scaly, etc.

In this invention, the aluminum powder can be used in a greater amount than in the prior art explosive compositions. If no sensitizer is added, the content of the aluminum powder is in the range of 10 to 70 % by weight, preferably in the range of 20 to 70 % by weight; whereas if a sensitizer is added, it is in the range of 10 to 70 % by weight. If the content of the aluminum powder is less than 10 % by weight, the fuel component will be insufficient to give reduced detonation performance; while if it exceeds 70 % by weight, inactive aluminum powder remains in the resulting composition to reduce the detonation performance.

The preferred compounding ratio of the respective components in the W/O explosive composition in the first aspect of this invention is as follows: 40 to 90 parts by weight of an inorganic oxidizer salt; 7 to 30 parts by weight of water; 0.5 to 10 parts by weight of a carbonaceous fuel; 0.5 to 10 parts by weight of an emulsifier; 1 to 40 parts by weight of a sensitizer; 1 to 50 % by volume of an organic gas-retaining agent having an average particle size of 10 to 4,000 µm ; and 10 to 70 % by weight of an aluminum powder having an average particle size of not more than 1 mm . Meanwhile, the preferred compounding ratio of the respective components in the second aspect of this invention is as follows: 40 to 90 parts by weight of an inorganic oxidizer salt; 7 to 30 parts by weight of water; 0.5 to 10 parts by weight of a carbonaceous fuel; 0.5 to 10 parts by weight of an emulsifier; 1 to 40 parts by weight of a sensitizer; 1 to 50 % by volume of an organic gas-retaining agent; and 10 to 70 % by weight of an aluminum powder.

If the content of the inorganic oxidizer salt is less than 40 % by weight, the detonation performance of the resulting composition will be lowered; whereas if it exceeds 90 % by weight, solubility thereof will be reduced. If the water content is less than 7 % by weight, solubility of the inorganic oxidizer salt will be lowered; whereas if it exceeds 30 % by weight, the contents of the other components will relatively be smaller to easily lower the detonation performance of the resulting composition. Addition of the carbonaceous fuel in an amount of less than 0.5 % by weight cannot give a very fine emulsion to provide small contact area; whereas if it exceeds 10 % by weight, the content of the inorganic oxidizer salt will relatively be smaller. If the content of the emulsifier is less than 0.5 % by weight, stability of the emulsion tends to be lowered; whereas if it exceeds 10 % by weight, detonation performance of the resulting composition can hardly be improved. If the content of the sensitizer is less than 1 % by weight, the resulting composition shows insufficient denotation reliability; whereas if it exceeds 40 % by weight, danger in the handling of the resulting composition will be increased. If the content of the organic gas-retaining agent is less than 1 % by volume, cap-sensitivity of the resulting composition may be reduced and explosion may be interrupted; whereas if it exceeds 50 % by volume, the underwater explosion energy tends to be lowered. If the aluminum powder is added in an amount of more than or less than the specified range of 10 to 70 % by weight, the detonation performance of the resulting explosive composition tends to be lowered.

The present W/O explosive composition can be prepared, for example, in the following manner.

An inorganic oxidizer salt, optionally together with a sensitizer and a chelating agent, is dissolved in a hot water (ca. 60 to 100 °C) to prepare an aqueous solution of inorganic oxidizer salt. Meanwhile, a carbonaceous fuel and an emulsifier are mixed by heating at a temperature where they assume a liquid state, usually at 70 to 90 °C, to prepare a combustible material mixture. Next, the aqueous solution of the inorganic oxidizer salt and the combustible material mixture prepared above are mixed by stirring at a temperature of 60 to 90 °C at a rate of about 600 to 6,000 rpm to provide a W/O emulsion. Subsequently, an organic gas-retaining agent and an aluminum powder are admixed to the resulting W/O emulsion to give a W/O explosive composition.

The thus obtained W/O explosive composition characteristically shows a particularly enhanced underwater explosion energy owing to the organic gas-retaining agent employed as the gas-retaining agent and also aluminum powder incorporated therein, since the emulsion membrane cannot easily be damaged by the organic gas-retaining agent unlike by the inorganic gas-retaining agent, and since the organic gas-retaining agent has a smaller specific gravity than the inorganic gas-retaining agent, and thus the proportion of the emulsion will be greater to allow the aluminum powder to be incorporated in an increased amount.

The underwater explosion energy can be divided into shock energy (Es) and bubble energy (Eb). The ratio of Eb to Es is usually about 3, and the combination of these two energy values Es and Eb is the total underwater explosion energy (see Encyclopedia of Explosives, Vol. 10, 1983, published by American Army Armament Research and Development Command).

Incidentally, the present W/O explosive composition is of high safety, since it is an emulsion type hydrated explosive.

## BEST MODE FOR CARRYING OUT THE INVENTION

Preferred embodiments of this invention will now be described below by way of Examples in comparison with Comparative Examples; wherein part(s) mean part(s) by weight.

### (Examples 1 to 6)

A W/O explosive composition was prepared using ammonium nitrate as the inorganic oxidizer salt, sorbitan monooleate as the emulsifier, a microcrystalline wax as the carbonaceous fuel, single-bubble assemblies of polystyrene having an average particle size of 300 µm as the gas retaining agent, hydrazine nitrate as the sensitizer and an aluminum powder having an average particle size of 30 µm. The proportion of the respective components are as shown in the following Tables 1 and 2.

The procedure of preparing the W/O explosive composition is as follows: Ammonium nitrate and hydrazine nitrate were dissolved in water by heating at about 85°C. Meanwhile, a mixture of the microcrystalline wax and sorbitan monooleate was melted at about 85°C, and the solution prepared above was added to the melted mixture, followed by stirring by an agitating blade to effect emulsification. The gas-retaining agent and aluminum powder were admixed to the resulting emulsion to provide a W/O explosive composition. Underwater explosion energy was determined for the thus obtained W/O explosive composition, and the results are also shown in Tables 1 and 2.

