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54 **Method for preparing novel emulsion-type explosive compositions.**

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Description

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,
5 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
10 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.

15 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.

20 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.

25 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.

30 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
35 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.

40 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
45 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
50 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
55 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 increases the compatibility of the aqueous and the oil phase, thus assisting in the formation of the emulsion.

5 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.

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
10 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
15 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 between 30 and 90% by weight of the composition.

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
20 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 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
25 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, derivatives and others of similar chemical nature.

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

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
35 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 be accelerated by suitable catalysts.
- 40 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 peroxides can be used instead of hydrogen peroxide.
4. Persulphates which decompose in the aqueous phase, e.g. potassium persulphate and ammonium
45 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 method is thermal or photolytic, preferably thermal decomposition of the chemical initiators.

The emulsion must form before polymerization has appreciably progressed.

50 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 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
55 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 pour out freely, i.e. have low viscosity, and/or are produced by techniques requiring low shearing forces.

5 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 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
10 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-acid esters such as sorbitan sesquioleate, sorbitan monooleate, sorbitan monopalmitate, sorbitan monostearate, sorbitan triolate and sorbitan tristearate. Also included are polyoxyethylene sorbital, lanoline fatty-
15 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
25 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 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
30 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 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
35 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 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
40 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 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
45 -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 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
50 cartridges or more in diameter, depending on the viscosity and the suitable added components.

The invention is illustrated by the following examples, in which the percentages are indicated by weight.

EXAMPLE 1

55 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 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 (18.35 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.

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.

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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.

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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.

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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.

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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.

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

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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	18,35	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	-	-	-	-	-	-	-	-	1,50	-
Maleic anhydride	-	-	-	-	-	-	-	-	-	1,27
Ammonium persulphate	-	-	0,01	-	0,01	0,01	-	-	0,01	0,01
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	5,24	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)	4700	4600	4400	5500	5100	5000	5300	5600	5400	5300
conf. Fe, 50 mm, 5°C	5	7	5	>30	>26	>28	>35	>37	>28	>28
Failure after (weeks)										

EXAMPLE 2

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

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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 cartridgeed in paper (32 mm diameter). The detonation velocity of the emulsion 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 16 were prepared according to the invention as follows:

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 cartridgeed in paper (32 mm in diameter). The detonation velocity of the emulsion initiated with a number 8 detonator was 5000 m/s. The emulsion was stored at 10°C and periodically tested in the same manner. The emulsion could still be detonated after 56 weeks.

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 cartridgeed 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:

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

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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 (1.17 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 n° 8 detonator.

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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	4700	5000	4900	5300	5100	5100
(m/s) Paper, 32 mm, 5°C	22	56	>63	>70	>67	>75
Failure after (weeks)						

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;
 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.
- 5
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 claim 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.
- 15 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.
- 20 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.
7. A method according to claim 6, characterised in that at least one monomer comprises hydroxyl, amine, acid or methoxymethyl reactive functional groups.
- 25 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.
- 30 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 acrylamides.
- 35 10. A method according to claim 1, characterised in that polymerization is initiated by a chemical initiator.
- 40 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.
- 45 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.
- 50 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.
- 55 16. A method according to claim 1, characterised in that polymerization is initiated by electromagnetic radiation.
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.

- 5
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.
- 10
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, micro-crystalline waxes, benzene, toluene, xylenes, asphalt materials, polymer oils and waxes, animal oils and waxes, elastomers and vegetable oils and waxes such as epoxydated soya oil and mixtures thereof.
- 15
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.
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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.
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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.
- 30
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.
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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.
- 40
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.
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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.
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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 sensitising 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.

55 **Patentansprüche**

1. Verfahren zur Herstellung einer neuen Sprengstoff-Zusammen-setzung vom Emulsionstyp umfassend eine kontinuierliche Brenn-stoffphase und eine, diskontinuierliche darin dispergiertewasserige Phase,

wobei die wässrige Phase oxidierende Salze und eine makromolekulare Struktur enthält, dadurch gekennzeichnet, daß es die folgenden Stufen umfaßt:

