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E-28006 Madrid(ES)(54) **Method for preparing novel emulsion-type explosive compositions.**

(57) The invention provides a novel explosive composition in emulsion, comprising an oxidizing agent, a fuel, an emulsifying agent and a polymer structure which envelopes the discontinuous oxidizing phase, supplementing the interfacial structure of the emulsifying system --used. The invention also provides a method for their preparation consisting in forming an aqueous solution of oxidizing salts and of one or more low molecular-weight organic monomers capable of polymerizing by - -addition. The aqueous solution is emulsified in a fuel in the presence of the emulsifying agent so as subsequently to bring about polymerization, straight-chain or cross linking polymerization of the monomers. Polymerization occurs basically at the interface and adjacent areas, producing an enveloping macrostructure - -which increases the stability of the emulsion.

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METHOD FOR PREPARING NOVEL EMULSION-TYPE EXPLOSIVE COMPOSITIONS

The invention relates to a method for preparing "water in oil" emulsion type explosive compositions and to the compositions obtained therefore. The compositions comprise an organic fuel as continuous phase, and as -discontinuous phase an aqueous solution containing oxidizing salts among other components.

Explosive compositions of the "water in oil" emulsion type are widely used since they combine good results --with great safety during use.

However, as they are based on dispersing a relatively large volume of aqueous phase in a continuous oil --phase, stability problems are frequent. These problems are difficult to solve without losing effectiveness in other respects.

In some cases, for example, use has been made of - different kinds of polymers as components in the oil --phase, thus increasing the stability of the emulsion and of the bubbles of gas occluded therein during the process of sensitization, owing to the effect of the polymers on the rheological properties of the continuous phase. This is the aim of the following inventions.

US PS 4 548 660. This patent describes the addition to the oil phase of a polymer in the group formed by -epoxy resins, unsaturated polyester resins, polybutene, polyisobutylene, petroleum resin, butadiene resin and ethylene-vinyl acetate copolymers.

US PS 4 470 855. This patent discloses incorporation in the main oil component (paraffin wax) of a polymer which contains ethyl radicals and acts as a modifier of flow properties.

US PS 4 496 505. The same as before; the patent discloses incorporation in the oil phase of acrylate/methacrylate copolymers and olefinic copolymers.

GB PS 2 098 976. In this case the oil phase comprises acrylonitrile/butylacrylate or vinyl acetate/ethylene -copolymers or a mixture of the two, together with conventional fuels.

US PS 4 343 668. In this case the continuous fuel --phase is formed by a liquid polymer that can be cross-linked to give a thermo-stable resin.

US PS 4 525 225. In this patent, which is on the same lines as those previously described, the oil phase used is a mixture of polyester and styrene.

In all cases, the resulting increase in stability of the system is always accompanied by a drastic change in rheological properties, which limits the range of application of the resulting compositions.

In order directly to stabilize the droplets of the -dispersed liquid phase themselves US PS 4 602 970 discloses polymerizing the emulsifying agent so as to combine adjacent molecules of emulsifying agent at the interface. The practical results, however, do not show a great improvement over the prior art, since the conventional emulsifiers required to prepare the emulsion are unsuitable for polymerization. This is because the emulsifiers are derived from oleic, linoleic and linolenic acid and have double bonds at the centres of molecules containing 18 carbon atoms. It is well known that the reactivity of double bonds decreases when the polar -character of the molecule decreases and, also, when -the distance between the double bond and the ends of the molecule increases. For these reasons it is very difficult for emulsifying agents conventionally used in explosive emulsions to be polymerized sufficiently as to form a macrostructure that effectively stabilizes the dispersed drops, so that the improvements obtained are not significant.

The object of the invention is a novel emulsion explosive composition having a greater stability than existing explosive emulsions without the need for substantially varying its rheological conditions or methods of manufacture. The novel emulsion explosive compositions have a hydrated polymer macrostructure which envelops the - aqueous oxidizing phase and is located in the boundaries of the interface produced by the emulsifying agent system. The production of this macrostructure is based on a novel method for forming the final explosive composition. The method consists in adding to the aqueous solution one or more low molecular-weight organic compounds (hereinafter called monomers) capable of polymerizing by addition. These monomers polymerize "in situ" once the emulsion -system has been formed. Polymerization occurs mainly in the interface of the emulsion and at its boundaries since the monomers are organic products and have some affinity for the organic continuous phase. The monomers have double bonds at the ends of the molecule enabling them to polymerize via radicals. Polymerization is initiated preferably by a chemical initiator although other kinds of initiation are possible, e.g. thermal or photochemical.

Owing to the organic nature of the monomers, polymerization occurs mainly at the interface and adjacent areas, resulting in an enveloping macrostructure, thick enough as to increase the stability of the emulsion without a substantial influence in its viscosity. The stability of the macrostructure can be increased by using monomers having more than one double bond or suitable functional groups for chemical cross-linking.