Incidentally, measurement of the underwater explosion energy was carried out by laying the explosive at the water depth of 4 m in a pool for determining underwater explosion energy and measuring the shock pulse of the exploded explosive by means of a pressure gauge (Tolmarine gauge) set at the same water depth and at an arbitrary distance so as to calculate Es value and Eb value, respectively. The total energy was obtained by combining the Es and Eb values in terms of the relative ratio to the values obtained in Comparative Example 1, according to the following equation.

$$\text{Total energy ratio} = \frac{Esn + Ebn}{Eso + Ebo}$$

In the above equation, Eso and Ebo are the values obtained in Comparative Example 1, while Esn and Ebn are the values obtained in Comparative Control Examples.

### (Comparative Example 1)

A W/O explosive composition was prepared in the same manner as in Examples 1 to 6, except that the aluminum powder was omitted. The thus prepared W/O explosive composition was tested in the same manner as in Example 1, and the results are as shown in Table 3.

### (Comparative Example 2)

A W/O explosive composition was prepared in the same manner as in Example 3, except that the organic gas-retaining agent was replaced by GMB having an average particle size of 50 µm as the inorganic gas-retaining agent. The thus prepared W/O explosive composition was tested in the same manner as in Examples 1 to 6, and the results are as shown in Table 3.

Table 1

Table 2

Table 3

The outer percentage of the aluminum powder shown in Tables 1 to 3 is indicated by % by weight per 100 parts by weight of the W/O explosive composition excluding the aluminum powder.

As can be seen from Tables 1 to 3, the W/O explosive compositions obtained in Examples 1 to 6 each showed a high total energy of 116 to 213 as the underwater explosion energy over the one obtained in Comparative Example 1, provided that the value of Comparative Example 1 is 100, and the explosive compositions obtained in Examples 5 and 6 each showed a value more than twice the value of the Comparative Example 1.

On the contrary, the W/O explosive composition of Comparative Example 1 showed only a low level of underwater explosion energy, since it does not contain an aluminum powder although it contains an organic gas-retaining agent. Meanwhile, the W/O explosive composition of Comparative Example 2 found difficulty in maintaining the shape of the W/O explosive and did not explode. This was because it uses a combination of an aluminum powder and GMB as the inorganic gas-retaining agent, and the aluminum powder was used in an increased amount.

The Es value of the W/O explosive (a standard W/O explosive composition) in Comparative Example 1 is about 0.7 MJ/kg; the Eb value thereof, about 2.1 MJ/kg; and the total energy, about 2.8 MJ/kg. Meanwhile, the total energy of the W/O explosive composition in each Example is increased to about 3.2 MJ/kg (Example 1) to 6.0 MJ/kg (Example 6).

(Example 7)

A W/O explosive was prepared using the explosive composition as shown in Table 4 in the following manner:

To 10.5 parts of water were added 74.4 parts of ammonium nitrate as the inorganic oxidizer salt, 10 parts of hydrazine nitrate as the sensitizer and 0.5 part of sodium ethylenediaminetetraacetate as the chelating agent, and they were dissolved well with heating at 90°C to prepare an aqueous solution of inorganic oxidizer salt. Meanwhile, 2.3 parts of Waxrex 602 as the carbonaceous fuel and 2.3 parts of sorbitan monooleate as the emulsifier were mixed with heating at 90°C to prepare a combustible material mixture. To the resulting mixture was added slowly the aqueous solution of inorganic oxidizer salt to effect emulsification by stirring at 650 rpm with heating at 90°C.

After completion of emulsification, the resulting emulsion was further stirred at 1,600 rpm for one minute to provide a W/O emulsion. Subsequently, 0.7 part of an organic gas-retaining agent having an average particle size of 300 µm and 11 parts of an aluminum powder were admixed to the W/O emulsion at 60 to 80°C to give a W/O explosive composition. Underwater explosion energy was determined for the thus obtained W/O explosive composition, and the results are as shown in the following Table 7.

(Example 8)

A W/O explosive composition was prepared as shown in Table 4 in the same manner as in Example 7, except that the sensitizer and chelating agent were omitted and that the content of the aluminum powder was changed. Performance of the resulting W/O explosive composition was evaluated, and the results are as shown in Table 7.

As can be seen from Table 7, the explosive composition prepared here showed a higher total energy ratio than that prepared in Example 7.

(Example 9)

A W/O explosive composition was prepared as shown in Table 4 substantially in the same manner as in Example 7, except that the content of the aluminum powder was increased. Performance of the resulting W/O explosive composition was evaluated, and the results are as shown in Table 7.

As can be seen from Table 7, the explosive composition prepared here showed a higher total energy ratio than that prepared in Example 7.

(Example 10)

A W/O explosive composition was prepared as shown in Table 5 substantially in the same manner as in Example 8, except that the content of the aluminum powder was increased. Performance of the resulting W/O explosive composition was evaluated, and the results are as shown in Table 8.

As can be seen from Table 8, the explosive composition prepared here showed a higher total energy ratio than that prepared in Example 8.

(Example 11)

A W/O explosive composition was prepared as shown in Table 5 substantially in the same manner as in Example 9, except that the content of the aluminum powder was increased. Performance of the resulting W/O explosive composition was evaluated, and the results are as shown in Table 8.

As can be seen from Table 8, the explosive composition prepared here showed a higher total energy ratio than that prepared in Example 9.

(Example 12)

A W/O explosive composition was prepared as shown in Table 5 substantially in the same manner as in Example 11, except that the content of the aluminum powder was increased. Performance of the resulting W/O explosive composition was evaluated, and the results are as shown in Table 8.

As can be seen from Table 8, the explosive composition prepared here showed a slightly higher total energy ratio than that prepared in Example 11.

(Example 13)

A W/O explosive composition was prepared as shown in Table 6 substantially in the same manner as in Example 10, except that the content of the aluminum powder was increased. Performance of the resulting W/O explosive composition was evaluated, and the results are as shown in Table 9.

As can be seen from Table 9, the explosive composition prepared here showed a slightly higher total energy ratio than that prepared in Example 10.

(Example 14)

A W/O explosive composition was prepared as shown in Table 6 substantially in the same manner as in Example 12, except that the content of the aluminum powder was increased. Performance of the resulting W/O explosive composition was evaluated, and the results are as shown in Table 9.