- (a) Herstellung einer wässrigen Lösung, die hauptsächlich oxidierende anorganische Salze und mindestens ein polymerisierbares organisches Monomer enthält;
 - 5 (b) Herstellung einer mit der wässrigen Lösung nicht mischbaren Ölmischung, die hauptsächlich Kohlenwasserstoff Brennstoffe und ein oder mehrere Emulgiermittel enthält;
 - (c) Herstellung einer Emulsion vom "Wasser-in-Öl-Typ" aus den in den vorhergehenden Stufen hergestellten Mischungen, und
 - 10 (d) Polymerisieren des oder der in der dispergierten wässrigen Phase enthaltenen Monomers oder Monomeren nach Bildung der Emulsion.
2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß das oder die in der wässrigen Phase enthaltene(n) Monomer oder die Monomeren mindestens eine Doppelbindung im Molekül enthalten.
 - 15 3. Verfahren nach Anspruch 1 und 2, dadurch gekennzeichnet, daß das Monomer oder die Monomeren vorzugsweise ausgewählt sind aus der Gruppe umfassend Acrylsäure, Methacrylsäure, Itaconsäure, Fumarsäure, Crotonsäure, Maleinsäureanhydrid, Acrylamid, Acrylaldehyd, Allylamin, Allylalkohol, Acrylnitril und deren Derivate.
 - 20 4. Verfahren nach den Ansprüchen 1 und 3, dadurch gekennzeichnet, daß das Monomere oder die Monomeren in Anteilen enthalten sind, die zwischen 0.01 und 20 Gew.% der Endzusammensetzung variieren.
 - 25 5. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß das Monomere, oder im Fall von mehr als einem Monomeren, mindestens eines davon mehr als eine Doppelbindung besitzen.
 6. Verfahren nach den Ansprüchen 1 und 2, dadurch gekennzeichnet, daß das Monomere, oder im Fall von mehr als einem Monomeren mindestens eines davon eine reaktive funktionelle Gruppe besitzt.
 - 30 7. Verfahren nach Anspruch 6, dadurch gekennzeichnet, daß mindestens ein Monomeres Hydroxyl-, Amin-, Säure- oder Methoxy-methyl-reaktive funktionelle Gruppen umfaßt.
 8. Verfahren nach den Ansprüchen 6 und 7, dadurch gekennzeichnet, daß der Zusammensetzung eine organische Verbindung zugefügt wird, die dazu fähig ist, mit den funktionellen Gruppen des vorhandenen Monomeren oder der Monomeren unter Vernetzung zu reagieren.
 - 35 9. Verfahren nach Anspruch 8, dadurch gekennzeichnet, daß die organische Verbindung, die zugefügt wird, zur Gruppe gehört, die folgende Liste umfaßt: Melamin, Formaldehyd, Benzoquanamine, Diepoxydianhydride, phenolische Harze, Tetraalkyltitanate, Diisocyanate, Dimethoxymethylharnstoff, Trimethylolmelaminmethylolat, butyliertes Trimethylolmelamin, butyliertes Methylolbenzoquanamin, Bismethoxymethylharnstoffe, Bismethoxymethylenharnstoff und ähnliche Aminoharze, Polyole und Polymere, die mit n-Methylol-Acrylamiden erhalten werden.
 - 40 10. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die Polymerisation durch einen chemischen Initiator initiiert wird.
 - 45 11. Verfahren nach Anspruch 10, dadurch gekennzeichnet, daß der Initiator zu der wässrigen Lösung zugegeben wird, kurz bevor sich die Emulsion bildet, damit vorher keine nennenswerte Polymerisation der Monomeren stattfindet.
 - 50 12. Verfahren nach Anspruch 10, dadurch gekennzeichnet, daß der Initiator zur Ölphase zugegeben wird.
 13. Verfahren nach den Ansprüchen 10 bis 12, dadurch gekennzeichnet, daß die Polymerisation durch Initiatoren vom Redox-Typ initiiert wird.
 - 55 14. Verfahren nach den Ansprüchen 10 bis 12, dadurch gekennzeichnet, daß die chemische Initiierung durch thermische Zersetzung einer Azo-, Peroxid-, Peracetat- oder Hydroperoxid-Verbindung verursacht wird.