The addition of monomers instead of polymers to the aqueous phase has other advantages due to the

low molecular weight of the monomer compared with the polymer. Emulsions tend to form with smaller drop size, since the aqueous phase containing the monomer has a much lower viscosity than it would have if the polymer itself were added. The presence of the monomer actually facilitates the formation of smaller drops since it is soluble in water and in a large number of organic compounds and to some extent
 5 increases the compatibility of the aqueous and the oil phase, thus assisting in the formation of the emulsion.

The water-in-oil emulsion-type explosive compositions according to the invention can have a wide range of viscosity and can be used in bulk pumpable form or cartridge in rolls 25 mm. or more in diameter, so as to be sensitive to the multiplier and to the detonator in both cases.

10 The emulsion comprises a continuous phase containing one or various hydrocarbon fuels, and a discontinuous phase comprising a supersaturated solution of inorganic oxidizing salts and a polymer macrostructure produced by polymerization of the partial or totally water soluble monomers added to the aqueous solution before forming the emulsion. This is formed by means of emulsifying agents.

The inorganic oxidizing salts used according to the invention are e.g. nitrates, chlorates and perchlorates of ammonium and alkali and alkaline earth metals. The salts can be used alone or in mixtures of two or more. The following are representative inorganic salts, ammonium nitrate, sodium nitrate, potassium nitrate, calcium nitrate, magnesium nitrate, ammonium perchlorate, sodium perchlorate, potassium perchlorate, magnesium perchlorate and others known in the art. The proportion of the salts in the emulsion is
 15 between 30 and 90% by weight of the composition.

20 Preferably, use is made of a mixture of ammonium nitrate in a percentage of at least 50% by weight of the total composition, and sodium nitrate, the proportion of which in the emulsion varies between 5 and 30% and preferably between 10 and 20%.

The amount of water in the discontinuous phase of the emulsion may be selected depending on the intended use of the emulsion and can vary between approximately 0 and 30% by weight of the total
 25 composition. Preferably the proportion is between 10 and 20%.

According to the invention, one or more organic products having at least one double bond, and therefore capable of polymerization by addition, are added to the salts solution. These products are partly or totally soluble in water and form part of the group comprising acrylic aldehyde, acrylamide, acrylic acid, methacrylic acid, itaconic acid, acrylonitrile, allyl amine, allyl alcohol, maleic anhydride, crotonic acid,
 30 derivatives and others of similar chemical nature.

The proportions of these products vary between 0.1 and 10% by weight of the total composition, preferably between 0.2 and 4%.

Among monomers completely soluble in water, use is preferably made of those having greater power of penetration in the oil phase.

35 Although polymerization can be initiated by any of the existing methods of radical polymerization, initiation is preferably made by chemical initiators which, when subjected to heat or electromagnetic radiation or chemical reaction, undergo homolytic fission into radicals having greater reactivity than the monomeric radicals. The following reaction systems can be used for producing radicals:

1. Thermal decomposition, usually applicable to organic, peroxide or azo compounds, e.g. benzoyl peroxide, dicumyl peroxide, methylethyl ketone peroxide, or α , α -azobisisobutyronitrile. Decomposition can
 40 be accelerated by suitable catalysts.

2. Photolytic decomposition, applicable to metal iodides and alkyls and azo compounds such as azobisisobutyronitrile.

3. Redox reactions such as the reaction between a ferrous ion and hydrogen peroxide. Alkyl
 45 peroxides can be used instead of hydrogen peroxide.

4. Persulphates which decompose in the aqueous phase, e.g. potassium persulphate and ammonium persulphate.

Polymerization can be initiated in the aqueous phase or in the oil phase. In the first case, redox and persulphate reactions are generally used. In the case of initiation in the continuous oil phase, the usual
 50 method is thermal or photolytic, preferably thermal decomposition of the chemical initiators.

The emulsion must form before polymerization has appreciably progressed.

If the polymerization is initiated from the oily phase, the initiator can be added without any restriction at any time after the emulsion forms. This method of initiation enables polymerization to be restricted in simple manner to the interface. If the initiator is added to the aqueous phase, the concentration of
 55 monomer and initiator must be such that the emulsion forms before the polymerization process has appreciably advanced. By suitable selection of the concentration of monomer, concentration of initiator, temperature and concentration of catalyst, any person skilled in the art can ensure that polymerization occurs substantially in a reasonably short interval of time after forming the emulsion.

The polymer macrostructure formed during polymerization gives great mechanical stability to the drop, inhibiting the growth of inorganic crystals and thus increasing the life of the emulsion. As the macrostructure is located in the interface and the boundaries of the drops, its presence does not affect the rheological properties of the emulsion. For this reason, special interest - - attaches to those emulsions which need to
 5 pour out - -freely, i.e. have low viscosity, and/or are produced by techniques requiring low shearing forces.