As can be seen from Table 9, the explosive composition prepared here showed a slightly higher total energy ratio than that prepared in Example 12.

(Example 15)

A W/O explosive composition was prepared as shown in Table 6 substantially in the same manner as in Example 13, except that the content of the aluminum powder was increased. Performance of the resulting W/O explosive composition was evaluated, and the results are as shown in Table 9.

As can be seen from Table 9, the explosive composition prepared here showed a slightly higher total energy ratio than that prepared in Example 13.

It should be noted here that the abbreviations used in the following Tables 4 to 6 stand for the respective compound as shown below.

MMA nitrate: Monomethylamine nitrate
Hyd nitrate: Hydrazine nitrate
EDA nitrate: Ethylenediamine nitrate
EDTA: Sodium ethylenediaminetetraacetate
SMO: Sorbitan monooleate
SMG: Monoglyceride stearate
Wax (1): Waxrex 602
Wax (2): Microcrystalline Wax 160
Wax (3): Polywax 500

| | |
|---|---|
| GMB: | Glass microballoon (particle size: 20 to 140 µm; average particle size: 60 µm) |
| SMB: | Shirasu microballoon (particle size: 30 to 150 µm; average particle size: 75 µm) |
| RMB (1): | Polyvinylidene chloride type resin microballoon (particle size: 10 to 100 µm; average particle size 30 µm) |
| Expanded polystyrene foam (1): | Obtained by prefoaming an expanded polystyrene foam beads (particle size: 180 to 700 µm; average particle size: 300 µm) |

Table 4
Table 5
Table 6
Table 7
Table 8
Table 9

(Comparative Example 3)

A W/O explosive composition was prepared as shown in Table 10 in the same manner as in Example 1, except that the aluminum powder was omitted. Performance of the resulting W/O explosive composition was evaluated, and the results are as shown in Table 16.

The thus prepared explosive composition is a standard composition for calculating the respective energy ratio.

(Comparative Example 4)

A W/O explosive composition was prepared as shown in Table 10 in the same manner as in Example 7, except that the content of the aluminum powder was reduced. Performance of the resulting W/O explosive composition was evaluated, and the results are as shown in Table 16.

As can be seen from Table 16, the explosive composition prepared here showed a lower total energy ratio than that prepared in Example 7.

(Comparative Example 5)

A W/O explosive composition was prepared as shown in Table 10 in the same manner as in Example 7, except that the content of the aluminum powder was increased. Performance of the resulting W/O explosive composition was evaluated, and the results are as shown in Table 16. This explosive composition did not explode.

(Comparative Example 6)

A W/O explosive composition was prepared as shown in Table 11 substantially in the same manner as in Comparative Example 4, except that an aluminum powder having a greater particle size was used. Performance of the resulting W/O explosive composition was evaluated, and the results are as shown in Table 17. This explosive composition did not explode.

(Comparative Example 7)

A W/O explosive composition was prepared as shown in Table 11 substantially in the same manner as in Comparative Example 5, except that an aluminum powder having a greater particle size was used. Performance of the resulting W/O explosive composition was evaluated, and the results are as shown in Table 17. This explosive composition did not explode.

(Comparative Example 8)

A W/O explosive composition was prepared as shown in Table 11 substantially in the same manner as in Example 8, except that the content of the aluminum powder was reduced. Performance of the resulting W/O explosive composition was evaluated, and the results are as shown in Table 17.

As can be seen from Table 17, the explosive composition prepared here showed a lower total energy ratio than that prepared in Example 8.

(Comparative Example 9)

A W/O explosive composition was prepared as shown in Table 12 substantially in the same manner as in Example 8, except that the content of the aluminum powder was increased. Performance of the resulting W/O explosive composition was evaluated, and the results are as shown in Table 18. This explosive composition did not explode.

(Comparative Example 10)

A W/O explosive composition was prepared as shown in Table 12 substantially in the same manner as in Comparative Example 8, except that an aluminum powder having a greater particle size was used. Performance of the resulting W/O explosive composition was evaluated, and the results are as shown in Table 18. This explosive composition did not explode.

(Comparative Example 11)

A W/O explosive composition was prepared as shown in Table 12 substantially in the same manner as in Comparative Example 9, except that an aluminum powder having a greater particle size was used. Performance of the resulting W/O explosive composition was evaluated, and the results are as shown in Table 18. This explosive composition did not explode.

(Comparative Example 12)

As can be seen from Table 19, the explosive composition prepared here showed a lower total energy ratio than that prepared in Example 9.

(Comparative Example 13)

A W/O explosive composition was prepared as shown in Table 13 substantially in the same manner as in Example 9, except that a resin microballoon (RMB) having a smaller average particle size was used as the gas-retaining agent. Performance of the resulting W/O explosive composition was evaluated, and the results are as shown in Table 19.

As can be seen from Table 19, the explosive composition prepared here showed a lower total energy ratio than that prepared in Example 9.

(Comparative Example 14)

A W/O explosive composition was prepared as shown in Table 13 substantially in the same manner as in Example 9, except that an expanded polystyrene foam having a greater average particle size was used as the gas-retaining agent. Performance of the resulting W/O explosive composition was evaluated, and the results are as shown in Table 19. This explosive composition did not explode.

(Comparative Example 15)

A W/O explosive composition was prepared as shown in Table 14 substantially in the same manner as in Example 10, except that the organic gas-retaining agent used as the gas-retaining agent was replaced by a Shirasu microballoon (SMB) which is an inorganic gas-retaining agent. Performance of the resulting W/O explosive composition was evaluated, and the results are as shown in Table 20.

As can be seen from Table 20, the explosive composition prepared here showed a lower total energy ratio than that prepared in Example 10.

(Comparative Example 16)

A W/O explosive composition was prepared as shown in Table 14 substantially in the same manner as in Example 10, except that a resin microballoon (RMB) having a smaller average particle size was used as the gas-retaining agent. Performance of the resulting W/O explosive composition was evaluated, and the results are as shown in Table 20.

As can be seen from Table 20, the explosive composition prepared here showed a lower total energy ratio than that prepared in Example 10.

