Abstract:
The present invention relates to the field of explosive emulsions. The present invention more specifically focuses on the use of a composition comprising at least a block copolymer a sorbitan ester and lecithin as emulsifier system for explosive emulsions.
EMULSIFIER SYSTEM FOR EXPLOSIVE EMULSIONS

The present invention relates to the field of explosive emulsions. The present invention more specifically focuses on the use of a composition comprising at least a block copolymer, a sorbitan ester and lecithin as emulsifier system for explosive emulsions.

BACKGROUND OF THE INVENTION

An explosive material is a reactive substance that contains a great amount of potential energy that can produce an explosion if released suddenly. Three kinds of explosives are known:

- A primary explosive is an explosive that is extremely sensitive to stimuli such as impact, friction, heat, static electricity, or electromagnetic radiation. A relatively small amount of energy is required for initiation. For example, Nitroglycerine and silver azide are primary explosives.

- A secondary explosive is less sensitive than a primary explosive and requires substantially more energy to be initiated but is safer to handle and store. A secondary explosive is usually initiated by a smaller quantity of a primary explosive. We can cite TNT as secondary explosive.

- Tertiary explosives, also called blasting agents, are so insensitive to shock that they cannot be reliably detonated by practical quantities of a primary explosive only. They instead require an intermediate explosive booster of secondary explosive. Known tertiary explosives are ammonium nitrate and ammonium perchlorate.

Among the many uses of explosives and blasting agents - ranging from pyrotechnics to munitions or propulsion - the large-scale mining, quarrying and tunneling construction operations are the most important by far.

Ammonium nitrate, $\text{NH}_4\text{NO}_3$, is a white crystalline solid, highly soluble in water and can be shipped and stored and mixed with fuel oil when needed. The industrial production entails the acid-base reaction of ammonia with nitric acid:
HNO₃ + NH₃ → NH₄NO₃

Ammonia is used as anhydrous gas and the nitric acid is concentrated. The reaction is violent owing to its highly exothermic nature. After the solution is formed, typically at about 83% concentration, the excess water is evaporated to an ammonium nitrate (AN) content of 95% to 99.9% concentration (AN melt), depending on grade. The AN melt is then made into prills or small beads in a spray tower, or into granules by spraying and tumbling in a rotating drum. The prills or granules may be further dried, cooled, and then coated with a waxy anti-caking material to prevent caking and enhance flowability. These prills or granules are the typical AN products in commerce. Ammonium nitrate is mainly used in production of fertilizers and explosive materials. The consumption for explosives has grown because of its safety advantage over other products such as dynamite. For the manufacture of civil explosives low density industrial grade AN prills are used (technical grade ammonium nitrate, TGAN, also called explosives-grade ammonium nitrate, EGAN) which are intentionally made very porous to allow for the rapid uptake of liquid fuel oil. They are small-sized (average diameter range between 1.4 to 2.0 mm), low-moisture content, non-setting, porous spheres which are a lower density than agricultural grade AN used for fertilizer (because of the higher density, agricultural grade AN prills will not properly absorb the fuel oil and blasting performance will suffer). The particle density of the TGAN prills is such that, when liquid fuel is properly applied to and mixed with them, the prills absorb the fuel uniformly which enhances reactivity.

As TGAN based explosives, we distinguish:

- Ammonium nitrate fuel oil (ANFO), which is made of about 94% ammonium nitrate and 6% fuel oil. ANFO accounts for more than 70% of the total explosives in mining, quarrying, and tunneling construction or wherever dry conditions exist.

- Emulsion explosives, which are water in oil (W/O)-emulsions, i.e. a supersaturated aqueous solution of AN forming the disperse internal phase surrounded by a continuous external fuel oil phase and stabilized by an emulsifier.
Heavy ANFO emulsions (also called heavy ANFO blends) are mixtures of ANFO and bulk emulsion that most commonly contain 40% emulsion to 75% emulsion.

The choice of the emulsion stabilizer is perhaps the most important task contributing to the success or failure of modern bulk emulsion programs. The emulsifier should have the ability to form a structured bilayer stabilizing densely packed droplets of supersaturated dispersed AN phase in a fuel phase, so that the tendency, in an emulsion at rest, for droplets to coalesce and for crystallization of salts to spread from nucleated droplets to their dormant neighbors is suppressed including the ability to preserve bilayer integrity dynamically when the W/O-emulsion is sheared, e.g. when being pumped. W/O-emulsifiers (HLB-Value 4-6), such as sorbitan monooleate, are surfactants of choice.

Existing emulsification systems used in emulsion explosives are generally based on three different technologies. Traditionally, sorbitan monooleate has been the emulsifier of choice for AN explosive emulsions, as described in US 3,447,978, although other sorbitan esters, such as sorbitan sesquioleate, sorbitan monolaurate, sorbitan monopalmitate, sorbitan mono stearate and sorbitan tristearate. The mono and glycerides of fat-forming fatty acids are also useful as Water-in-Oil type emulsifying agents.

The second system is one based on PIBSA (polyisobutene succinic anhydride). These PIBSA systems are typically produced from the reaction between PIB (polyisobutylene) with maleic anhydride as described in EP 1585773.

The third type of emulsification system generally used for emulsion explosives is based on PIB-lactone chemistry. These systems are typically produced by reacting a PIBSA with a suitable amine such as triethanolamine, diethanolamine or monoethanolamine, as described in US 5,500,062.

Combinations of the above types of emulsification systems are also known for use in emulsion explosives. For example, blends of sorbitan monooleate and either PIBSA or PIB-lactone based emulsifiers or sorbitan monooleate and soybean lecithin (US 5,076,867) are known.
In addition to stability, explosive emulsion compositions are generally evaluated for their explosive properties (e.g., total energy, velocity of detonation, detonation sensitivity, etc.) and also for their shelf life (e.g., flexibility of storage conditions and preservation of explosive properties over time). A particular composition may have ideal explosive properties but very poor shelf life characteristics rendering it virtually unsuitable for common use.

The main issue with sorbitan monooleate is that it is not stable at pH below 5, thus the emulsion containing it generally has a poor shelf life. This is a problem because an explosive emulsion is supposed to be at a pH below 5 for the gasification step. This step is necessary to produce in situ an amount of gas sufficient for the explosivity, in the form of microbubbles, generally through the addition of sodium nitrite to a low pH system.

Explosive emulsion compositions also have to maintain their explosive properties at temperatures below the crystallization temperature of the ammonium nitrate solution once the emulsion has been formed. For that purpose, fudge point depressants are generally added into the emulsion composition. Known fudge point reducers are sodium nitrate, calcium nitrate, monomethylamine nitrate (MMAN) and hexamine nitrate solution (HNS).

Fudge point depressants reduce the crystallization temperature of the emulsion, but they also unfortunately desensitize the emulsion.

The fudge point of such a solution is the temperature at which the nuclei of ammonium nitrate crystals begin to form when a concentrated aqueous solution of ammonium nitrate is cooled. The fudge point of a concentrated aqueous solution of ammonium nitrate is in a general way proportional to the concentration of the solution. (US 3,026,716)

The fudge point is the lowest temperature at which the solid oxidizer is fully soluble in the water.

That's why it remains a need to better control the stability of emulsions (i.e. avoiding demixion coalescence, flocculation and/or creaming) in the field of explosive products, if possible with less surfactant and also to extend the shelf life of explosive emulsion even at pH below 5, or even better below 2, without using fudge point depressants.
There is thus a need for new emulsifiers systems, that would provide an emulsification (droplets size) and/or a stability as good as and/or better than those of current emulsifiers or emulsifier mixtures, advantageously at lower amounts, and that would also allow a better shelf life of the explosive emulsion even at pH below 5, or even better below 2, without desensitizing the explosive emulsion.

**BRIEF SUMMARY OF THE INVENTION**

In this context, the inventors have discovered that the use of a composition comprising a block copolymer selected from the group consisting of:

- (block A)-(block B) di-block copolymers,
- (block A)-(block B)-(block A) tri-block copolymers, and
- (block B)-(block A)-(block B) tri-block copolymers,

wherein block A is a hydrophilic block, block B is a hydrophobic block, and block A or block B comprises units deriving from mono-alpha-ethylenically unsaturated monomers,

a sorbitan ester,

and lecithin,

as emulsifier system for explosive emulsions, allows promoting the stability of explosive emulsion.

It also has the advantage of providing a longer shelf life without the use of fudge point reducers. Indeed, surprisingly, it has been found that the use of a composition according to the invention allows to use a fewer quantity of emulsifier in the emulsion without affecting the stability and even improving the shelf life at low pH.