Apart from specific location of the polymer in the peripheral area of the drop, addition of a monomer to the aqueous phase in order to polymerize it after the emulsion has been formed has a further advantage as compared with initial addition of polymers to the aqueous phase. In view of the large increase in viscosity in the aqueous phase after a polymer dissolves in it, the replacement of the polymer by a monomer before the
 10 emulsion forms increases oil phase-aqueous phase viscosity ration, thus reducing the size of the drops of emulsion for a given shearing force. This increases the stability and sensitivity of the emulsion by increasing the contact surface between the oxidizing agent and fuel.

According to the invention the emulsifying agent can be any of the kinds normally used in this class of emulsions and can be used alone or in combination. The emulsifying agents can include e.g. sorbitan fatty-
 15 acid esters such as sorbitan sesquioleate, sorbitan monooleate, sorbitan monopalmitate, sorbitan monostearate, sorbitan triolate and sorbitan tristearate. Also included are -polyoxyethylene sorbital, lanoline fatty-acid alkyl esters, polyalkylene esters, substituted oxazolines, fatty-alcohol phosphate esters, fatty alkanol amides, ethoxy fatty ethers, soya lecithin, lanoline derivatives, fatty-acid mono- and diglycerides, and salts of fatty acids and fatty amines.

If the emulsifier has double bonds in the molecule, it can sometimes form part of the macrostructure occurring during polymerization in some extent. Acceptable emulsification is usually obtained when the emulsifying agent amount is from 0.1 to 6%, preferably 0.2 to 4% and particularly preferably 0.5 to 3% by
 20 weight of the total explosive composition.

For the purpose of the present invention, the continuous organic hydrophobic phase of the "water in oil" emulsion normally comprises a hydrocarbon or carbonaceous fuel of mineral, animal or vegetable origin and liquid or solid at ambient temperature (in that case it should be liquid under the conditions for forming the emulsion).

The suitable organic compounds include aromatic and aliphatic saturated and unsaturated hydrocarbons and derivatives thereof and mixtures of any of them. The preferred compounds include mineral oil, diesel
 30 oil, paraffin oil and wax, petroleum distillates, benzene, toluene, xylene, epoxy soya oil, dinitrotoluene and mixtures thereof. The rheological properties of the system can be controlled by adding waxes to the continuous organic --phase. In general, the total continuous organic phase -corresponds to values between 1 and 20%, preferably - -between 2 and 10% by weight of the total explosive composition.

The compositions according to the invention can also include auxiliary or additional fuels. These include
 35 -those which can be added to the aqueous phase, e.g. glucose, sucrose, fructose, maltose, molasses, glycols, formamide, urea, hexamethylene tetramide, methylamine nitrate, hexamethylene tetramine nitrate and other organic nitrates. Additional fuels include solid materials in particle form such as carbon, graphite, sulphur, aluminium, magnesium and perchlorates. The proportions of additional fuel can vary, depending on the desired characteristics of the final explosive emulsion, but are usually between 0 and 20%, preferably
 40 between 0.5 and 10% by weight of the total explosive composition.

According to the invention, the explosive composition also contains a discontinuous gaseous component in order to increase its sensitivity and simultaneously reduce its density to values preferably between 0.7 and 1.4 g/cc. Bubbles of air or gas can be incorporated in -the explosive composition by mixing hollow
 45 spheres -such as glass microspheres, resin microspheres or porous particles such as perlite or by mechanical agitation or injection or bubbling of gas through the composition, or by chemical production of gas "in situ" by adding products such as hydrogen peroxide, sodium nitrite, sodium carbonate, N,N -dinitrous pentamethylene tetramine, nitrous acid or salts thereof which decompose in acid solutions, and organic foaming - -agents such as dinitrous components and diisocyanates. The gaseous component is normally added to the emulsion when cool and forms part of the emulsion in a proportion which varies
 50 between 0.01 and 60% by volume of the final explosive composition.

The explosive compositions according to the invention can be used either in bulk form or in 25 mm cartridges or more in diameter, depending on the viscosity and the suitable added components.

The invention is illustrated by the following examples, which are in no case limitative and in which the percentages are indicated by weight.

EXAMPLE 1

In order to show the advantages of explosive compositions of "water in oil" emulsion type according to the invention as compared with conventional bulk explosive emulsions, ten different compositions were prepared and tested (Table 1).

Composition 1 corresponded to a conventional explosive emulsion and was prepared and tested in accordance with the following operative procedure:

A mixture of ammonium nitrate (59.70 parts), sodium nitrate (18.35 parts) and water (13.80 parts) was heated to 70°C with vigorous stirring until an aqueous solution formed. The aqueous solution was added at the same temperature, with agitation, to a solution of sorbitan monooleate (1.40 parts) in paraffin oil (5.25 parts). Agitation was continued until a uniform emulsion was obtained. Next, glass microspheres (1.50 parts) were added and mixed to obtain a homogeneous mixture. The density of the final mixture at 25°C was 1.25 g/cc and its viscosity was 653 p. The detonation velocity at 5°C, confined in iron 50 mm in diameter and initiated by a 17 g pentrite multiplier, was 4700 m/s. The emulsion was stored at -10°C and periodically tested as described. The explosive failed after 5 weeks.