(Comparative Example 17)

A W/O explosive composition was prepared as shown in Table 14 substantially in the same manner as in Example 10, except that an expanded polystyrene foam having a greater average particle size was used as the gas retaining agent. Performance of the resulting W/O explosive composition was evaluated, and the results are as shown in Table 20. This explosive composition did not explode.

(Comparative Example 18)

A W/O explosive composition was prepared as shown in Table 15 substantially in the same manner as in Comparative Example 3, except that the content of the organic gas-retaining agent was increased. Performance of the resulting W/O explosive composition was evaluated, and the results are as shown in Table 21. This explosive composition did not explode.

(Comparative Example 19)

A W/O explosive composition was prepared as shown in Table 15 substantially in the same manner as in Comparative Example 3, except that the organic gas-retaining agent was omitted.

Performance of the resulting W/O explosive composition was evaluated, and the results are as shown in Table 21. This explosive composition did not explode.

(Comparative Example 20)

A W/O explosive composition was prepared as shown in Table 15 substantially in the same manner as in Comparative Example 3, except that the content of the organic gas-retaining agent was increased. Performance of the resulting W/O explosive composition was evaluated, and the results are as shown in Table 21. This explosive composition did not explode.

(Comparative Example 21)

A W/O explosive composition was prepared as shown in Table 15 substantially in the same manner as in Comparative Example 3, except that the organic gas-retaining agent and sensitizer were omitted. Performance of the resulting W/O explosive composition was evaluated, and the results are as shown in Table 21. This explosive composition did not explode.

It should be noted here that the abbreviations used in the following Tables 10 to 15 respectively stand for the compounds as shown below:

| | |
|---|---|
| Expanded St 300 μ: | An expanded polystyrene foam (average particle size: 300 μm) |
| Expanded St 4100 μ: | An expanded polystyrene foam (average particle size: 4100 μm) |
| RMB (2): | Polyvinylidene chloride type resin microballoon (particle size : 5 to 30 μm; average particle size: 8 μm) |

Table 10
Table 11
Table 12
Table 13
Table 14
Table 15
Table 16
Table 17
Table 18
Table 19
Table 20

Table 21

As shown in Tables 7 to 9, the W/O explosive compositions obtained in Examples 7 to 15 each showed a total energy value of underwater explosion energy of 116 to 213 which is considerably higher than the value in Comparative Example 3, provided that the total energy of Comparative Example 3 is 100. The total energy values of Examples 11, 12 and 13 are more than twice the value of Comparative Example 3.

On the contrary, the W/O explosive compositions of the respective Comparative Examples either did not explode at all, or showed a low underwater explosion energy.

The total energy in Comparative Example 3 was about 2.8 MJ/kg; whereas those of Examples were in the range of 3.2 MJ/kg (Example 7) to 6.0 MJ/kg (Example 14). It can be seen that the total energy values of Examples are considerably higher than that in Comparative Example 3.

It should be appreciated that this invention is not limited to the above Examples, and many other modifications and variations of this invention as hereinbefore set forth can be made without departing from the spirit and scope of the invention.

## Industrial Applicability

As has been described heretofore, since the present W/O explosive composition has a high underwater explosion energy, it can suitably be employed as an explosive for coal mining and other mining industries.

Table 1

| Example | | | 1 | 2 | 3 |
|---|---|---|---|---|---|
| Composition (% by-weight) | Aqueous oxidizer salt | Ammonium nitrate | 74 | 74 | 74 |
| | | Water | 10.5 | 10.5 | 10.5 |
| | Sensitizer | Hydrazine nitrate | 10.5 | 10.5 | 10.5 |
| | Emulsifier | Sorbitan monooleate | 2.2 | 2.2 | 2.2 |
| | Carbonaceous fuel | Microcrystalline wax | 2.2 | 2.2 | 2.2 |
| | Organic gas-retaining agent (Unit of the parenthesized values is volume %) | | 0.6 (18.5) | 0.6 (17.7) | 0.6 (16.6) |
| | Inorganic gas-retaining agent (Unit of the parenthesized values is volume %) | | - | - | - |
| | Aluminum powder (The parenthesized values are outer percentage) | | 10 (11) | 20 (25) | 30 (43) |
| Performance | Apparent specific gravity (g/cc) | | 1.17 | 1.29 | 1.34 |
| Underwater Explosion energy | Ratio of shock energy | | 101 | 122 | 130 |
| | Ratio of bubble energy | | 121 | 165 | 200 |
| | Ratio of total energy | | 116 | 154 | 183 |

Table 2

| Example | | | 4 | 5 | 6 |
|---|---|---|---|---|---|
| Composition (% by-weight) | Aqueous oxidizer salt | Ammonium nitrate | 74 | 74 | 74 |
| | | Water | 10.5 | 10.5 | 10.5 |
| | Sensitizer | Hydrazine nitrate | 10.5 | 10.5 | 10.5 |
| | Emulsifier | Sorbitan monooleate | 2.2 | 2.2 | 2.2 |
| | Carbonaceous fuel | Microcrystalline wax | 2.2 | 2.2 | 2.2 |
| | Organic gas-retaining agent (Unit of the parenthesized values is volume %) | | 0.6 (13.9) | 0.6 (11.1) | 0.6 (10.0) |
| | Inorganic gas-retaining agent (Unit of the parenthesized values is volume %) | | - | - | - |
| | Aluminum powder (The parenthesized values are outer percentage) | | 50 (100) | 65 (186) | 70 (233) |
| Performance | Apparent specific gravity (g/cc) | | 1.56 | 1.79 | 1.88 |
| Underwater Explosion energy | Ratio of shock energy | | 100 | 98 | 95 |
| | Ratio of bubble energy | | 245 | 250 | 252 |
| | Ratio of total energy | | 209 | 212 | 213 |