The present invention is also directed to a method for controlling the stability and/or improving the shelf life at low pH of an explosive water-in-oil emulsion comprising droplets of an aqueous phase dispersed in a hydrophobic phase, said method comprising the step of using in the emulsifier system comprising:

- a block copolymer selected from the group consisting of:
- (block A)-(block B) di-block copolymers,
- (block A)-(block B)-(block A) tri-block copolymers, and
- (block B)-(block A)-(block B) tri-block copolymers,

wherein block A is a hydrophilic block, block B is a hydrophobic block, and block A or block B comprises units deriving from mono-alpha-ethylenically unsaturated monomers,
- a sorbitan ester and
- lecithin.

The use of the emulsifier system comprising the block copolymer in a mixture with a sorbitan ester, in particular sorbitan monooleate, allows improving stability of explosive emulsions.

By "controlling the stability of an emulsion", it is meant that:

- the emulsion remains stable longer at temperatures below the fudge point with the emulsifier system than without it, for the same amount of other surfactants in the emulsion, and/or
- the emulsion with the emulsifier system remains stable longer than an emulsion with the block copolymer and without the sorbitan ester, at the same amount of surfactants, and/or
- the emulsion with the emulsifier system remains stable longer than an emulsion with the sorbitan ester and without the block copolymer, at the same amount of surfactants, and/or
- the emulsion with the emulsifier system remains stable as long as or longer than with another emulsifying system such as PIBSA at the same amount of other surfactants.

By "improving the shelf life at low pH", it is meant that:

- the emulsion remains stable longer at low pH (below 5, preferably between 5 and 1) with the emulsifier system than without it, for the same amount of other surfactants in the emulsion, and/or
- the emulsion with the emulsifier system remains stable longer at low pH (below 5, preferably between 5 and 1) than an emulsion with the block copolymer and without the sorbitan ester, at the same amount of surfactants, and/or
- the emulsion with the emulsifier system remains stable longer at low pH (below 5, preferably between 5 and 1) than an emulsion with the sorbitan ester and without the block copolymer, at the same amount of surfactants, and/or
- at low pH (below 5, preferably between 5 and 1), the emulsion with the emulsifier system remains stable as long as/or longer than with another emulsifying system such as PIBSA at the same amount of other surfactants.

Whereas increasing the stability of an emulsion without adding some more emulsifier (surfactant, polymer) is useful, lowering the amount of emulsifier (surfactant, polymer) without decreasing the stability is also possible according to the invention. The invention is thus cost-effective and environment friendly.

The invention is an alternative solution to the use of known emulsifiers or emulsifying systems, that provides at least the same properties, and to many extends advantages. These advantages include a good stability, a better shelf life at low pH, even at lower quantities.

By using the emulsifier system in an explosive emulsion, it is meant that the emulsifying system is comprised in the emulsion. It may for example have been added to an emulsion, to the compounds comprised in the emulsion, optionally premixed with some of them, prior to emulsifying, or to a dried emulsion or water, prior to mixing said dried emulsion with water to recover an emulsion.

Explosive emulsions may be prepared in a conventional way, mixing the aqueous phase and the hydrophobic phase, the surfactant, and the emulsifier system, optionally providing some
energy for emulsifying. Explosive emulsions may be for example prepared with a homogenizes

In a further aspect, the invention relates to a simple water-in-oil explosive emulsion comprising:

- droplets of an aqueous phase dispersed in a hydrophobic phase,
- an emulsifier system consisting of:
  - a block copolymer selected from the group consisting of:
    - (block A)-(block B) di-block copolymers,
    - (block A)-(block B)-(block A) tri-block copolymers, and
    - (block B)-(block A)-(block B) tri-block copolymers,

wherein block A is a hydrophilic block, block B is a hydrophobic block, and block A or block B comprises units deriving from mono-alpha-ethylenically unsaturated monomers,

- a sorbitan ester and
- lecithin.

**DETAILED DESCRIPTION OF THE INVENTION**

**Definitions**

In the present specification, the molecular weight of a polymer, a copolymer, a moiety, a graft, a side-chain, a core, a branch, a block or a backbone refers to the weight-average molecular weight of said polymer, copolymer, moiety, graft, side-chain, core, branch, block or backbone. The weight-average molecular weight of the polymer or copolymer can be measured by gel permeation chromatography (GPC). In the present specification, the molecular weight of a graft, side-chain, core, branch, block or backbone refers to the molecular weight calculated from the amounts of monomers, polymers, initiators and/or transfer agents used to make the said graft, side-chain, core, branch, block or backbone. The one skilled in the art knows how to calculate these molecular weights. The ratios by weight
between blocks refers to the ratios between the amounts of the compounds used to make said moieties, considering an extensive polymerization.

Typically, the molecular weight $M$ of a block, graft, side-chain, branch, core or $n$, backbone is calculated according to the following formula:

$$M = \sum_{i} M_i \times \frac{n_i}{n_{\text{precursor}}}$$

wherein $M_i$ is the molecular weight of a monomer $i$.

$n_i$ is the number of moles of a monomer $i$.

and $n_{\text{precursor}}$ is the number of moles of a compound the macromolecular chain of the block, graft, side-chain, branch, core or backbone will be linked to.

Said compound may be a transfer agent or a transfer group, a previous block, or a graft or reactive side-chain. If it is a previous block, the number of moles may be considered as the number of moles of a compound the macromolecular chain of said previous block has been linked to, for example a transfer agent or a transfer group. It may be also obtained by a calculation from a measured value of the molecular weight of said previous block. If two blocks are simultaneously grown from a previous block, at both ends, the molecular weight calculated according to the above formula should be divided by two.

In the present specification, a unit deriving from a monomer is understood as a unit that may be directly obtained from the said monomer by polymerizing. Thus, a unit deriving from an ester of acrylic or methacrylic acid does not encompass a unit of formula $-\text{CH-CH(COOH)}-$, $-\text{CH-C(CH}_3\text{(COOH)}-$, $-\text{CH-CH(OH)}-$, $-\text{CH-C(CH}_3\text{(OH)}-$, obtained for example by polymerizing an ester of acrylic or methacrylic acid, or a vinyl acetate, and then hydrolyzing. A unit deriving from acrylic acid or methacrylic acid encompasses for example a unit obtained by polymerizing a monomer (for example an alkyl acrylate or methacrylate) and then reacting (for example hydrolyzing) to obtain units of formula $-\text{CH-CH(COOH)}-$ or $-\text{CH-C(CH}_3\text{(COOH)}-$.
unit deriving from vinyl alcohol encompasses for example a unit obtained by polymerizing a monomer (for example a vinyl ester) and then reacting (for example hydrolyzing) to obtain units of formula \(-\text{CH-CH(OH)}-\) or \(-\text{CH-C(CH}_3\text{)(OH)}-\).

Emulsifier system

Block copolymer

The block copolymer comprises at least two different blocks, block A, and block B. It is selected from the group consisting of (block A)-(block B) di-block copolymers, (block A)-(block B)-(block A) tri-block copolymers, and (block B)-(block A)-(block B) tri-block copolymers. The block copolymer is a linear block copolymer. By linear it is meant that the blocks arrangement is linear. However, a block may be a block having a comb polymer structure, that is comprising repetitive units comprising a polymeric moiety (macromonomers).

A block is usually defined by repeating units it comprises. A block may be defined by naming a polymer, or by naming monomers it is derived from. In the present specification, a unit deriving from a monomer is understood as a unit that may be directly obtained from the said monomer by polymerizing. Thus, a unit deriving from an ester of acrylic or methacrylic acid does not encompass a unit of formula \(-\text{CH-CH(COOH)}-\), \(-\text{CH-C(CH}_3\text{)(COOH)}-\), \(-\text{CH-CH(OH)}-\), \(-\text{CH-C(CH}_3\text{)(OH)}-\) greater than, obtained for example by polymerizing an ester of acrylic or methacrylic acid, or a vinyl acetate, and then hydrolyzing. A unit deriving from acrylic acid or methacrylic acid encompasses for example a unit obtained by polymerizing a monomer (for example an alkyl acrylate or methacrylate) and then reacting (for example hydrolyzing) to obtain units of formula \(-\text{CH-CH(COOH)}-\) or \(-\text{CH-C(CH}_3\text{)(COOH)}-\). A unit deriving from vinyl alcohol encompasses for example a unit obtained by polymerizing a monomer (for example a vinyl ester) and then reacting (for example hydrolyzing) to obtain units of formula \(-\text{CH-CH(OH)}-\) or \(-\text{CH-C(CH}_3\text{)(OH)}-\).
A block may be a copolymer, comprising several kinds of repeating units, deriving from several monomers. Hence, block A and block B are different polymers, deriving from different monomers, but they may comprise some common repeating units (copolymers). Block A and Block B preferably do not comprise more than 50 percent of a common repeating unit (derived from the same monomer).

Block A is hydrophilic and block B is hydrophobic. Hydrophilic or Hydrophobic properties of a block refer to the property said block would have without the other block(s), that is the property of a polymer consisting of the same repeating units than said block, having the same molecular weight. By hydrophilic block, polymer or copolymer, it is meant that the block, polymer or copolymer does not phase separate macroscopically in water at a concentration from 0.01 percent and 10 percent by weight, at a temperature from 20 degrees centigrade to 30°C. By hydrophobic block, polymer or copolymer, it is meant that the block, polymer or copolymer does phase separate macroscopically in the same conditions.