Composition 2 was an explosive emulsion prepared according to the method described in US PS 4 602 970:

The procedure for composition 1 was repeated except that the oil phase comprised 1.40 parts of sorbitan monooleate, 5.24 parts of paraffin oil and 0.01 parts of α, α -azobisisobutyronitrile. The emulsion was kept at 80°C for one hour. The final density of the emulsion at 25°C was 1.24 g/cc and its viscosity was 674 p. The detonation velocity according to the test described in the previous case, was 4600 m/s. The emulsion was stored at 10°C and periodically tested as described. The explosive failed after 7 weeks.

Composition 3 was an explosive emulsion in which acrylamide had been polymerized in the aqueous phase before forming the emulsion:

A mixture of ammonium nitrate (59.70 parts), sodium nitrate (18.34 parts) and water (13.30 parts) was heated to 70°C with vigorous agitation until an aqueous solution formed. Next, 1.50 parts of acrylamide and 0.01 parts of ammonium persulphate were added. Polymerization occurred with total conversion, ending at the moment when the viscosity of the aqueous solution remained constant. The final viscosity at 70°C was 4 p. The hot aqueous solution was added, with agitation, to a solution of sorbitan monooleate (1.40 parts) in paraffin oil (4.25 parts). Agitation was continued until a uniform emulsion was obtained. Glass microspheres (1.50 parts) were then added and mixed to obtain a homogeneous mixture. The density of the final emulsion at 25°C was 1.24 g/cc and its viscosity was 601 p. The detonation velocity in the previously-described test was 4400 m/s. The emulsion was stored at 10°C and the detonation velocity was periodically tested. The explosive failed after 5 weeks.

Compositions 4 to 10 were prepared according to the present invention, keeping similar components as far as possible:

Composition 4:

A mixture of ammonium nitrate (59.70 parts), sodium nitrate (18.35 parts), acrylamide (1.50 parts) and water (13.30 parts) was heated to 80°C with vigorous agitation until an aqueous solution formed. The aqueous solution was added at the said temperature with agitation to an oily solution comprising 1.40 parts of sorbitan monooleate, 4.24 parts of paraffin oil and 0.01 parts of α, α -azobisisobutyronitrile. The emulsion was kept at 80°C for an hour, 1.5 parts of glass microspheres were then added. The final density of the emulsion at 25°C was 1.25 g/cc and its viscosity was 735 p. The detonation velocity according to the previously-described test was 5500 m/s. The emulsion was stored at 10°C and periodically the detonation velocity was tested as described. The emulsion explosive could still be detonated after 30 weeks.

Composition 5:

A mixture of ammonium nitrate (59.70 parts), sodium nitrate (8.35 parts) and water (13.30 parts) was heated to 70°C with vigorous agitation until an aqueous solution formed. Next, 1.50 parts of acrylamide and 0.01 parts of ammonium persulphate were added and immediately this final aqueous solution was added at the said temperature, with agitation, to an oily solution comprising 1.40 parts of sorbitan monooleate and 4.25 parts of paraffin oil, so that polymerization occurred after the emulsion had formed. The emulsion was kept at 70°C for an hour. The viscosity of the aqueous solution formed by ammonium nitrate, sodium nitrate, acrylamide and water at 70°C was less than 1 p. The viscosity of the final emulsion at 25°C was 714 p and its density was 1.24 g/cc. The detonation velocity according to the previously-

described test was 5100 m/s. The emulsion -was stored at 10°C and its detonation velocity was periodically measured. The emulsion explosive could still be detonated after 26 weeks.

5 Composition 6:

The method of operation was the same as for composition 5 except that acrylamide was replaced by N-hydroxymethyl acrylamide. The density of the final emulsion at 25°C was 1.25 g/cc and its viscosity was 709 p. The detonation velocity according to the previously-described test was 5000 m/s. The emulsion was stored at 10°C and its detonation velocity was periodically measured by the same test. The emulsion explosive could still be detonated after 28 weeks.

Composition 7:

The method was the same as for composition 4 except that 1.5 parts of acrylamide were replaced by 1,00 parts of acrylamide and 0,50 parts of N, N-bismethylene acrylamide. The viscosity of the final emulsion at 25°C was 731 p and its density was 1,24 g/cc. The detonation velocity according to the previously-described test was - 5300 m/s. The emulsion was stored at 10°C and its detonation velocity was periodically measured by the same test. After 35 weeks the emulsion could still be detonated.

Composition 8:

A mixture of ammonium nitrate (59,70 parts), sodium nitrate (18,35 parts) and water (13,30 parts) was heated to 70°C with vigorous agitation. Next, 1,00 parts of acrylamide and 0,50 parts of N,N-bismethylene acrylamide were added. When the monomers had dissolved, the hot aqueous solution was added with agitation to a solution of sorbitan monooleate (1,40 parts) and benzoyl peroxide (0,005 parts) in paraffin oil (4,24 parts). Agitation was continued until a uniform emulsion was obtained. After -cooling the emulsion to 40°C, glass microspheres (1,50 parts) and dimethyl paratoluidine (0,005 parts) were --added and mixed to obtain a homogeneous mixture. The density of the final emulsion at 25°C was 1,24 g/cc and its viscosity was 756 p. The detonation velocity in accordance with the previously-described test was 5600 m/s. The emulsion was stored at 10°C and the same detonation velocity test was periodically made. After 37 weeks the - emulsion could still be detonated.