Table 3

| Comparative Example | | | 1 | 2 |
|---|---|---|---|---|
| Composition (% by-weight) | Aqueous oxidizer salt | Ammonium nitrate | 74 | 74 |
| | | Water | 10.5 | 10.5 |
| | Sensitizer | Hydrazine nitrate | 10.5 | 10.5 |
| | Emulsifier | Sorbitan monooleate | 2.2 | 2.2 |
| | Carbonaceous fuel | Microcrystalline wax | 2.2 | 2.2 |
| | Organic gas-retaining agent (Unit of the parenthesized values is volume %) | | 0.6 (21) | - |
| | Inorganic gas-retaining agent (Unit of the parenthesized values is volume %) | | - | 7 (18) |
| | Aluminum powder (The parenthesized values are outer percentage | | - | 30 (43) |
| Performance | Apparent specific gravity (g/cc) | | 1.10 | 1.34 |
| Underwater Explosion energy | Ratio of shock energy | | 100 | - |
| | Ratio of bubble energy | | 100 | - |
| | Ratio of total energy | | 100 | - |

Table 4

| Example | | | 7 | 8 | 9 |
|---|---|---|---|---|---|
| Composition (parts by weight) | Aqueous inorganic oxidizer salt | $NH_4NO_3$ | 74.4 | 77.5 | 66.7 |
| | | $NaNO_3$ | - | 5.2 | 4.2 |
| | | Water | 10.5 | 11.7 | 9.2 |
| | Sensitizer | MMA nitrate | - | - | 15.0 |
| | | Hyd nitrate | 10.0 | - | - |
| | | EDA nitrate | - | - | - |
| | Chelating agent | EDTA | 0.5 | - | - |
| | | Tartaric acid | - | - | 0.3 |
| | Emulsifier | SMO | 2.3 | 2.8 | - |
| | | SMG | - | - | 2.3 |
| | Carbonaceous fuel | WAX (1) | 2.3 | - | - |
| | | WAX (2) | - | 2.8 | 0.4 |
| | | WAX (3) | - | - | 1.9 |
| | Gas-retaining agent (Unit of the parenthesized values is volume %) | RMB (1) | - | - | 1.3 (17.2) |
| | | Expanded polystyrene foam (1) | 0.7 (18.5) | 0.7 (17.7) | - |
| | Load of aluminum powder (Unit of the parenthesized values is % by weight) | | 11 (10) | 25 (20) | 43 (30) |

Table 5

| Example | | | 10 | 11 | 12 |
|---|---|---|---|---|---|
| Composition (parts by weight) | Aqueous inorganic oxidizer salt | $NH_4NO_3$ | 82.7 | 74.4 | 68.6 |
| | | $NaNO_3$ | - | - | 5.2 |
| | | Water | 11.7 | 10.5 | 11.2 |
| | Sensitizer | MMA nitrate | - | - | - |
| | | Hyd nitrate | - | - | 10.0 |
| | | EDA nitrate | - | 10.0 | - |
| | Chelating agent | EDTA | - | 0.5 | 0.4 |
| | | Tartaric acid | - | - | - |
| | Emulsifier | SMO | 2.8 | 2.3 | 2.3 |
| | | SMG | - | - | - |
| | Carbonaceous fuel | WAX (1) | 1.4 | 2.3 | - |
| | | WAX (2) | 1.4 | - | 0.4 |
| | | WAX (3) | - | - | 1.9 |
| | Gas-retaining agent (Unit of the parenthesized values is volume %) | RMB (1) | 1.3 (17.1) | 0.8 (11.1) | - |
| | | Expanded polystyrene foam (1) | - | 0.4 (7.2) | 0.7 (11.1) |
| | Load of aluminum powder (Unit of the parenthesized values is % by weight) | | 43 (30) | 100 (50) | 186 (65) |

Table 6

| Example | | | 13 | 14 | 15 |
|---|---|---|---|---|---|
| Composition (parts by weight) | Aqueous inorganic oxidizer salt | $NH_4NO_3$ | 77.5 | 74.4 | 82.7 |
| | | $NaNO_3$ | 5.2 | - | - |
| | | Water | 11.7 | 10.5 | 11.7 |
| | Sensitizer | MMA nitrate | - | - | - |
| | | Hyd nitrate | - | 10.0 | - |
| | | EDA nitrate | - | - | - |
| | Chelating agent | EDTA | - | 0.5 | - |
| | | Tartaric acid | - | - | - |
| | Emulsifier | SMO | 2.8 | 2.3 | 2.8 |
| | | SMG | - | - | - |
| | Carbonaceous fuel | WAX (1) | 2.8 | 2.3 | 2.8 |
| | | WAX (2) | - | - | - |
| | | WAX (3) | - | - | - |
| | Gas-retaining agent (Unit of the parenthesized values is volume %) | RMB (1) | 1.3 (13.2) | - | 1.3 (11.5) |
| | | Expanded polystyrene foam (1) | - | 0.7 (10.0) | - |
| | Load of aluminum powder (Unit of the parenthesized values is % by weight) | | 186 (65) | 233 (70) | 233 (70) |

Table 7

| Example | | 7 | 8 | 9 |
|---|---|---|---|---|
| Performance | Apparent specific gravity (g/cc) | 1.17 | 1.27 | 1.34 |
| Underwater Explosion energy | Ratio of shock energy | 101 | 117 | 134 |
| | Ratio of bubble energy | 121 | 148 | 202 |
| | Ratio of total energy | 116 | 138 | 184 |

Table 8

| Example | | 10 | 11 | 12 |
|---|---|---|---|---|
| Performance | Apparent specific gravity (g/cc) | 1.31 | 1.55 | 1.79 |
| Underwater Explosion energy | Ratio of shock energy | 122 | 102 | 97 |
| | Ratio of bubble energy | 180 | 248 | 250 |
| | Ratio of total energy | 165 | 210 | 211 |

Table 9

| Example | | 13 | 14 | 15 |
|---|---|---|---|---|
| Performance | Apparent specific gravity (g/cc) | 1.75 | 1.88 | 1.82 |
| Underwater Explosion energy | Ratio of shock energy | 95 | 95 | 92 |
| | Ratio of bubble energy | 230 | 252 | 235 |
| | Ratio of total energy | 188 | 213 | 189 |