It is further mentioned that the block copolymer may be soluble in water, ethanol, and/or in a hydrophobic compound. In a preferred embodiment, the block copolymer is soluble in water, ethanol or in a mixture of water and ethanol. The block copolymer may be introduced in the emulsion, or in the mixture of the compounds comprised in the emulsion, in a solid form, or in a solution form.

Preferably, block B comprises repeating units deriving from monomers selected from the group consisting of:
- dialkylsiloxane, such as dimethyl siloxane,
- alkylesters of an alpha-ethylenically-unsaturated, preferably mono-alpha-ethylenically-unsaturated, monocarboxylic acid, such as methylacrylate, ethylacrylate, n-propylacrylate, n-butylacrylate, methylmethacrylate, ethylmethacrylate, n-propylmethacrylate, n-butylmethacrylate, and 2-ethyl-hexyl acrylate, 2-ethyl-hexyl methacrylate, isoctyl acrylate, isoctyl methacrylate, lauryl acrylate, lauryl methacrylate,
- vinyl Versatate,
- acrylonitrile,
- vinyl nitriles, comprising from 3 to 12 carbon atoms,
- vinylamine amides, and
- vinylaromatic compounds such as styrene.

Preferred block B are poly(acrylic acid) block, or salts thereof and particularly are selected in the group consisting of: 2-ethyl-hexyl acrylate (A2EH), a mixture of 2-ethyl-hexyl acrylate (A2EH) and behenyl acrylate (80/20), a mixture of 2-ethyl-hexyl acrylate (A2EH) and lauryl acrylate (75/25), or a mixture of 2-ethyl-hexyl acrylate (A2EH) and isoctyl acrylate (75/25); preferably 2-ethyl-hexyl acrylate (A2EH).

Preferably, block A comprises repeating units deriving from monomers selected from the group consisting of:
- ethylene oxide,
- vinyl alcohol,
- vinyl pyrrolidone,
- acrylamide, methacrylamide,
- polyethylene oxide (meth)acrylate (i.e. polyethoxylated (meth)acrylic acid),
- hydroxyalkylesters of alpha-ethylenically-unsaturated, preferably mono-alpha- ethylenically-unsaturated, monocarboxylic acids, such as 2-hydroxyethylacrylate, and hydroxyalkylamides of alpha-ethylenically-unsaturated, preferably mono-alpha- ethylenically-unsaturated, monocarboxylic acids,
- dimethylaminoethyl (meth)acrylate, dimethylaminopropyl (meth)acrylate, ditertiobutylaminoethyl (meth)acrylate, dimethylnomethyl (meth)acrylamide, dimethylaminopropyl (meth)acrylamide;
- ethylenimine, vinylamine, 2-vinylpyridine, 4-vinylpyridine;
- trimethylammonium ethyl (meth)acrylate chloride, trimethylammonium ethyl (meth)acrylate methyl sulphate, dimethylammonium ethyl (meth)acrylate benzyl chloride, 4-benzoylbenzyl
dimethylammonium ethyl acrylate chloride, trimethyl ammonium ethyl (meth)acrylamido (also called 2-(acryloxy)ethyltrimethylammonium, TMAEAMS) chloride, trimethylammonium ethyl (meth)acrylate (also called 2-(acryloxy)ethyltrimethylammonium, TMAEAMS) methyl sulphate, trimethyl ammonium propyl (meth)acrylamido chloride, vinylbenzyl trimethyl ammonium chloride,

- diallyldimethyl ammonium chloride,

- monomers having the following formula:

\[
\begin{align*}
\text{H}_2\text{C} = \text{C} &- \text{Z} \left[ \text{CH}_2 \right]_n \text{N} \left[ \text{A} \right] \text{N}^{+} - \text{B} \left[ \text{N}^{+} \right] \text{R}^{5} - \text{R}^{6} \\
\text{R}^{1} & - \text{X} - \text{R}^{2} \left[ \text{X} - \text{R}^{2} \right] \\
\text{R}^{3} & \left[ \text{R}^{3} \right]_m \\
\end{align*}
\]

wherein

- \( R^1 \) is a hydrogen atom or a methyl or ethyl group;

- \( R^2, R^3, R^4, R^5 \) and \( R^6 \), which are identical or different, are linear or branched \( C_2 \text{–} C_6 \), preferably \( C_2 \text{–} C_4 \), alkyl, hydroxyalkyl or aminoalkyl groups;

- \( m \) is an integer from 1 to 10, for example 1;

- \( n \) is an integer from 1 to 6, preferably 2 to 4;

- \( Z \) represents a -C(0)0- or -C(0)NH- group or an oxygen atom;

- \( A \) represents a \((\text{CH}_2)_p\) group, \( p \) being an integer from 1 to 6, preferably from 2 to 4;

- \( B \) represents a linear or branched \( C_2 \text{–} C_{12} \), advantageously \( C_3 \text{–} C_6 \), polymethylene chain optionally interrupted by one or more heteroatoms or heterogroups, in particular \( O \) or \( NH \), and optionally substituted by one or more hydroxyl or amino groups, preferably hydroxyl groups;

- \( X \), which are identical or different, represent counterions, - alpha-ethylenically-unsaturated, preferably mono-alpha-ethylenically-unsaturated, monomers comprising a phosphate or phosphonate group,
- alpha-ethylenically-unsaturated, preferably mono-alpha-ethylenically-unsaturated, monocarboxylic acids, such as acrylic acid, methacrylic acid
- monoalkylesters of alpha-ethylenically-unsaturated, preferably mono-alpha-ethylenically-unsaturated, dicarboxylic acids,
- monoalkylamides of alpha-ethylenically-unsaturated, preferably mono-alpha-ethylenically-unsaturated, dicarboxylic acids,
- alpha-ethylenically-unsaturated, preferably mono-alpha-ethylenically-unsaturated, compounds comprising a sulphonic acid group, and salts of alpha-ethylenically-unsaturated, preferably mono-alpha-ethylenically-unsaturated, compounds comprising a sulphonic acid group, such as vinyl sulphonic acid, salts of vinyl sulfonic acid, vinylbenzene sulphonyl acid, salts of vinylbenzene sulphonyl acid, alpha-acylamidomethylpropanesulphonic acid, salts of alpha-acylamidomethylpropanesulphonic acid 2-sulphoethyl methacrylate, salts of 2-sulphoethyl methacrylate, acrylamido-2-methylpropanesulphonic acid (AMPS), salts of acrylamido-2-methylpropanesulphonic acid, and styrenesulphonate (SS).

Preferably block A is vinyl pyrrolidone.

While block B is usually a neutral block, block A might be discriminated as regard to its electrical behavior or nature. It means that block A may be a neutral block, or a polyionic block (a polyanionic block, or a polycationic block). It is further mentioned the electrical behavior or nature (neutral, polyanionic or polycationic) may depend on the pH of the emulsion. By polyionic it is meant that the block comprises ionic (anionic or cationic) repetitive units whatever the pH, or that the block comprises repetitive units that may be neutral or ionic (anionic or cationic) depending on the pH of the emulsion (the units are potentially ionic). A unit that may be neutral or ionic (anionic or cationic), depending on the pH of the composition, will be thereafter referred as an ionic unit (anionic or cationic), or as a unit deriving from an ionic monomer (anionic or cationic), whatever it is in a neutral form or in an ionic form (anionic or cationic).
Examples of polycationic blocks are blocks comprising units deriving from cationic monomers such as:

- aminoalkyl (meth)acrylates, aminoalkyl (meth)acrylamides, - monomers, including particularly (meth)acrylates, and (meth)acrylamides derivatives, comprising at least one secondary, tertiary or quaternary amine function, or a heterocyclic group containing a nitrogen atom, vinylamine or ethylenimine;
- diallyldialkyl ammonium salts;
- their mixtures, their salts, and macromonomers deriving from therefrom.