Composition 9:

The method was the same as for composition 5 except that acrylamide was replaced by acrylic acid and the -- initiator was 0.01 parts of ammonium persulphate and 0.01 parts of sodium metabisulphite. The density of the final emulsion at 25°C was 1.25 g/cc and its viscosity was 741 p. The detonation velocity in the previously-described test was 5400 m/s. The emulsion was stored at 10°C and its velocity was periodically measured by the same test. The emulsion explosive could still be detonated after 28 weeks.

Composition 10:

The method was the same as for composition 9 except that 13.53 parts of water were used instead of 13.30 -parts and the 1.5 parts of acrylic acid were replaced by 1.27 parts of maleic anhydride. The density of the final emulsion at 25°C was 1.25 g/cc and its viscosity was 713 p. The detonation velocity in the previously-described test was 5300 mn/s. The emulsion was stored at 10°C and its velocity was periodically measured by the same test. The emulsion explosive could still be detonated after 28 weeks.

As Table 1 shows, the compositions- according to the invention are considerably more stable than conventional compositions without apparent effect on other properties.

TABLE 1

| COMPONENTS | COMPOSITIONS | | | | | | | | | |
|--|--------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
| Ammonium nitrate | 59,70 | 59,70 | 59,70 | 59,70 | 59,70 | 59,70 | 59,70 | 59,70 | 59,70 | 59,70 |
| Sodium nitrate | 18,35 | 18,35 | 18,34 | 18,35 | 18,34 | 18,34 | 18,35 | 18,35 | 18,33 | 18,33 |
| Water | 13,80 | 13,80 | 13,30 | 13,30 | 13,30 | 13,30 | 13,30 | 13,30 | 13,30 | 13,53 |
| Acrylamide | - | - | 1,50 | 1,50 | 1,50 | - | 1,00 | 1,00 | - | - |
| N,N-bismethylene acrylamide | - | - | - | - | - | - | 0,50 | 0,50 | - | - |
| N-hydroxymethyl acrylamide | - | - | - | - | - | 1,50 | - | - | - | - |
| Acrylic acid | - | - | - | - | - | - | - | - | - | - |
| Maleic anhydride | - | - | - | - | - | - | - | - | 1,50 | - |
| Ammonium persulphate | - | - | 0,01 | - | 0,01 | 0,01 | - | - | 0,01 | 1,27 |
| Sodium metabisulphite | - | - | - | - | - | - | - | - | 0,01 | 0,01 |
| α,α -azobisisobutyronitrile | - | 0,01 | - | 0,01 | - | - | 0,01 | - | - | - |
| Benzoyl peroxide | - | - | - | - | - | - | - | 0,005 | - | - |
| Dimethyl paratoluidine | - | - | - | - | - | - | - | 0,005 | - | - |
| Sorbitan monooleate | 1,40 | 1,40 | 1,40 | 1,40 | 1,40 | 1,40 | 1,40 | 1,40 | 1,40 | 1,40 |
| Paraffin oil | 5,25 | 5,25 | 4,25 | 4,24 | 4,25 | 4,25 | 4,24 | 4,24 | 4,25 | 4,25 |
| Microspheres | 1,50 | 1,50 | 1,50 | 1,50 | 1,50 | 1,50 | 1,50 | 1,50 | 1,50 | 1,50 |
| Density (g/cc), 25°C | 1,25 | 1,24 | 1,24 | 1,25 | 1,24 | 1,25 | 1,24 | 1,24 | 1,25 | 1,25 |
| Viscosity (p), 25°C | 653 | 674 | 601 | 735 | 714 | 709 | 731 | 756 | 741 | 713 |
| Detonation velocity (m/s) conf. Fe. 050 mm, 50°C | 4700 | 4600 | 4400 | 5500 | 5100 | 5000 | 5300 | 5600 | 5400 | 5300 |
| Failure after (weeks) | 5 | 7 | 5 | >30 | >26 | >28 | >35 | >37 | >28 | >28 |

EXAMPLE 2

5 Similarity to example 1 various compositions in small-diameter cartridges were prepared and tested (Table 2).

Composition 11 was a conventional explosive emulsion and was prepared by the following procedure.