Table 10

| Comparative Example | | | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Composition<br>(parts by weight) | Aqueous inorganic oxidizer salt | $NH_4NO_3$ | 74.4 | 74.4 | 74.4 |
| | | $NaNO_3$ | — | — | — |
| | | Water | 10.5 | 10.5 | 10.5 |
| | Sensitizer | MMA nitrate | — | — | — |
| | | Hyd nitrate | 10.0 | 10.0 | 10.0 |
| | | EDA nitrate | — | — | — |
| | Chelating agent | EDTA | 0.5 | 0.5 | 0.5 |
| | | Tartaric acid | — | — | — |
| | Emulsifier | SMO | 2.3 | 2.3 | 2.3 |
| | | SMG | — | — | — |
| | Carbonaceous fuel | WAX (1) | 2.3 | 2.3 | 2.3 |
| | | WAX (2) | — | — | — |
| | | WAX (3) | — | — | — |
| | Gas-retaining agent (Unit of the parenthesized values is volume %) | | Expanded St<br>300μ<br>0.7<br>(21.0) | Expanded St<br>300μ<br>0.7<br>(19.7) | Expanded St<br>300μ<br>0.7<br>(8.9) |
| | Load of aluminum powder (Unit of the parenthesized values is % by weight) | Particle size<br>0.1 mm | — | 5.3<br>(5.0) | 300<br>(75) |
| | | 1.2 mm | — | — | — |

Table 11

| Comparative Example | | | 6 | 7 | 8 |
|---|---|---|---|---|---|
| Composition (parts by weight) | Aqueous inorganic oxidizer salt | $NH_4NO_3$ | 66.7 | 66.7 | 82.7 |
| | | $NaNO_3$ | 4.2 | 4.2 | – |
| | | Water | 9.2 | 9.2 | 11.7 |
| | Sensitizer | MMA nitrate | 15.0 | 15.0 | – |
| | | Hyd nitrate | – | – | – |
| | | EDA nitrate | – | – | – |
| | Chelating agent | EDTA | – | – | – |
| | | Tartaric acid | 0.3 | 0.3 | – |
| | Emulsifier | SMO | – | – | 2.8 |
| | | SMG | 2.3 | 2.3 | – |
| | Carbonaceous fuel | WAX (1) | – | – | 1.4 |
| | | WAX (2) | 0.4 | 0.4 | 1.4 |
| | | WAX (3) | 1.9 | 1.9 | – |
| | Gas-retaining agent (Unit of the parenthesized values is volume %) | | Expanded St<br>$300\mu$<br>0.7<br>(19.8) | Expanded St<br>$300\mu$<br>0.7<br>(8.9) | Expanded St<br>$300\mu$<br>0.7<br>(19.4) |
| | Load of aluminum powder (Unit of the parenthesized values is % by weight) | Particle size 0.1 mm | – | – | 5.3<br>(5.0) |
| | | 1.2 mm | 5.3<br>(5.0) | 300<br>(75) | – |

Table 12

| Comparative Example | | | 9 | 10 | 11 |
|---|---|---|---|---|---|
| Composition (parts by weight) | Aqueous inorganic oxidizer salt | $NH_4NO_3$ | 82.7 | 77.5 | 77.5 |
| | | $NaNO_3$ | — | 5.2 | 5.2 |
| | | Water | 11.7 | 11.7 | 11.7 |
| | Sensitizer | MMA nitrate | — | — | — |
| | | Hyd nitrate | — | — | — |
| | | EDA nitrate | — | — | — |
| | Chelating agent | EDTA | — | — | — |
| | | Tartaric acid | — | — | — |
| | Emulsifier | SMO | 2.8 | — | — |
| | | SMG | — | 2.8 | 2.8 |
| | Carbonaceous fuel | WAX (1) | 1.4 | — | — |
| | | WAX (2) | 1.4 | 0.5 | 0.5 |
| | | WAX (3) | — | 2.3 | 2.3 |
| | Gas-retaining agent (Unit of the parenthesized values is volume %) | | Expanded St<br>300μ<br>0.7<br>(8.7) | Expanded St<br>300μ<br>0.7<br>(19.5) | Expanded St<br>300μ<br>0.7<br>(8.7) |
| | Load of aluminum powder (Unit of the parenthesized values is % by weight) | Particle size 0.1 mm | 300<br>(75) | — | — |
| | | 1.2 mm | — | 5.3<br>(5.0) | 300<br>(75) |

Table 13

| Comparative Example | | | 12 | 13 | 14 |
|---|---|---|---|---|---|
| Composition<br>(parts by weight) | Aqueous inorganic oxidizer salt | $NH_4NO_3$ | 68.6 | 68.6 | 68.6 |
| | | $NaNO_3$ | 5.2 | 5.2 | 5.2 |
| | | Water | 11.2 | 11.2 | 11.2 |
| | Sensitizer | MMA nitrate | — | — | — |
| | | Hyd nitrate | — | — | — |
| | | EDA nitrate | 10.0 | 10.0 | 10.0 |
| | Chelating agent | EDTA | 0.4 | 0.4 | 0.4 |
| | | Tartaric acid | — | — | — |
| | Emulsifier | SMO | 2.3 | 2.3 | 2.3 |
| | | SMG | — | — | — |
| | Carbonaceous fuel | WAX (1) | — | — | — |
| | | WAX (2) | 2.3 | 2.3 | 2.3 |
| | | WAX (3) | — | — | — |
| | Gas-retaining agent (Unit of the parenthesized values is volume %) | | GMB<br>7.0<br>(16.0) | RMB (2)<br>2.5<br>(18.0) | Expanded St<br>4100μ<br>0.3<br>(15.3) |
| | Load of aluminum powder (Unit of the parenthesized values is % by weight) | Particle size 0.1 mm | 43<br>(30) | 43<br>(30) | 43<br>(30) |
| | | 1.2 mm | — | — | — |