15. Verfahren nach Anspruch 14, dadurch gekennzeichnet, daß die thermische Zersetzung des Initiators katalysiert wird, damit die Zersetzung bei Temperaturen unterhalb von 80° C stattfindet.
- 5 16. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die Polymerisation durch elektromagnetische Strahlung initiiert wird.
17. Verfahren nach Anspruch 1, dadurch gekennzeichnet daß zusätzlich zu den Monomeren zur wässerigen Lösung ein Übertragungsmittel zugegeben werden kann.
- 10 18. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die anorganischen oxidierenden Salze ausgewählt sind unter Nitraten, Chloraten oder Perchloraten von Ammonium und Alkali -oder Erdalkalimetallen.
- 15 19. Verfahren nach den Ansprüchen 1 und 18, dadurch gekennzeichnet, daß der Anteil der verwendeten anorganischen oxidierenden Salze zwinschen 20 und 90 Gew.-% der Endzusammensetzung liegt.
- 20 20. Verfahren gemäß Anspruch 1, dadurch gekennzeichnet, daß die wasserunlöslichen Kohlenwasserstoff-Brennstoffe aliphatisch, alicyklisch und/oder aromatisch sein können und gesättigt und/oder ungesättigt sein können.
- 25 21. Verfahren nach Anspruch 20, dadurch gekennzeichnet, daß der Kohlenwasserstoff-Brennstoff ausgewählt ist aus der folgenden Gruppe: Heizöl, Dieselöl, destillierte Öle, Kerosin, Naphtha, Paraffinöle und -Wachse, mikrokristalline Wachse, Benzol, Toluol, Xylole, Asphaltmaterialien, polymere Öle und Wachse, tierische Öle und Wachse, Elastomere und pflanzliche Öle und Wachse, wie z.B. epoxydiertes Sojabohnenöl, und Mischungen davon.
- 30 22. Verfahren nach den Ansprüchen 1, 20 und 21, dadurch gekennzeichnet, daß die Kohlenwasserstoff-Brennstoffe in Mengen zwischen 2 und 30 Gew % der Endzusammensetzung enthalten sind.
- 35 23. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die in der Ölphase enthaltenen Emulgiermittel ausgewählt sind aus der Gruppe gebildet aus Sorbitanestern, Pentaerythritestern, Fettsäureglyceriden, alkoxylierten Alkoholen, alkoxylierten Phenolen, alkoxylierten Fettsäureaminen, Polyoxyalkylensorbitanestern, Glykol-und Polyoxyalkylenestern, Säureamiden, Fettamiden, quarternären Aminen, Alkyloxazolinen, Alkenyloxazolinen, Imidazolinen, Alkylsulfonaten, Alkylarylsulfonaten, Alkylsulfosuccinaten, Alkylphosphat, Alkylphenosphaten, phosphatierten, Estern, Lecithin, Lanolinderivaten, und Copolymeren von Polyoxyalkylenglycol und 12-Hydroxystearinpolysäure.
- 40 24. Verfahren nach den Ansprüchen 1 und 23, dadurch gekennzeichnet, daß die Emulgiermittel in Anteilen zwischen 0.2 und 7% der Endzusammensetzung enthalten sind.
- 45 25. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die Zusammensetzung durch Einbau einer diskontinuierlichen gasförmigen Phase sensibilisiert wird, um eine Enddichte zwischen 0.7 und 1.4 g/cm³ zu erhalten.
- 50 26. Verfahren nach Anspruch 25, dadurch gekennzeichnet, daß die diskontinuierliche Phase durch direkte Injektion von Luft, Occlusion, Zusatz von Gasentwicklern und Zusatz von Hohlkügeln, wie z.B. Gasmikrokugeln, Polymerenmikrokugeln, Perlit, vulkanischen Mikrokugeln und Flugaschen eingebaut werden kann.
- 55 27. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß Hilfsbrennstoffe, wie z.B. Aluminium-Silicium-Legierungen, Ferrosilicium, Kohlehydrate, Amine, Amide, Schwefel und Kohlenstoff, in die Zusammensetzung eingebaut werden können.
28. Verfahren nach Anspruch 27, dadurch gekennzeichnet, daß die Hilfsbrennstoffe in Anteilen unterhalb von 25 Gew.-% der Endzusammensetzung eingebaut werden.
29. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die Sensibilität der Zusammensetzung durch Zugabe von Hilfs-Sensibilisierungsmitteln, wie z.B. nitrierten Aminen, Nitrotoluolen, PETN, PDX, HMX,

Nitrocellulose oder Mischungen davon erhöht werden kann.