Examples of cationic monomers include:

- dimethylaminoethyl (meth)acrylate, dimethylaminopropyl (meth)acrylate, ditertiobutylaminoethyl (meth)acrylate, dimethylaminomethyl (meth)acrylamide, dimethylaminopropyl (meth)acrylamide;
- ethylenimine, vinylamine, 2-vinylpyridine, 4-vinylpyridine;
- trimethylammonium ethyl (meth)acrylate chloride, trimethylammonium ethyl (meth)acrylate methyl sulphate, dimethylammonium ethyl (meth)acrylate benzyl chloride, 4-benzoylbenzyl dimethylammonium ethyl acrylate chloride, trimethyl ammonium ethyl (meth)acrylamido (also called 2-(acryloxy)ethyltrimethylammonium, TMAEAMS) chloride, trimethylammonium ethyl (meth)acrylate (also called 2-(acryloxy)ethyltrimethylammonium, TMAEAMS) methyl sulphate, trimethyl ammonium propyl (meth)acrylamido chloride, vinylbenzyl trimethyl ammonium chloride,
- diallyldimethyl ammonium chloride,
- monomers having the following formula:

$$\begin{array}{c}
\text{X}^- \\
\text{H}_2\text{C}==\text{C}--\text{Z}--\text{CH}_2\text{n}\text{N}^+\text{A}--\text{N}^+\text{B}--\text{N}^+\text{R}_5 \\
\text{R}_1 \\
\text{R}_2 \\
\text{R}_3 \\
\text{R}_4 \\
\text{R}_5 \\
\text{R}_6
\end{array}$$

wherein
- **R**\textsubscript{1} is a hydrogen atom or a methyl or ethyl group;
- **R**\textsubscript{2}, **R**\textsubscript{3}, **R**\textsubscript{4}, **R**\textsubscript{5} and **R**\textsubscript{6}, which are identical or different, are linear or branched \(\text{C}_{\text{t}}\text{C}_{\text{s}}\), preferably \(\text{C}_{\text{t}}\text{C}_{\text{t}}\), alkyl, hydroxyalkyl or aminoalkyl groups;
- **m** is an integer from 1 to 10, for example 1;
- **n** is an integer from 1 to 6, preferably 2 to 4;
- **Z** represents a \(-\text{C}(0)0-\) or \(-\text{C}(0)\text{NH}-\) group or an oxygen atom;
- **A** represents a \((\text{CH}_2)_p\) group, \(p\) being an integer from 1 to 6, preferably from 2 to 4;
- **B** represents a linear or branched \(\text{C}_2\text{C}_2\), advantageously \(\text{C}_3\text{C}_5\), polymethylene chain optionally interrupted by one or more heteroatoms or heterogroups, in particular O or NH, and optionally substituted by one or more hydroxyl or amino groups, preferably hydroxyl groups;
- **X**, which are identical or different, represent counterions, and their mixtures, and macromonomers deriving therefrom.

Examples of anionic blocks are blocks comprising units deriving from anionic monomers selected from the group consisting of:

- alpha-ethylenically-unsaturated monomers comprising a phosphate or phosphonate group,
- alpha-ethylenically-unsaturated monocarboxylic acids,
- monoalkylesters of alpha-ethylenically-unsaturated dicarboxylic acids,
- monoalkylamides of alpha-ethylenically-unsaturated dicarboxylic acids,
- alpha-ethylenically-unsaturated compounds comprising a sulphonic acid group, and salts of alpha-ethylenically-unsaturated compounds comprising a sulphonic acid group.

Preferred anionic blocks include blocks comprising deriving from at least one anionic monomer selected from the group consisting of:

- acrylic acid, methacrylic acid,
- vinyl sulphonic acid, salts of vinyl sulfonic acid,
- vinylbenzene sulphonic acid, salts of vinylbenzene sulphonic acid,
- alpha-acrylamidomethylpropanesulphonic acid, salts of alpha-acrylamidomethylpropanesulphonic acid.
- 2-sulphoethyl methacrylate, salts of 2-sulphoethyl methacrylate,
- acrylamido-2-methylpropanesulphonic acid (AMPS), salts of acrylamido-2-methylpropanesulphonic acid, and
- styrenesulfonate (SS).

Examples of neutral blocks (block A or block B) are blocks comprising units deriving from at least one monomer selected from the group consisting of:
- alkyl oxides, such as ethylene oxide, and propylene oxide,
- acrylamide, methacrylamide,
- amides of alpha-ethylenically-unsaturated, preferably mono-alpha-ethylenically-unsaturated, monocarboxylic acids,
- esters of an alpha-ethylenically-unsaturated, preferably mono-alpha-ethylenically-unsaturated, monocarboxylic acid, for example alkyl esters such as such as methylacrylate, ethylacrylate, n-propylacrylate, n-butylacrylate, methylethacrylate, ethylethacrylate, n-propylethacrylate, n-butylethacrylate, 2-ethyl-hexyl acrylate, or hydroxyalkyi esters such as 2-hydroxyethylacrylate,
- polyethylene and/or polypropylene oxide (meth)acrylates (i.e. polyethoxylated and/or polypropoxylated (meth)acrylic acid),
- vinyl alcohol,
- vinyl pyrrolidone,
- vinyl acetate, vinyl Versatate,
- vinyl nitriles, preferably comprising from 3 to 12 carbon atoms,
- acrylonitrile,
- vinylamine amides,
- vinyl aromatic compounds, such as styrene, and
- mixtures thereof.

Block A or Block B derives from mono-alpha-ethylenically unsaturated monomers. In a preferred embodiment, both block A and block B derive from mono-alpha-ethylenically
unsaturated monomers. More precisely, it is meant that for block A and/or block B, at least 50 percent of the repeating units are mono-alpha-ethylenically-unsaturated monomers derived units.

The monomers listed above, except alkyl oxides such as ethylene oxide and propylene oxide, are mono-alpha-unsaturated monomers.

In a preferred embodiment, the block copolymer is a di-block copolymer.

The di-block polymer itself is advantageously soluble in the hydrophobic phase described below.

We even prefer low Mws amphiphilic di-block copolymers with a very short water-soluble block (A) and a longer block (B).

In a preferred embodiment, block B is a poly(acrylic acid) block, or a salt thereof. Advantageously, block B is a poly(2-ethyl-hexyl acrylate) block. The poly(acrylic acid) block may be polyanionic or neutral.

In a preferred embodiment, block B is a poly(acrylic acid) block, or a salt thereof and block A is a poly(vinylpyrrolidone) block, and the block copolymer is more preferably a di-block copolymer (p(A2EH)-p(VP) di-block copolymer).

Method of preparation of the block copolymer

There are several methods for making block copolymers. Some methods for making such copolymers are provided below.

It is possible for example to use anionic polymerization with sequential addition of 2 monomers as described for example by Schmolka, J. Am. Oil Chem. Soc. 1977, 54, 110; or alternatively Wilczek-Veraet et al., Macromolecules 1996, 29, 4036. Another method which can be used consists in initiating the polymerization of a block polymer at each of the ends of another block polymer as described for example by Katayose and Kataoka, Proc. Intern. Symp. Control. Rel. Bioact. Materials, 1996, 23, 899.
In the context of the present invention, it is recommended to use living or controlled polymerization as defined by Quirk and Lee (Polymer International 27, 359 (1992)). Indeed, this particular method makes it possible to prepare polymers with a narrow dispersity and in which the length and the composition of the blocks are controlled by the stoichiometry and the degree of conversion. In the context of this type of polymerization, there are more particularly recommended the copolymers which can be obtained by any so-called living or controlled polymerization method such as, for example:

- free-radical polymerization controlled by xanthates according to the teaching of Application WO 98/58974 and Patent US 6,153,705,
- free-radical polymerization controlled by dithioesters according to the teaching of Application WO 98/01478,
- free-radical polymerization controlled by dithioesters according to the teaching of Application WO 99/351 78,
- free-radical polymerization controlled by dithiocarbamates according to the teaching of Application WO 99/35177,
- free-polymerization using nitroxide precursors according to the teaching of Application WO 99/03894,
- free-radical polymerization controlled by dithiocarbamates according to the teaching of Application WO 99/31 144,
- free-radical polymerization controlled by dithiocarbazates according to the teaching of Application WO 02/26836,
- free-radical polymerization controlled by halogenated Xanthates according to the teaching of Application WO 00/75207 and US Application 09/980,387,
- free-radical polymerization controlled by dithiophosphoroesters according to the teaching of Application WO 02/10223,
- free-radical polymerization controlled by a transfer agent in the presence of a disulphur compound according to the teaching of Application WO 02/22688,
- atom transfer radical polymerization (ATRP) according to the teaching of Application WO
96/30421, - free-radical polymerization controlled by initiators according to the teaching of
- free-radical polymerization controlled by degenerative transfer of iodine according to the
teaching of Tatemoto et al., Jap. 50, 127, 991 (1975), Daikin Kogyo Co Ltd Japan, and
Matyjaszewski et al., Macromolecules, 28, 2093 (1995),
- group transfer polymerization according to the teaching of Webster O.W., "Group Transfer
7, edited by H.F. Mark, N.M. Bikales, C.G. Overberger and G. Menges, Wiley Interscience,
New York, 1987,
- radical polymerization controlled by tetraphenylethane derivatives (D. Braun et al.,
Macromol. Symp., 111, 63 (1996)),
- radical polymerization controlled by organocobalt complexes (Wayland et al., J. Am. Chem.
Soc, 1 16, 7973 (1994)).