Table 14

| Comparative Example | | | 15 | 16 | 17 |
|---|---|---|---|---|---|
| Composition (parts by weight) | Aqueous inorganic oxidizer salt | $NH_4NO_3$ | 82.7 | 82.7 | 82.7 |
| | | $NaNO_3$ | — | — | — |
| | | Water | 11.7 | 11.7 | 11.7 |
| | Sensitizer | MMA nitrate | — | — | — |
| | | Hyd nitrate | — | — | — |
| | | EDA nitrate | — | — | — |
| | Chelating agent | EDTA | — | — | — |
| | | Tartaric acid | — | — | — |
| | Emulsifier | SMO | — | — | — |
| | | SMG | 2.8 | 2.8 | 2.8 |
| | Carbonaceous fuel | WAX (1) | 2.8 | 2.8 | 2.8 |
| | | WAX (2) | — | — | — |
| | | WAX (3) | — | — | — |
| | Gas-retaining agent (Unit of the parenthesized values is volume %) | | SMB<br>7.4<br>(16.1) | RMB (2)<br>2.5<br>(18.0) | Expanded St<br>4100μ<br>0.3<br>(15.1) |
| | Load of aluminum powder (Unit of the parenthesized values is % by weight) | Particle size 0.1 mm | 43<br>(30) | 43<br>(30) | 43<br>(30) |
| | | 1.2 mm | — | — | — |

Table 15

| Comparative Example | | | 18 | 19 | 20 | 21 |
|---|---|---|---|---|---|---|
| Composition<br>(parts by weight) | Aqueous inorganic oxidizer salt | $NH_4NO_3$ | 74.4 | 74.4 | 77.5 | 77.5 |
| | | $NaNO_3$ | – | – | 5.2 | 5.2 |
| | | Water | 10.5 | 10.5 | 11.7 | 11.7 |
| | Sensitizer | MMA nitrate | – | – | – | – |
| | | Hyd nitrate | 10.0 | 10.0 | – | – |
| | | EDA nitrate | – | – | – | – |
| | Chelating agent | EDTA | – | – | – | – |
| | | Tartaric acid | 0.5 | 0.5 | – | – |
| | Emulsifier | SMO | 2.3 | 2.3 | 2.8 | 2.8 |
| | | SMG | – | – | – | – |
| | Carbonaceous fuel | WAX (1) | – | – | 1.4 | 1.4 |
| | | WAX (2) | 0.4 | 0.4 | 1.4 | 1.4 |
| | | WAX (3) | 1.9 | 1.9 | – | – |
| | Gas-retaining agent (Unit of the parenthesized values is volume %) | | Expanded St<br>300μ<br>1.8<br>(53.0) | – | Expanded St<br>300μ<br>1.8<br>(52.0) | – |
| | Load of aluminum powder (Unit of the parenthesized values is % by weight) | Particle size 0.1 mm | – | – | – | – |
| | | 1.2 mm | – | – | – | – |

Table 16

| Comparative Example | | 3 | 4 | 5 |
|---|---|---|---|---|
| Performance | Apparent specific gravity (g/cc) | 1.10 | 1.11 | 2.01 |
| Underwater Explosion energy | Ratio of shock energy | 100 | 100 | - |
| | Ratio of bubble energy | 100 | 108 | - |
| | Ratio of total energy | 100 | 105 | - |

Table 17

| Comparative Example | | 6 | 7 | 8 |
|---|---|---|---|---|
| Performance | Apparent specific gravity (g/cc) | 1.12 | 2.01 | 1.10 |
| Underwater Explosion energy | Ratio of shock energy | - | - | 92 |
| | Ratio of bubble energy | - | - | 95 |
| | Ratio of total energy | - | - | 94 |

Table 18

| Comparative Example | | 9 | 10 | 11 |
|---|---|---|---|---|
| Performance | Apparent specific gravity (g/cc) | 2.00 | 1.11 | 2.00 |
| Underwater Explosion energy | Ratio of shock energy | - | - | - |
| | Ratio of bubble energy | - | - | - |
| | Ratio of total energy | - | - | - |

Table 19

| Comparative Example | | 12 | 13 | 14 |
|---|---|---|---|---|
| Performance | Apparent specific gravity (g/cc) | 1.40 | 1.34 | 1.25 |
| Underwater Explosion energy | Ratio of shock energy | 116 | 120 | - |
| | Ratio of bubble energy | 158 | 175 | - |
| | Ratio of total energy | 145 | 161 | - |

Table 20

| Comparative Example | | 15 | 16 | 17 |
|---|---|---|---|---|
| Performance | Apparent specific gravity (g/cc) | 1.39 | 1.33 | 1.25 |
| Underwater Explosion energy | Ratio of shock energy | 108 | 110 | - |
| | Ratio of bubble energy | 132 | 158 | - |
| | Ratio of total energy | 119 | 143 | - |

Table 21

| Comparative Example | | 18 | 19 | 20 | 21 |
|---|---|---|---|---|---|
| Performance | Apparent specific gravity (g/cc) | 0.55 | 1.41 | 0.52 | 1.40 |
| Underwater Explosion energy | Ratio of shock energy | - | - | - | - |
| | Ratio of bubble energy | - | - | - | - |
| | Ratio of total energy | - | - | - | - |

## Claims

1. A water-in-oil emulsion explosive composition containing a continuous phase consisting of a carbonaceous fuel component; a disperse phase consisting of an aqueous solution of inorganic oxidizer salt; an emulsifier; and an organic gas-retaining agent having an average particle size of 10 to 4,000 $\mu$m; and wherein said explosive composition contains 10 to 70 % by weight of an aluminum powder having an average particle size of not greater than 1 mm based on the total amount of the explosive composition.

2. A water-in-oil emulsion explosive composition according to Claim 1, wherein the shape of the aluminum powder is spherical or scaly.

3. A water-in-oil emulsion explosive composition according to Claim 1, wherein the organic gas-retaining agent is at least one selected from the group consisting of polystyrene, polyethylene and polyvinylidene chloride.

4. A water-in-oil emulsion explosive composition according to Claim 1, wherein the content of the organic gas-retaining agent is 1 to 50 % by volume based on the total amount of the explosive composition.

5. A water-in-oil emulsion explosive composition according to Claim 1, wherein the inorganic oxidizer salt contains ammonium nitrate as a major component.