30. Verfahren nach Anspruch 29, dadurch gekennzeichnet, daß die Hilfs-Sensibilisierungsmittel in Anteilen unterhalb von 30 Gew.-% der Endzusammensetzung zugegeben werden.

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31. Neue Sprengstoff-Zusammensetzung in Emulsionsform, erhalten gemäß dem Verfahren nach einem der vorhergehenden Ansprüche

Revendications

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1. Procédé de préparation de nouvelles compositions explosives du type émulsion comprenant une phase combustible continue et une phase aqueuse discontinue qui y est dispersée, ladite phase aqueuse contenant des sels oxydants et une structure macromoléculaire, caractérisé en ce qu'il comprend les étapes suivantes :

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a) Préparer une solution aqueuse comprenant principalement les sels inorganiques oxydants et au moins un monomère organique polymérisable ;

b) Préparer un mélange d'huiles non miscible avec la solution aqueuse et contenant principalement des hydrocarbures combustibles et un ou plusieurs agents émulsionnants ;

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c) Former une émulsion du type "eau dans l'huile" à partir des mélanges préparés aux stades précédents, et

d) Polymériser, après formation de l'émulsion, le monomère ou les monomères contenus dans la phase aqueuse dispersée.

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2. Procédé selon la revendication 1, caractérisé en ce que le monomère ou les monomères incorporés dans la phase aqueuse portent au moins une double liaison sur la molécule.

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3. Procédé selon les revendications 1 et 2, caractérisé en ce que le monomère ou les monomères sont choisis, de préférence, dans le groupe comprenant l'acide acrylique, l'acide méthacrylique, l'acide itaconique, l'acide fumarique, l'acide crotonique, l'anhydride maléique, l'acrylamide, l'aldéhyde acrylique, l'allyl amine, l'alcool allylique, l'acrylonitrile et leurs dérivés.

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4. Procédé selon les revendications 1 et 3, caractérisé en ce que le monomère ou les monomères sont incorporés à une proportion qui varie entre 0,01 et 20% en poids de la composition finale.

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5. Procédé selon la revendication 1, caractérisé en ce que le monomère ou au moins l'un d'entre eux, s'il y en a plus d'un, a plus d'une double liaison.

6. Procédé selon les revendications 1 et 2, caractérisé en ce que le monomère ou au moins l'un d'entre eux, s'il y en a plus d'un, a un groupe fonctionnel réactif.

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7. Procédé selon la revendication 6, caractérisé en ce qu'au moins un monomère comprend des groupes réactifs fonctionnels hydroxyle, amine, acide ou méthoxyméthyle.

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8. Procédé selon les revendications 6 et 7, caractérisé en ce qu'un composé organique capable de réagir avec les groupes fonctionnels du ou des monomères existants et de former des réticulations est ajouté à la composition.

9. Procédé selon la revendication 8, caractérisé en ce que le composé organique qui est ajouté appartient au groupe comprenant des résines telles que les suivantes : mélamine, formaldéhyde, benzoguanamines, diépoxy dianhydrides, phénolique, tétraalkyl titanates, diisocyanates, diméthoxyméthyl urée, méthylolate de triméthylol mélamine, triméthylol mélamine butylée, méthylol benzoguanamine butylée, bisméthoxyméthyl urées, bisméthoxyméthylène urée et résines aminées similaires, polyols et polymères obtenus avec les n-méthylol acrylamides.

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10. Procédé selon la revendication 1, caractérisé en ce que la polymérisation est amorcée par un initiateur chimique.

11. Procédé selon la revendication 10, caractérisé en ce que l'initiateur est ajouté à la solution aqueuse

immédiatement avant que l'émulsion ne se forme de manière qu'aucune polymérisation appréciable des monomères ne se produise au préalable.