Preferred processes are sequenced living free-radical polymerization processes, involving
the use of a transfer agent. Preferred transfer agents are agents comprising a group of
formula -S-C(S)-Y-, -S-C(S)-S-, or -S-P(S)-Y-, or -S-P(S)-S-, wherein Y is an atom different
from sulfur, such as an oxygen atom, a nitrogen atom, and a carbon atom. They include
dithioester groups, thioether-thione groups, dithiocarbamate groups, dithiphosphorosters,
dithiocarbazates, and xanthate groups. Examples of groups comprised in preferred transfer
agents include groups of formula -S-C(S)-NR-NR'\_2, -S- C(S)-NR-N=CR'\_2, -S-C(S)-0-R, -S-
C(S)-CR=CR'\_2, and -S-C(S)-X, wherein R and R' are or identical or different hydrogen atoms,
or organic groups such as hydrocarbyl groups, optionally substituted, optionally comprising
heteroatoms, and X is an halogen atom. A preferred polymerization process is a living radical
polymerization using xanthates.
Copolymers obtained by a living or controlled free-radical polymerization process may comprise at least one transfer agent group at an end of the polymer chain. In particular embodiment such a group is removed or deactivated.

A "living" or "controlled" radical polymerization process used to make the block copolymers comprises the steps of: a) reacting a mono-alpha-ethylenically-unsaturated monomer, at least a free radicals source compound, and a transfer agent, to obtain a first block, the transfer agent being bounded to said first block, b1) reacting the first block, another mono-alpha-ethylenically-unsaturated monomer, and, optionally, at least a radical source compound, to obtain a di-block copolymer, b2) optionally, repeating n times (n being equal to or greater than 0) step b1) to obtain a (n-2)-block copolymer, and then c) optionally, reacting the transfer agent with means to render it inactive.

For example, a "living" or "controlled" radical polymerization process used to make the di-block copolymers comprises the steps of: a) reacting a mono-alpha-ethylenically-unsaturated monomer, at least a free radicals source compound, and a transfer agent, to obtain a first block, the transfer agent being bounded to said first block, b) reacting the first block, another mono-alpha-ethylenically-unsaturated monomer, and, optionally, at least a radical source compound, to obtain a di-block copolymer, and then c) optionally, reacting the transfer agent with means to render it inactive.

During step a), a first block of the polymer is synthesized. During step b), b1), or b2), another block of the polymer is synthesized.

Examples of transfer agents are transfer agents of the following formula (I):

\[
\begin{align*}
\text{C - S - R} \\
\text{w}
\end{align*}
\]

(1)

wherein:
R represents an $R^0_-$, $R^2R^2_-'N$- or $R^3_-$ group, $R^2$ and $R^2'$, which are identical or different, representing (i) an alkyl, acyl, aryl, alkene or alkyne group or (ii) an optionally aromatic, saturated or unsaturated carbonaceous ring or (iii) a saturated or unsaturated heterocycle, it being possible for these groups and rings (i), (ii) and (iii) to be substituted, $R^3$ representing H, Cl, an alkyl, aryl, alkene or alkyne group, an optionally substituted, saturated or unsaturated (hetero)cycle, an alkylthio, alkoxy carbonyl, aryloxy carbonyl, carboxyl, acyloxy, carbamoyl, cyano, dialkyi- or diarylphosphonato, or dialkyi- or diarylphosphinato group, or a polymer chain, 

$R^1$ represents (i) an optionally substituted alkyl, acyl, aryl, alkene or alkyne group or (ii) a carbonaceous ring which is saturated or unsaturated and which is optionally substituted or aromatic or (iii) an optionally substituted, saturated or unsaturated heterocycle or a polymer chain, and

The $R^1$, $R^2$, $R^2'$ and $R^3$ groups can be substituted by substituted phenyl or alkyl groups, substituted aromatic groups or the following groups: oxo, alkoxy carbonyl or aryloxy carbonyl (-COOR), carboxyl (-COOH), acyloxy (-O$_2$CR), carbamoyl (-CONR$_2$), cyano (-CN), alkylcarbonyl, alkyllaryl carbonyl, arylcarbonyl, arylalkyl carbonyl, isocyanato, phthalimido, maleimido, succinimido, amidino, guanidino, hydroxyl (-OH), amino (-NR$_2$), halogen, allyl, epoxy, alkoxy (-OR), S-alkyl, S-aryl or silyl, groups exhibiting a hydrophilic or ionic nature, such as alkaline salts of carboxylic acids or alkaline salts of sulphonic acid, poly(alkylene oxide) (PEO, PPO) chains, or cationic substituents (quaternary ammonium salts), R representing an alkyl or aryl group.

Preferably, the transfer agent of formula (I) is a dithiocarbonate chosen from the compounds of following formulae (IA), (IB) and (IC):
\[ S \]
\[ w \]
\[ C - S - R^1 \quad (IA) \]
\[ / \]
\[ O-R^2 \]
\[ R^2_\ldots \ldots (O - C - S - R^1)_p \quad (IB) \]
\[ II \]
\[ S \]
\[ R^{i\prime}_\ldots \ldots (S - C - O - R^2)_p \quad (IC) \]
\[ II \]
\[ S \]

wherein:

- \( R^2 \) and \( R^{2\prime} \) represent (i) an alkyl, acyl, aryl, alkene or alkyne group or (ii) an optionally aromatic, saturated or unsaturated carbonaceous ring or (iii) a saturated or unsaturated heterocycle, it being possible for these groups and rings (i), (ii) and (iii) to be substituted,

- \( R^1 \) and \( R^{1\prime} \) represent (i) an optionally substituted alkyl, acyl, aryl, alkene or alkyne group or (ii) a carbonaceous ring which is saturated or unsaturated and which is optionally substituted or aromatic or (iii) an optionally substituted, saturated or unsaturated heterocycle or a polymer chain, and

- \( p \) is between 2 and 10.

Other examples of transfer agents are transfer agents of the following formulae (II) and (III):

![Formula II](attachment:formula_ii.png)

(II)

![Formula III](attachment:formula_iii.png)

(III)
wherein

R\(^1\) is an organic group, for example a group \(R^1\) as defined above for transfer agents of formulae (I), (IA), (IB), and (IC),

\(R^2, R^3, R^4, R^7, \text{ and } R^8\) which are identical or different are hydrogen atoms or organic groups, optionally forming rings. Examples of \(R^2, R^3, R^4, R^7, \text{ and } R^8\) organic groups include hydrocarbyls, substituted hydrocarbyls, heteroatom-containing hydrocarbyls, and substituted heteroatom-containing hydrocarbyls.

The mono-alpha-ethylenically-unsaturated monomers and their proportions are chosen in order to obtain the desire properties for the block(s). According to this process, if all the successive polymerizations are carried out in the same reactor, it is generally preferable for all the monomers used during one stage to have been consumed before the polymerization of the following stage begins, therefore before the new monomers are introduced. However, it may happen that monomers of the preceding stage are still present in the reactor during the polymerization of the following block. In this case, these monomers generally do not represent more than 5 mole percent of all the monomers. The polymerization can be carried out in an aqueous and/or organic solvent medium. The polymerization can also be carried out in a substantially neat melted form (bulk polymerization), or according to a latex type process in an aqueous medium.

**Properties of the block copolymer**

The weight-average molecular weight of the block copolymer is preferably comprised between 1000 and 100000 g/mol. It is more preferably comprised between 2000 and 20000 g/mol. Within these ranges, the weight ratio of each block may vary. It is however preferred that each block has a molecular weight above 500 g/mol, and preferably above 1000 g/mol.
Within these ranges, the weight ratio between block A and block B (ratio block B / block A) is preferably of from 40/60 to 95/5, and more preferably of from 50/50 to 95/5.

For the preferred di-block copolymer according to the invention, and in particular for p(A2EH)-p(VP) di-block copolymer, p(A2EH) has a molecular weight below 40000 g/mol, preferably below 20000 g/mol and even more preferably between 1000 and 20000 g/mol.

For the preferred di-block copolymer according to the invention, and in particular for p(A2EH)-p(VP) di-block copolymer, p(VP) has a molecular weight below 5000 g/mol, preferably below 3000 g/mol and even more preferably between 1000 and 3000 g/mol.

Sorbitan ester

Quantity

A Sorbitan ester is also present in the emulsifier system, the weight ratio between the amount of the block copolymer and the amount of the sorbitan ester may vary.

This is usually a matter of cost, performance and environment impact. Thus, the weight ratio between the amount of the block copolymer and the amount of the sorbitan ester together with the block copolymer is typically of from 1 percent to 50 percent, being preferably from 5 percent to 20 percent, for example of from about 10 percent.

Nature

The sorbitan ester is advantageously selected in the group consisting of

- sorbitan monolaurate,
- sorbitan monooleate,
- sorbitan tristearate,
- sorbitan tristearate, polyoxyethylene sorbitol hexastearate, lactylated mono- and diglycerides of fat-forming fatty acids, ethylene glycol fatty acid ester, mono- and diglycerides of fat-forming fatty acids, mono- and di glycerides from the glycerolysis of edible fats, propylene glycol fatty acid ester, propylene glycol monostearate, ethylene
glycol fatty acid ester, sorbitan sesquioleate, polyoxyethylene sorbitol 4.5 oleate, glycerol monostearate, sorbitan partial fatty esters, high-molecular-weight fatty amine blend.