A mixture of ammonium nitrate (59.10 parts), sodium nitrate (18.20 parts) and water (13.60 parts) was heated to 70°C with vigorous agitation until an aqueous solution formed. The aqueous solution was added at said temperature, with rapid agitation, to a mixture of sorbitan monooleate (2.70 parts), paraffin oil (0.70 parts), paraffin wax (1.50 parts) and microcrystalline wax (1.90 parts) heated to 65°C. Agitation was continued until a uniform emulsion was obtained. Next, glass microspheres (2.30 parts) were added and mixed to obtain a homogeneous mixture. The density of the final mixture at 25°C was 1.16 g/cc. The final mixture was cartridged in paper (32 mm diameter). The detonation velocity of the emulsions initiated with a number 8 detonator was 4700 m/s. The emulsion was stored at 10°C and periodically tested. The emulsion failed after 22 weeks.

Compositions 12 to 6 were prepared according to the invention as follows:

20 Composition 12:

A mixture of ammonium nitrate (59.10 parts), sodium -nitrate (18.20 parts) and water (13.10 parts) was heated to 80°C with vigorous agitation until an aqueous solution formed. 1.50 parts of acrylamide were then added. The final solution was added at said temperature with agitation to a mixture of sorbitan monooleate (2.70 parts), paraffin oil (0.69 parts), paraffin Wax (1.17 parts), microcrystalline wax (1.67 parts) and α,α -azobisisobutyronitrile (0.01 parts) heated to 80°C. The emulsion was kept at 80°C for an hour. Glass microspheres (2.30 parts) were then added and mixed to obtain a homogeneous mixture. The density of the final mixture at 25°C was 1.6 g/cc. The final mixture was cartridged in paper (32 mm in diameter). The detonation velocity of the emulsion initiated with a number 8 detonator was 5000 mn/s. The emulsion was stored at 10°C and periodically tested in the same manner. The emulsion could still be detonated after 56 weeks.

35 Composition 13:

A mixture of ammonium nitrate (59.10 parts), sodium nitrate (18.18 parts) and water (13.10 parts) was heated to 70°C with vigorous agitation until an aqueous solution formed. 1.50 parts of acrylic acid, 0.01 parts of ammonium sulphate and 0.01 parts of sodium metabisulphite were then added. The final solution was immediately added, with agitation, to a mixture of sorbitan monooleate (2.70 parts), paraffin oil (0.70 parts), paraffin wax (1.17 parts) and microcrystalline wax (1.67 parts) heated to 65°C. Agitation was continued until a uniform emulsion was obtained. Glass microspheres (2.30 parts) were then added and mixed to obtain a homogeneous mixture. The density of the final mixture at 25°C was 1.17 g/cc. The final mixture was cartridged in paper (32 mm in diameter). The detonation velocity of the emulsion initiated with a number 8 detonator was 4900 m/s. The emulsion was stored at 10°C and periodically tested as before. After 63 weeks the emulsion could still be detonated.

Composition 14:

50 The method was the same as for composition 13 except that acrylic acid was replaced by N-hydroxymethyl acrylamide and the initiator was ammonium persulphate only. The density of the final emulsion at 25°C was 1.16 g/cc. The emulsion was wrapped in paper 32 mm diameter. The detonation velocity of the emulsion initiated with a number 8 detonator was 5300 m/s. The emulsion was stored at 10°C and periodically tested as before. The emulsion - -could still be detonated after 70 weeks.

Composition 15:

The method was the same as for composition 12 except that 13.33 parts of water were used instead of 13.10 and the 1.50 parts of acrylamide were replaced by 1.27 parts of maleic anhydride. The density of the final emulsion -at 25°C was 1.16 g/cc. The emulsion was rolled in paper 32 mm in diameter. The detonation velocity of the emulsion initiated with a number 8 detonator was 5100 m/s . The emulsion was stored at 10°C and periodically tested as before. The emulsion could still be detonated after 67 weeks.

Composition 16:

A mixture of ammonium nitrate (59.10 parts), sodium nitrate (18.20 parts) and water (13.10 parts) was heated to 70°C with vigorous agitation. Next, 1.00 parts of -acrylamide and 0.50 parts of N-N-bismethylene acrylamide were added. After the monomers had dissolved, the hot -aqueous solution was added with rapid agitation, a hot mixture (65°C) of sorbitan monooleate (2.70 parts), paraffin oil (0.69 parts), paraffin wax (1.7 parts), microcrystalline wax (1.67 parts) and benzoyl peroxide - -(0.005 parts). Agitation was continued until a uniform - emulsion was obtained. Next, glass microspheres (2.30 parts) and dimethyl aniline (0.005 parts) were added and mixed to obtain a homogeneous mixture. The density of the final emulsion at 25°C was 1.17 g/cc. The emulsion was cartridged in paper (32 mm diameter). The detonation velocity of the emulsion initiated with a number 8 detonator was 5100 m/s . The emulsion was stored at 10°C and periodically tested as before. The emulsion could still be detonated after 75 weeks.

As Table 2 shows, the method according to the invention gives compositions having appreciably improved --stability in small diameter cartridged emulsions initiated with a no 8 detonator.