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12. Procédé selon la revendication 10, caractérisé en ce que l'initiateur est ajouté à la phase d'huile.
13. Procédé selon les revendications 10 à 12, caractérisé en ce que la polymérisation est amorcée par un initiateur du type rédox.
- 10 14. Procédé selon les revendications 10 à 12, caractérisé en ce que l'initiation chimique est produite par décomposition thermique d'un composé azo, peroxyde, peracétate ou hydroperoxyde.
- 15 15. Procédé selon la revendication 14, caractérisé en ce que la décomposition thermique de l'initiateur est catalysée de manière que la décomposition se produise à des températures inférieures à 80 ° C.
- 16 16. Procédé selon la revendication 1, caractérisé en ce que la polymérisation est amorcée par rayonnement électromagnétique.
17. Procédé selon la revendication 1, caractérisé en ce qu'un agent de transfert peut être ajouté à la solution aqueuse en plus des monomères.
- 20 18. Procédé selon la revendication 1, caractérisé en ce que les sels inorganiques oxydants sont choisis parmi les nitrates, chlorates ou perchlorates d'ammonium et de métaux alcalins ou alcalino-terreux.
- 25 19. Procédé selon les revendications 1 et 18, caractérisé en ce que la proportion des sels inorganiques oxydants utilisés est comprise entre 20 et 90% en poids de la composition finale.
- 30 20. Procédé selon la revendication 1, caractérisé en ce que les hydrocarbures combustibles insolubles dans l'eau peuvent être aliphatiques, alicycliques et/ou aromatiques et peuvent être saturés et/ou insaturés.
- 35 21. Procédé selon la revendication 20, caractérisé en ce que l'hydrocarbure combustible est choisi dans le groupe suivant : fuel-oil, diesel, huiles distillées, kérosène, naphte , huiles et cires de paraffine, cires microcristallines, benzène, toluène, xylènes, matériaux d'asphalte, huiles et cires de polymère, huiles et cires animales, élastomères et huiles et cires végétales comme de l'huile de soja époxydée et leurs mélanges.
- 40 22. Procédé selon les revendications 1, 20 et 21 caractérisé en ce que les hydrocarbures combustibles sont incorporés en quantités comprises entre 2 et 30% en poids de la composition finale.
- 45 23. Procédé selon la revendication 1, caractérisé en ce que les agents émulsionnants incorporés dans la phase d'huile sont choisis dans le groupe formé des sorbitan esters, pentaérythritol esters, glycérides d'acide gras, alcools alcoylés, phénols alcoylés, amines grasses alcoylées, polyoxyalkylène sorbitan esters, glycol et polyoxyalkylène esters, amides d'acide, amides gras, amines quaternaires, alkyl oxazolines, alkényl oxazolines, imidazolines, sulfonates d'alkyle, sulfonates d'alkyl aryle, sulfosuccinates d'alkyle, phosphate d'alkyle, phosphates d'alkylène, esters phosphatés, lécithine, dérivés de lanoline, et copolymères de polyoxyalkylène glycol et de polyacide hydroxystéarique.
- 50 24. Procédé selon les revendications 1 et 23, caractérisé en ce que les agents émulsionnants sont incorporés à des proportions comprises entre 0,2 et 7% de la composition finale.
- 55 25. Procédé selon la revendication 1, caractérisé en ce que la composition est sensibilisée par incorporation d'une phase gazeuse discontinue afin d'obtenir une densité finale comprise entre 0,7 et 1,4 g/cm³.
26. Procédé selon la revendication 25, caractérisé en ce que la phase discontinue peut être incorporée par injection directe d'air, occlusion, addition de générateurs de gaz et addition de sphères creuses comme des microsphères de verre, des microsphères de polymère, de la perlite, des microsphères volcaniques et des cendres volantes.

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27. Procédé selon la revendication 1, caractérisé en ce que des combustibles auxiliaires peuvent être incorporés dans la composition comme de l'aluminium, des alliages aluminium-silice, du ferrosilicium, des carbohydrates, des amines, des amides, du soufre et du carbone.
- 5 28. Procédé selon la revendication 27, caractérisé en ce que les combustibles auxiliaires sont incorporés à des proportions inférieures à 25% en poids de la composition finale.
29. Procédé selon la revendication 1, caractérisé en ce que la sensibilité de la composition peut être accrue par addition d'agents sensibilisants auxiliaires tels que des amines nitrées, du nitrotoluène, PETN, PDX, HMX, de la nitrocellulose ou leurs mélanges.
- 10 30. Procédé selon la revendication 29, caractérisé en ce que les agents sensibilisants auxiliaires sont ajoutés à des proportions inférieures à 30% en poids de la composition finale.
- 15 31. Nouvelle composition explosive en émulsion obtenue selon le procédé de l'une quelconque des revendications précédentes.

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