Sorbitan monooleate is particularly preferred because it has the optimum hydrophilic-lipophilic balance (HLB) for making W/O emulsions (water/oil), and as it is nonionic, it is not affected by the hardness of water. In addition, sorbitan monooleate usually needs to be introduced in a lower quantity than the others emulsifiers, for the same stability.

Lecithin and in particular from soybean is added in the composition acting as emulsifier system. It is particularly advantageous to have a SMO:Lecithin weight ratio between 50:50 and 90:10.

The presence of lecithin in combination with SMO in particular at this ratio, together with the diblock copolymer, provides the best results in terms of stability of the final explosive emulsion.

In a particularly preferred embodiment according to the invention, the composition acting as emulsifier system is a blend comprising:

- poly(2-ethyl-hexyl acrylate)-poly(vinylpyrrolidone) diblock copolymer (p(A2EH)-p(VP) di-block copolymer, p(A2EH) having a molecular weight below 40000 g/mol, preferably below 20000 g/mol and even more preferably between 1000 and 20000 g/mol and p(VP) has a molecular weight below 5000 g/mol, preferably below 3000 g/mol and even more preferably between 1000 and 3000 g/mol, also known under the name Rhodibloc RS sold by Rhodia,
- sorbitan monooleate (SMO), and
- lecithin (L)

Preferably, in the above preferred emulsifier system, the blend comprises:

- from 5 to 40% by weight of diblock copolymer,
from 40 to 70% by weight of sorbitan monooleate and,
- from 20 to 45% by weight of lecithin.

This blend, at this ratio, provides the best results in terms of stability of the final explosive emulsion.

Explosive emulsion
General composition of an emulsion explosive contains an aqueous phase, a hydrophobic phase, the emulsifier system according to the invention and optional additional ingredients such as gassing agents, sensitizers and further emulsifier.

Aqueous phase
The aqueous phase is based on water, and may comprise some further ingredients, such as active agents.
In a particular embodiment, the hydrophilic phase is a hydrophilic phase of an explosive emulsion. Such a phase comprises water, an oxygen-donating compound and optionally other water-soluble additives. Examples of oxygen-donating compounds include ammonium nitrate. In such a hydrophilic phase, the water content usually varies in the range 1-30 weight percent, preferably in the range 10-20 weight percent.
Active agents that may be comprised in aqueous phase include organic or inorganic compounds, as long as they are water-soluble or water-dispersible. They may be solubilized in a hydrophilic solvent that is miscible with water, such as methanol, ethanol, propylene glycol, glycerol. Actives may also be in a solid form, dispersed in the aqueous phase.

Hydrophobic phase
The hydrophobic phase is not miscible with the aqueous phase. It is often referred to an oily phase. By "not miscible", it is meant that the ingredient or mixture of ingredients of the hydrophobic phase is not more than 10 weight percent soluble in water, at a temperature
comprised between 20 degrees centigrade and the emulsion-preparation temperature or
emulsion-use temperature.
In a particular embodiment, the hydrophobic phase is selected in the group consisting of fuel
oil, such as a fraction obtained from petroleum distillation, diesel, kerosene, methyl esters or
biodiesel, waxes (e.g. microcrystalline wax, paraffin wax and slack wax). Preferably, the fuel
oil is selected from the group comprising kerosene, diesel oil, lubricating oils, mineral oil and
paraffin, more preferably diesel oil and refined mineral oil. Alternatively, the fuel oil may be
selected from non-petroleum based oils and waxes, for example the fuel oil may be selected
from the group comprising glyceride oils, vegetable oils, vegetable waxes, ester oils and
silicone oils, and mixtures thereof.

Optional additional Ingredients
Gassing Agents are small hollow microspheres of glass or resinous materials, such as
phenol-formaldehyde, urea-formaldehyde, Expancel®, and copolymers of vinylidene chloride
and acrylonitrile. Suitable porous materials include expanded minerals such as perlite, and
expanded polymers such as polystyrene.
Chemical gassing systems are preferred, such as
- Sodium nitrite/thiourea
- Sodium nitrite/sulfamic acid
- Sodium nitrite/sodium thiocyanate
- Hydrazine hydrate/sodium dichromate
- Sodium bicarbonate/acetic acid.
Sodium nitrite / sulfamic acid is particularly preferred.

A sensitizer can be employed to provide a critical diameter, that is the smallest charge
diameter in which the explosive will detonate reliably at the temperature given. Sensitizers
may be selected from the group consisting of particulate atomized aluminum or other metallic
particles. Examples of other particulate molecular explosives are pentaerythritol tetranitrate
(PETN), cyclotrimethylene trinitramine (RDX), trinitrotoluene (TNT), cyclotetramethylene tetranitramine (HMX), and nitrocellulose.

The emulsion optionally comprises an emulsifier different from the emulsifier system. The emulsifier may be a surfactant or a polymer. It is mentioned that the emulsion may comprise no optional emulsifier, less than 4 percent by weight (based on the total weight of the emulsion), or more than (or equal to) 4 percent by weight. As the emulsifier system has also emulsifying properties, the emulsifier different from it may also be referred to as a co-emulsifier. A large variety of emulsifiers or mixture of emulsifiers may be used. That usually depends on the phases and on what the emulsion is used for.

Preferred surfactants, as emulsifiers different from the emulsifier system, have a HLB of lower than or equal to 10, and may be selected from the group consisting of ethoxylated alcohols, ethoxylated alkyl phenols, and ethoxylated castor oils. Examples of such surfactants include:

- diethylene glycol fatty acid ester polyoxyethylene stearyl ether, polyoxyethylene oleyl ether, polyoxyethylene sorbitol beeswax derivative, polyoxyethylene cetyl ether, diethylene glycol monolaurate, sorbitan monopalmitate, sorbitan monoooleate polyoxyethylene ester mixed fatty and resin acids blend,
- polyoxypropylene mannitol dioleate, polyoxyethylene sorbitol lanolin derivative,
- polyoxyethylene sorbitol esters of mixed fatty and resin acids,
- polyoxyethylene fatty acid,
- polyoxyethylene sorbitol oleate,
- polyoxyethylene sorbitan monostearate,
- polyoxyethylene sorbitol tallow esters,
- polyoxyethylene sorbitol tall oil, polyoxyethylene lauryl ether,
- polyoxyethylene sorbitan monooleate.
Quantities

The amount of aqueous phase is usually of from 10 to 99 weight percent, relative to the weight of the hydrophobic phase, emulsifier system, and aqueous phase. It is preferably of from 50 to 98 weight percent, and even more preferably 90% to 96%.

The amount of emulsifier system is usually of from 0.1 to 10 weight percent of the amount of aqueous phase. It is preferably of from 0.1 to 5 weight percent.

Process of preparation of the explosive emulsion

The emulsion may be prepared by any process known by the one skilled in the art. Usually a process for preparing the emulsion comprises the steps of introducing in a recipient the compounds the emulsion comprises (water, hydrophobic phase compound, emulsifier system), and mixing with adding energy in the system (vigorous mixing), for example with a homogenizer. In an embodiment the emulsifier system is added to the hydrophobic phase prior to mixing with adding energy. The emulsifier system may be introduced in several forms: solid, solution, premix with another compound... In another embodiment the emulsifier system is added into an emulsion which has already been prepared.

Specific language is used in the description so as to facilitate the understanding of the principle of the invention. It should, however, be understood that no limitation of the scope of the invention is envisaged by the use of this specific language. Modifications, improvements and perfections may especially be envisaged by a person skilled in the technical field concerned, on the basis of his own general knowledge.

The term "and/or" includes the meanings "and", "or" and also all the other possible combinations of elements connected to this term.
Other details or advantages of the invention will emerge more clearly in the light of the examples given below, purely for indicative purposes.

**BRIEF DESCRIPTION OF THE DRAWINGS**

Figure 1 - Gasification curve (density=f(time)) for examples of the example part below.

**EXAMPLES**

**Ingredients:**
- Block copolymer = a di-block copolymer PA2EH-b-PVP (A2EH meaning 2-ethylhexyl acrylate, VP meaning vinyl pyrrolidone), the weight-average molecular weight of the PA2EH block being 13500 g/mol, and the weight-average molecular weight of the PVP block being 2300 g/mol, commercially available Rhodibloc RS by Solvay.
- Sorbitan monooleate sold under the trademark Dhaytan® S80 by Solvay.
- Hydrophobic phase: fuel oil = diesel (Oleo Diesel S500) from Petrobras Distribuidora S.A.
- Aqueous phase: water, ammonium nitrate (Ultraprill Egan from Vale fertilizantes S.A.) and sulfamic acid from Casa Americana de Artigos para Laboratorio Ltda.
- PIBSA (polyisobutene succinic anhydride)
- Lecithin from Granol Ind. E Com. E exportagao S.A.
- Sodium nitrite from Labsynth Produtos para Laboratorio Ltda.