TABLE 2

| COMPONENTS | COMPOSITIONS | | | | | |
|---|--------------|-------|-------|-------|-------|-------|
| | 11 | 12 | 13 | 14 | 15 | 16 |
| Ammonium nitrate | 59,10 | 59,10 | 59,10 | 59,10 | 59,10 | 59,10 |
| Sodium nitrate | 18,20 | 18,20 | 18,18 | 18,19 | 18,20 | 18,20 |
| Water | 13,60 | 13,10 | 13,10 | 13,10 | 13,33 | 13,10 |
| Acrylamide | - | 1,50 | - | - | - | 1,00 |
| N,N-bismethylene acrylamide | - | - | - | - | - | 0,30 |
| N-hydroxymethyl acrylamide | - | - | - | 1,50 | - | - |
| Acrylic acid | - | - | 1,50 | - | - | - |
| Maleic anhydride | - | - | - | - | 1,27 | - |
| Ammonium persulphate | - | - | 0,01 | 0,01 | - | - |
| Sodium metabisulphite | - | - | 0,01 | - | - | - |
| α,α -azobisisobutyronitrile | - | 0,01 | - | - | 0,01 | - |
| Benzoyl peroxide | - | - | - | - | - | 0,005 |
| Dimethyl analine | - | - | - | - | - | 0,005 |
| Sorbitan monooleate | 2,70 | 2,70 | 2,70 | 2,70 | 2,70 | 2,70 |
| Paraffin oil | 0,70 | 0,69 | 0,70 | 0,70 | 0,69 | 0,69 |
| Paraffin wax | 1,50 | 1,17 | 1,17 | 1,17 | 1,17 | 1,17 |
| Microcrystalline wax | 1,90 | 1,67 | 1,67 | 1,67 | 1,67 | 1,67 |
| Microspheres | 2,30 | 2,30 | 2,30 | 2,30 | 2,30 | 2,30 |
| Density (g/cc), 25°C | 1,16 | 1,16 | 1,17 | 1,16 | 1,16 | 1,17 |
| Detonation velocity (m/s) Paper, 32 mm, 5°C | 4700 | 5000 | 4900 | 5300 | 5100 | 5100 |
| Failure after (weeks) | 22 | 56 | >63 | >70 | >67 | >75 |

Claims

1.- A method for preparing novel emulsion type explosive compositions comprising a continuous fuel phase --and a discontinuous aqueous phase dispersed therein, --said aqueous phase containing oxidizing salts and a macromolecular structure, characterised in that it comprises the following steps:

a) Preparing an aqueous solution mainly comprising oxidizing inorganic salts and at least one polymerizable organic monomer;

b) Preparing an oil mixture non-miscible with the aqueous solution and mainly containing hydrocarbon fuels and one or more emulsifying agents;

5 c) Forming a "water in oil" type emulsion from the mixtures prepared in the previous stages, and

d) Polymerizing, after formation of the emulsion, the monomer or monomers contained in the dispersed - aqueous phase.

2.- A method according to claim 1, characterised in that the monomer or monomers included in the aqueous phase bear at least one double bond on the molecule.

10 3.- A method according to claims 1 and 2, characterised in that the monomer or monomers are chosen preferably among the group comprising acrylic acid, methacrylic acid, itaconic acid, fumaric acid, crotonic acid, maleic anhydride, acrylamide, acryl aldehyde, allyl - amine, allyl alcohol, acrylonitrile and derivatives - thereof.

4.- A method according to claims 1 and 3, characterised in that the monomer or monomers are incorporated in a proportion which varies between 0.01 and 20% by weight of the final composition.

5.- A method according to claim 1 characterised in that the monomer or at least one of them if there are more than one, has more than one double bond.

6.- A method according to claims 1 and 2, characterised in that the monomer, or at least one of them if there are more than one, has a reactive functional - group.

20 7.- A method according to claim 6, characterised in that at least one monomer comprises hydroxyl, amine, acid or methoxymethyl reactive functional groups.

8.- A method according to claims 6 and 7, characterised in that an organic compound capable of reacting with the functional groups of the existing monomer or monomers and forming cross-links is added to the composition.

25 9.- A method according to claim 8, characterised in that the organic compound which is added belongs to the group comprising resins of the following: melamine, formaldehyde, benzoguanamines, diepoxy dianhydrides, phenolic, tetraalkyl titanates, diisocyanates, dimethoxymethyl urea, trimethylol melamine methylolate, butylated trimethylol melamine, butylated methylol benzoguanamine, bismethoxymethyl ureas, bismethoxymethylene - urea and similar amino resins, polyols and polymers obtained with n-methylol acrylamidés.

30 10.- A method according to claim 1, characterised in that polymerization is initiated by a chemical initiator.

11.- A method according to claim 10, characterised in that the initiator is added to the aqueous solution immediately before the emulsion forms, so that no appreciable polymerization of monomers occurs beforehand.

12.- A method according to claim 10, characterised in that the initiator is added to the oleous phase.

13.- A method according to claims 10 to 12, characterised in that polymerization is initiated by redox type initiators.