6. A water-in-oil emulsion explosive composition according to Claim 1, wherein the contents of the carbonaceous fuel component, inorganic oxidizer salt containing ammonium nitrate as a major component, water, emulsifier, organic gas-retaining agent and aluminum powder are 1 to 10 % by weight, 40 to 80 % by weight, 7 to 30 % by weight, 1 to 5 % by weight, 1 to 50 % by volume and 10 to 70 % by weight, respectively, based on the total amount of the explosive composition.

7. A water-in-oil emulsion explosive composition according to Claim 1, which further contains a sensitizer.

8. A water-in-oil emulsion explosive composition comprising a continuous phase consisting of a carbonaceous fuel component; a disperse phase consisting of an aqueous solution of inorganic oxidizer salt; an emulsifier; a sensitizer; an organic gas-retaining agent; and an aluminum powder.

9. A water-in-oil emulsion explosive composition according to Claim 8, wherein the shape of the aluminum powder is of spherical or scaly.

10. A water-in-oil emulsion explosive composition according to Claim 8, wherein the organic gas-retaining agent is at least one selected from the group consisting of polystyrene, polyethylene and polyvinylidene chloride.

11. A water-in-oil emulsion explosive composition according to Claim 8, wherein the content of the organic gas-retaining agent is 1 to 50 % by volume based on the total amount of the explosive composition.

12. A water-in-oil emulsion explosive composition according to Claim 8, wherein the sensitizer is at least one selected from the group consisting of monomethylamine nitrate, hydrazine nitrate and ethylenediamine nitrate.

**13.** A water-in-oil emulsion explosive composition according to Claim 8, containing hydrazine nitrate as the sensitizer and further a chelating agent.

**14.** A water-in-oil emulsion explosive composition according to Claim 13, wherein the content of the hydrazine nitrate is 1 to 20 % by weight based on the total amount of the explosive composition and the content of the chelating agent is 0.1 to 10 % by weight based on the amount of the hydrazine nitrate.

**15.** A water-in-oil emulsion explosive composition according to Claim 8, wherein the inorganic oxidizer salt contains ammonium nitrate as a major component.

**16.** A water-in-oil emulsion explosive composition according to Claim 8, wherein the contents of the carbonaceous fuel component, inorganic oxidizer salt containing ammonium nitrate as a major component, water, emulsifier, sensitizer, organic gas-retaining agent and aluminum powder are 1 to 10 % by weight, 40 to 80 % by weight, 7 to 30 % by weight, 1 to 5 % by weight, 1 to 20 % by weight, 1 to 50 % by volume and 10 to 70 % by weight, respectively, based on the total amount of the explosive composition.

## Amended claims

**1.** (Amended) A water-in-oil emulsion explosive composition comprising 1 to 10 % by weight of a carbonaceous fuel component as a continuous phase; 40 to 80 % by weight of an inorganic oxidizer salt consisting mainly of ammonium nitrate and 7 to 30 % by weight of water as a disperse phase; 1 to 5 % by weight of an emulsifier; 1 to 50 % by volume of an organic gas-retaining agent having an average particle size of 10 to 4,000 μm and 10 to 70 % by weight of an aluminum powder having an average particle size of 0.01 to 1 μm, based on the total amount of the explosive composition.

**2.** A water-in-oil emulsion explosive composition according to Claim 1, wherein the shape of the aluminum powder is spherical or scaly.

**3.** A water-in-oil emulsion explosive composition according to Claim 1, wherein the organic gas-retaining agent is at least one selected from the group consisting of polystyrene, polyethylene and polyvinylidene chloride.

**4.** (Deleted)

**5.** (Deleted)

**6.** (Deleted)

**7.** (Amended) A water-in-oil emulsion explosive composition according to Claim 1, which further contains 1 to 20 % by weight of a sensitizer based on the total amount of the explosive composition.

**8.** (Deleted)

**9.** (Deleted)

**10.** (Deleted)

**11.** (Deleted)

**12.** (Amended) A water-in-oil emulsion explosive composition according to Claim 7, wherein the sensitizer is at least one selected from the group consisting of monomethylamine nitrate, hydrazine nitrate and ethylenediamine nitrate.

**13.** (Amended) A water-in-oil emulsion explosive composition according to Claim 12, containing hydrazine nitrate as the sensitizer and further a chelating agent.

**14.** (Amended) A water-in-oil emulsion explosive composition according to Claim 13, wherein the content of the chelating agent is 0.1 to 10 % by weight based on the amount of the hydrazine nitrate.

**15.** (Deleted)

**16.** (Deleted)

**17.** (Added) A water-in-oil emulsion explosive composition according to Claim 1, wherein the content of the aluminum powder is 20 to 70 % by weight based on the total amount of the explosive composition.

# INTERNATIONAL SEARCH REPORT

International Application No PCT/JP90/01068

**I. CLASSIFICATION OF SUBJECT MATTER** (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int. Cl$^5$ C06B47/14

**II. FIELDS SEARCHED**

Minimum Documentation Searched [7]

| Classification System | Classification Symbols |
|---|---|
| IPC | C06B47/14 |

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

**III. DOCUMENTS CONSIDERED TO BE RELEVANT** [9]

| Category * | Citation of Document, [11] with indication, where appropriate, of the relevant passages [12] | Relevant to Claim No. [13] |
|---|---|---|
| X | JP, A, 60-90887 (Nippon Oil and Fats Co., Ltd.),<br>22 May 1985 (22. 05. 85)<br>& EP, A1, 142271 & US, A, 4543137<br>& CA, A1, 1217058 | 1 - 16 |
| X | JP, A, 62-207791 (Nippon Oil and Fats Co., Ltd.),<br>12 September 1987 (12. 09. 87)<br>& EP, A2, 237274 & US, A, 4,732,626 | 1 - 16 |

* Special categories of cited documents: [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

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**IV. CERTIFICATION**

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|---|---|
| Date of the Actual Completion of the International Search<br>October 30, 1990 (30. 10. 90) | Date of Mailing of this International Search Report<br>November 13, 1990 (13. 11. 90) |
| International Searching Authority<br>Japanese Patent Office | Signature of Authorized Officer |

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