**Emulsification procedure:**
- Heating of the oxidizing solution (the mixture of water and ammonium nitrate) at 80°C with subsequent vacuum filtration and adjust the dilution volume;
- Heating of the emulsifier mixture to 80°C;
- Pre-emulsion using centrifugal propeller shaft agitator, addition of oxidant solution (pH 1.7) to emulsifier with vigorous stirring;
- Refining of the pre-emulsion for 10 minutes with vigorous stirring in a planetary mixer.
Equipments:
- Pre-emulsion: Fisatom stirrer, model 715, rotation 500 rpm, a centrifugal propeller shaft.
- For Refining of the Emulsion: Planetary Mixer Arno Deluxe, 8 speed.
- Details of crystals: Microscope Metallographic Bioptika B500 lens LM Plan 100x0,80, transmitted light.

1. Thermal Cycling Stability:

Samples

Table 1 - Samples for thermal cycling stability tests

<table>
<thead>
<tr>
<th>Trial #</th>
<th>Total weight (g)</th>
<th>Em. (g)</th>
<th>Diesel (g)</th>
<th>Amm. Nitrate (g)</th>
<th>Water (g)</th>
<th>PIBSA (g) (1)</th>
<th>SMO (g)</th>
<th>Lecithin (g)</th>
<th>Rhodi bloc RS (g) (2)</th>
<th>SA (g)</th>
<th>Em. % (3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>800</td>
<td>14.08</td>
<td>35.84</td>
<td>588.8</td>
<td>147.2</td>
<td>28.16</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1.17</td>
<td>1.76</td>
</tr>
<tr>
<td>C2</td>
<td>800</td>
<td>14.08</td>
<td>49.92</td>
<td>588.8</td>
<td>147.2</td>
<td>0</td>
<td>14.08</td>
<td>0</td>
<td>0</td>
<td>1.17</td>
<td>1.76</td>
</tr>
<tr>
<td>C3</td>
<td>800</td>
<td>14.08</td>
<td>49.92</td>
<td>588.8</td>
<td>147.2</td>
<td>0</td>
<td>8.59</td>
<td>5.49</td>
<td>0</td>
<td>1.17</td>
<td>1.76</td>
</tr>
<tr>
<td>Inv1</td>
<td>800</td>
<td>14.08</td>
<td>47.81</td>
<td>588.8</td>
<td>147.2</td>
<td>0</td>
<td>8.59</td>
<td>3.38</td>
<td>4.22</td>
<td>1.17</td>
<td>1.76</td>
</tr>
</tbody>
</table>

Em. = Emulsifier
Amm. Nitrate = Ammonium nitrate
SA = Sulfamic acid
(1) 50% weight Mineral oil
(2) 50% weight Mineral oil
(3) Calculated over the total mass

In the following stability tests, the emulsion explosive compositions C1, C2, C3 and Inv1 as described in table 1 above were used. Each emulsion was subjected to thermal cycling stability test. This test is described below.

Tests
- A sample of 100ml of the emulsion was placed in a sealed plastic container. The container was placed in a freezer set at a constant temperature of -10°C and left for a period of 24 hours (1st cycle). After 24 hours, the container was removed from the freezer and allowed to equilibrate to room temperature and left for a period of 24 hours (2nd
cycle). Then the container was placed in an oven set at a constant temperature of 70°C and left for a period of 24 hours (3rd cycle). The container was then removed from the oven and allowed to equilibrate to room temperature.

- Each sample was then evaluated using microscopy. The sequence of 3 cycles was repeated 2 times with 2 batches of samples: first batch was evaluated after each cycle (1st, 2nd and 3rd) and second batch was evaluated only at the end of the sequence (after 3rd cycle).

Results

The results of the thermal cycling tests are shown in Table 2 below.

<table>
<thead>
<tr>
<th>Trial #</th>
<th>Emulsifier</th>
<th>1st cycle (a)</th>
<th>2nd cycle (a)</th>
<th>3rd cycle (a)</th>
<th>After 3 cycle (b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>PIBSA</td>
<td>OK</td>
<td>OK</td>
<td>C</td>
<td>C</td>
</tr>
<tr>
<td>C2</td>
<td>SMO</td>
<td>C</td>
<td>C</td>
<td>C</td>
<td>C</td>
</tr>
<tr>
<td>C3</td>
<td>SMO+LECITHIN</td>
<td>OK</td>
<td>C</td>
<td>C</td>
<td>C</td>
</tr>
<tr>
<td>Inv1</td>
<td>SMO+LECITHIN + Rhodibloc RS 15%</td>
<td>OK</td>
<td>OK</td>
<td>C</td>
<td>OK</td>
</tr>
</tbody>
</table>

- C Occurrence of crystallization
- OK without crystallization
- (a) Readings after each step
- (b) Readings after the last step of the 3rd cycle

The presence of crystals was observed using a microscope with 100X magnification.

Conclusion

The sample according to the invention showed a better stability than the comparative examples as no crystallization was observed after the 3rd cycle. The presence of crystals at 3rd step when reading after each step is probably due to the contamination caused by the previous readings.
2. Gasification Stability:

Samples:

Table 3 - Samples for gasification tests

<table>
<thead>
<tr>
<th>Samples</th>
<th>NH3NO3 (g)</th>
<th>Water (g)</th>
<th>Sulfamic acid (g)</th>
<th>SMO (g)</th>
<th>Lecithin (g)</th>
<th>Diesel (g)</th>
<th>Rhodibloc RS (g)</th>
<th>PIBSA (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inv.2</td>
<td>612.31</td>
<td>134.41</td>
<td>1.17</td>
<td>5.08</td>
<td>2</td>
<td>43.71</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td>C4</td>
<td>612.31</td>
<td>134.41</td>
<td>1.17</td>
<td>0</td>
<td>0</td>
<td>36.64</td>
<td>0</td>
<td>16.64</td>
</tr>
<tr>
<td>C5</td>
<td>612.31</td>
<td>134.41</td>
<td>1.17</td>
<td>5.08</td>
<td>3.24</td>
<td>44.96</td>
<td>0</td>
<td></td>
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Tests

- Addition of 0.2% solution of Sodium Nitrite at 20% concentration, to observe the variation in density of the gassed emulsion compared with PIBSA additive emulsion.

- The pH of all emulsions in the gasification process is 1.7.

- Made readings at initial time (time =0), and after 5, 10 and 15 minutes.

- Readings made with the same volume, and variation on the mass.

- After 15 minutes the upper limit for density is 1.15 g/ml.

Results

Fig.1 shows the gasification curve of the tests.

Conclusion

Inv2 presents the highest stability to heat compared to tests using PIBSA (C4) and SMO + Lecithin (C5).

We observed that the PIBSA behaves differently compared to other tests. The gasification rate of the SMO alone and SMO + Lecithin + Rhodibloc is greater than that of the PIBSA.
CLAIMS

1. Use of a composition comprising
   • a block copolymer selected from the group consisting of:
     - (block A)-(block B) di-block copolymers,
     - (block A)-(block B)-(block A) tri-block copolymers, and
     - (block B)-(block A)-(block B) tri-block copolymers,

   wherein block A is a hydrophilic block, block B is a hydrophobic block, and block A or
   block B comprises units deriving from mono-alpha-ethylenically unsaturated monomers,
   • a sorbitan ester, and
   • lecithin

   as emulsifier system for explosive emulsions.

2. Use according to claim 1, wherein the block copolymer is a (block A)-(block B) di-block
   copolymer.

3. Use according to claim 1 or 2, wherein block B comprises repeating units deriving from
   monomers selected from the group consisting of:
   - dialkylsiloxane, such as dimethyl siloxane,
   - alkylesters of an alpha-ethylenically-unsaturated, preferably mono-alpha-ethylenically-
     unsaturated, monocarboxylic acid, such as methylacrylate, ethylacrylate, n-
     propylacrylate, n-butylacrylate, methylmethacrylate, ethylmethacrylate, n-
     propylmethacrylate, n-butylmethacrylate, and 2-ethyl-hexyl acrylate, 2-ethyl-hexyl
     methacrylate, isoctyl acrylate, isoctyl methacrylate, lauryl acrylate, lauryl
     methacrylate,
   - vinyl Versatate,
   - acrylonitrile,
   - vinyl nitriles, comprising from 3 to 12 carbon atoms,
- vinylamine amides, and
- vinylaromatic compounds such as styrene.