14.- A method according to claims 10 to 12, characterised in that chemical initiation is brought about by thermal decomposition of an azo, peroxide, peracetate or hydroperoxide compound.

15.- A method according to claim 14, characterised in that thermal decomposition of the initiator is catalyzed so that the decomposition occurs at temperatures below 80°C.

16.- A method according to claim 1, characterised in that polymerization is initiated by electromagnetic radiation.

45 17.- A method according to claim 1, characterised in that a transference agent can be added to the aqueous solution in addition to the monomers.

18.- A method according to claim 1, characterised in that the inorganic oxidizing salts are chosen among nitrates, chlorates or perchlorates of ammonium and alkaline or alkaline earth metals.

19.- A method according to claims 1 and 18, characterised in that the proportion of inorganic oxidizing - salts used is between 20 and 90% by weight of the final composition.

20.- A method according to claim 1, characterised in that the water-insoluble hydrocarbon fuels can be aliphatic, alicyclic and/or aromatic and can be saturated and/or unsaturated.

21.- A method according to claim 20, characterised in that the hydrocarbon fuel is selected from the following group: fuel oil, diesel oil, distilled oils, kerosene, naphtha, paraffin oils and waxes, microcrystalline waxes, benzene, toluene, xylenes, asphalt materials, polymer oils and waxes, animal oils and waxes, elastomers and vegetable oils and waxes such as epoxylated soya oil and mixtures thereof.

22.- A method according to claims 1, 20 and 21, characterised in that the hydrocarbon fuels are incorporated in quantities between 2 and 30 percent by weight of the final composition.

23.- A method according to claim 1, characterised in that the emulsifying agents incorporated in the oleous phase are chosen among the group formed by sorbitan esters, pentaerythritol esters, fatty acid glycerides, alkoxyated alcohols, alkoxyated phenols, alkoxyated fatty amines, polyoxyalkylene sorbitan esters, glycol and polyoxyalkylene esters, acid amides, fatty amides, quaternary amines, alkyl oxazolines, alkenyl oxazolines, imidazolines, alkyl sulphonates, alkyl aryl sulphonates, alkyl sulphosuccinates, alkyl phosphate, alkylene phosphates, phosphated esters, lecithin, lanoline derivatives, and copolymers of polyoxyalkylene glycol and 12 hydroxystearic polyacid.

24.- A method according to claims 1 and 23, characterised in that the emulsifying agents are incorporated in proportions between 0.2 and 7% of the final composition.

25.- A method according to claim 1, characterised in that the composition is sensitized by incorporating a discontinuous gaseous phase in order to obtain a final density between 0.7 and 1.4 g/cm³.

26.- A method according to claim 25, characterised -in that the discontinuous phase can be incorporated by direct injection of air, occlusion, addition of gas generators and addition of hollow spheres such as glass microspheres, polymer microspheres, perlite, volcanic microspheres and flying ashes.

27.- A method according to claim 1, characterised -in that auxiliary fuels can be incorporated in the composition such as aluminium, aluminium-silicon alloys, ferrosilicon, carbohydrates, amines, amides, sulphur and carbon.

28.- A method according to claim 27, characterised in that the auxiliary fuels are incorporated in proportions below 25% by weight of the final composition.

29.- A method according to claim 1, characterised in that the sensitivity of the composition can be increased by adding auxiliary sensitizing agents such as nitrated amines, nitrotoluenes, PETN, PDX, HMX, nitrocellulose or mixtures thereof.

30.- A method according to claim 29, characterised in that the auxiliary sensitizing agents are added in proportions below 30% by weight of the final composition.

31.- A novel explosive composition in emulsion obtained in accordance to the method of any of the preceding claims.



| DOCUMENTS CONSIDERED TO BE RELEVANT | | | |
|--|--|--|---|
| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | CLASSIFICATION OF THE APPLICATION (Int. Cl.4) |
| A | EP-A-0 107 226 (THE DOW CHEMICAL CO.) * Page 3, line 32 - page 5, line 32; page 6, lines 17-28; page 7, line 9 - page 8, line 21; claims; page 9, lines 8-31 * | 1-4,6,7 ,10,13, 14,17- 24 | C 06 B 47/14 C 08 F 2/32 |
| A | US-A-4 524 175 (F.W. STANLEY Jr.) * Column 6, lines 12-33; column 7, lines 11-33; column 2, lines 48-58; claims * | 1 | |
| A | EP-A-0 183 890 (SCAN COIN S.A.) * Claims; page 4, example * | 1,31 | |
| D,A | US-A-4 525 225 (M. CECHANSKI) * Column 8, line 27 - column 9, line 37; claims * | 1,31 | |
| A | US-A-4 739 008 (P.M. ROBINSON et al.) | | |
| | | | TECHNICAL FIELDS SEARCHED (Int. Cl.4) |
| | | | C 06 B C 08 F |
| The present search report has been drawn up for all claims | | | |
| Place of search THE HAGUE | | Date of completion of the search 22-03-1989 | Examiner SCHUT, R.J. |
| CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document | | | |