4. Use according to anyone of claims 1 to 3, wherein block B is poly(acrylic acid) block, or salts thereof and particularly are selected in the group consisting of: 2-ethyl-hexyl acrylate (A2EH), a mixture of 2-ethyl-hexyl acrylate (A2EH) and behenyl acrylate (80/20), a mixture of 2-ethyl-hexyl acrylate (A2EH) and lauryl acrylate (75/25), or a mixture of 2-ethyl-hexyl acrylate (A2EH) and iso-octyl acrylate (75/25); preferably 2-ethyl-hexyl acrylate (A2EH).

5. Use according to anyone of claims 1 to 4, wherein block A comprises repeating units deriving from monomers selected from the group consisting of:
- ethylene oxide,
- vinyl alcohol,
- vinyl pyrrolidone,
- acrylamide, methacrylamide,
- polyethylene oxide (meth)acrylate (i.e. polyethoxylated (meth)acrylic acid),
- hydroxyalkylesters of alpha-ethylenically-unsaturated, preferably mono-alpha- ethylenically-unsaturated, monocarboxylic acids, such as 2-hydroxyethylacrylate, and hydroxyalkylamides of alpha-ethylenically-unsaturated, preferably mono-alpha- ethylenically-unsaturated, monocarboxylic acids,
- dimethylaminoethyl (meth)acrylate, dimethylaminopropyl (meth)acrylate, ditertiobutylaminoethyl (meth)acrylate, dimethylaminomethyl (meth)acrylamide, dimethylaminopropyl (meth)acrylamide;
- ethylenimine, vinylamine, 2-vinylpyridine, 4- vinylpyridine;
- trimethylammonium ethyl (meth)acrylate chloride, trimethylammonium ethyl (meth)acrylate methyl sulphate, dimethylammonium ethyl (meth)acrylate benzyl chloride, 4-benzoylbenzyl dimethylammonium ethyl acrylate chloride, trimethyl ammonium ethyl (meth)acrylamido (also called 2-(acryloxy)ethyltrimethylammonium, TMAEAMS) chloride, trimethylammonium ethyl
(meth)acrylate (also called 2- (acryloxy)ethyltrimethylammonium, TMAEAMS) methyl sulphate, trimethyl ammonium propyl, (meth)acrylamido chloride, vinylbenzyl trimethyl ammonium chloride,
- diallyldimethyl ammonium chloride,
- monomers having the following formula:

\[
\begin{align*}
\text{H}_2\text{C} &= \text{C} - \text{Z} - \left[ \text{CH}_2 \right]_n \text{N}^+ \text{A} \text{N}^+ \text{B} \text{N}^+ \text{R}_5 \\
\text{R}_1 & \quad \text{X}^- & \quad \text{R}_2 & \quad \text{X}^- & \quad \text{R}_4 & \quad \text{X}^-
\end{align*}
\]

wherein
- \( R_1 \) is a hydrogen atom or a methyl or ethyl group;
- \( R_2, R_3, R_4, R_5 \), which are identical or different, are linear or branched \( \text{C}_6 \text{C}_6 \), preferably \( \text{C}_2-\text{C}_4 \), alkyl, hydroxyalkyl or aminoalkyl groups;
- \( m \) is an integer from 1 to 10, for example 1;
- \( n \) is an integer from 1 to 6, preferably 2 to 4;
- \( \text{Z} \) represents a \(-\text{C}(0)\text{O}-\) or \(-\text{C}(0)\text{NH}-\) group or an oxygen atom;
- \( \text{A} \) represents a \((\text{CH}_2)_p\) group, \( p \) being an integer from 1 to 6, preferably from 2 to 4;
- \( \text{B} \) represents a linear or branched \( \text{C}_2-\text{C}_{12} \), advantageously \( \text{C}_3-\text{C}_6 \), polymethylene chain optionally interrupted by one or more heteroatoms or heterogroups, in particular \( \text{O} \) or \( \text{NH} \), and optionally substituted by one or more hydroxyl or amino groups, preferably hydroxyl groups;
- \( X \), which are identical or different, represent counterions, - alpha-ethylenically-unsaturated,
- preferably mono-alpha-ethylenically-unsaturated, monomers comprising a phosphate or phosphonate group,
- alpha-ethylenically-unsaturated, preferably mono-alpha-ethylenically-unsaturated, monocarboxylic acids, such as acrylic acid, methacrylic acid
- monoalkylesters of alpha-ethylenically-unsaturated, preferably mono-alpha-ethylenically-unsaturated, dicarboxylic acids,
- monoalkylamides of alpha-ethylenically-unsaturated, preferably mono-alpha-ethylenically-unsaturated, dicarboxylic acids,
- alpha-ethylenically-unsaturated, preferably mono-alpha-ethylenically-unsaturated, compounds comprising a sulphonic acid group, and salts of alpha-ethylenically-unsaturated, preferably mono-alpha-ethylenically-unsaturated, compounds comprising a sulphonic acid group, such as vinyl sulphonic acid, salts of vinyl sulfonic acid, vinylbenzene sulphonic acid, salts of vinylbenzene sulphonic acid, alpha-acrylamidomethylpropanesulphonic acid, salts of alpha-acrylamidomethylpropanesulphonic acid 2-sulphoethyl methacrylate, salts of 2-sulphoethyl methacrylate, acrylamido-2-methylpropanesulphonic acid (AMPS), salts of acrylamido-2-methylpropanesulphonic acid, and styrenesulfonate (SS).

6. Use according to anyone of claims 1 to 5, wherein block A is vinyl pyrrolidone.

7. Use according to anyone of claims 1 to 6, wherein the emulsifier system composition is a blend comprising:
   - poly(2-ethyl-hexyl acrylate)-poly(vinylpyrrolidone) diblock copolymer (p(A2EH)-p(VP) di-block copolymer, p(A2EH) having a molecular weight below 40000 g/mol, preferably below 20000 g/mol and even more preferably between 1000 and 20000 g/mol and p(VP) has a molecular weight below 5000 g/mol, preferably below 3000 g/mol and even more preferably between 1000 and 3000 g/mol, also known under the name Rhodibloc RS sold by Rhodia,
   - sorbitan monooleate (SMO), and
   - lecithin (L).

8. Use according to claim 7, wherein the blend comprises:
   - from 5 to 40% by weight of diblock copolymer,
from 40 to 70% by weight of sorbitan monooleate and,
- from 20 to 45% by weight of lecithin.

9. A simple water-in-oil explosive emulsion comprising:
- droplets of an aqueous phase dispersed in a hydrophobic phase,
- an emulsifier system comprising:
  - a block copolymer selected from the group consisting of:
    - (block A)-(block B) di-block copolymers,
    - (block A)-(block B)-(block A) tri-block copolymers, and
    - (block B)-(block A)-(block B) tri-block copolymers,
  wherein block A is a hydrophilic block,- block B is a hydrophobic block, and block A or block B comprises units deriving from mono-alpha-ethylenically unsaturated monomers,
  - a sorbitan ester, and
  - lecithin.

10. An emulsion according to claim 9, further comprising a chemical gassing system selected in the group consisting of:
- Sodium nitrite/thiourea
- Sodium nitrite/sulfamic acid
- Sodium nitrite/sodium thiocyanate
- Hydrazine hydrate/sodium dichromate
- Sodium bicarbonate/acetic acid.
Sodium nitrite/sulfamic acid being preferred.

11. An emulsion according to claim 9 or 10, wherein the emulsifier system composition is a blend comprising:
poly(2-ethyl-hexyl acrylate)-poly(vinylpyrrolidone) diblock copolymer (p(A2EH)-p(VP) di-block copolymer, p(A2EH) having a molecular weight below 40000 g/mol, preferably below 20000 g/mol and even more preferably between 1000 and 20000 g/mol and p(VP) has a molecular weight below 5000 g/mol, preferably below 3000 g/mol and even more preferably between 1000 and 3000 g/mol, also known under the name Rhodibloc RS sold by Rhodia,
- sorbitan monooleate (SMO), and
- lecithin (L).

12. An emulsion according to claim 11, wherein the blend comprises:
- from 5 to 40% by weight of diblock copolymer,
- from 40 to 70% by weight of sorbitan monooleate and,
- from 20 to 45% by weight of lecithin.

13. An emulsion according to anyone of claims 10 to 12, wherein the amount of emulsifier system is from 0.1 to 10 weight percent of the amount of aqueous phase, preferably of from 0.1 to 5 weight percent.
FIG. 1
**INTERNATIONAL SEARCH REPORT**

**A. CLASSIFICATION OF SUBJECT MATTER**

INV. C06B23/00 C06B47/14

According to International Patent Classification (IPC) or to both national classification and IPC

**ADD.**

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

C06B

Electronic database consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

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- **X** Further documents are listed in the continuation of Box C.  
- **X** See patent family annex.

* Special categories of cited documents:
  
  "A" document defining the general state of the art which is not considered to be of particular relevance
  
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  "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
  
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**Date of the actual completion of the international search**

22 August 2016

**Date of mailing of the international search report**

31/08/2016

**Name and mailing address of the ISA/**

Kappen, Sascha
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