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RHEOLOGY MODIFICATION AND MODIFIERS

The present invention relates to explosives compositions and methods for modifying the rheology of explosives compositions using associative thickeners.

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Civilian mining, quarrying and excavation industries commonly use bulk or packaged explosive formulations as a principal method for breaking rocks and ore for mining, building tunnels, excavating and similar activities. Explosive compositions typically used in these applications include emulsion-based explosive compositions.

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Water-in-oil emulsion explosive compositions were first disclosed by Bluhm in United States Patent 3,447,978 and comprise (a) a discontinuous aqueous phase comprising discrete droplets of an aqueous solution of inorganic oxygen-releasing salts; (b) a continuous water-immiscible organic phase throughout which the droplets are dispersed and (c) an emulsifier which forms an emulsion of the droplets of oxidiser salt solution throughout the continuous organic phase. Where these types of emulsions comprise very little water or adventitious water only in the discontinuous phase they are more correctly referred to as melt-in-fuel emulsion explosives.

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In emulsion explosives, emulsifiers are generally used to decrease interfacial tension between the aqueous and oil phases. Molecules of the emulsifier locate at the interface between the aqueous droplet and continuous hydrocarbon phase. The emulsifier molecules are oriented with the hydrophilic head group in the aqueous droplet and the lipophilic tail in the continuous hydrocarbon phase. Emulsifiers stabilise the emulsion, inhibiting coalescence of the aqueous droplets and phase separation. Emulsifiers also inhibit crystallisation of oxidiser salt in the aqueous droplets. Uncontrolled crystallisation can lead to emulsion breakdown and reduction in detonation sensitivity of the emulsion explosive composition.

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Generally the emulsions themselves are not detonable and in order to form an explosive composition, the emulsion must be mixed with sensitising agents such as a self

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explosive (e.g. trinitrotoluene or nitroglycerine) or a discontinuous phase of void agents. Suitable void agents include glass microballoons, plastic microballoons, expanded polystyrene beads and gas bubbles including bubbles of entrained air.

5 Emulsions are often blended with ANFO-based explosive compositions to provide explosives which are commonly referred to as "heavy ANFO's". Compositions comprising blends of emulsion and AN or ANFO are described for example in Australian Patent Application No. 29408/71 (Butterworth) and US Patents 3,161,551 (Egly et al) and 4,357,184 (Binet et al).

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When explosives are used in the mining industry, ore and rock is fractured by drilling blastholes in the area to be blasted, and then filling the blastholes with bulk or packaged explosive compositions which are subsequently detonated. Bulk explosives are generally less expensive per unit mass than packaged explosives hence bulk explosives are preferred,
15 particularly at large mine sites where many hundreds of tonnes of explosives may be needed for a single blast. Packaged explosives also suffer the drawback that they must be manually loaded into blastholes whereas bulk explosives are able to be readily loaded by mechanised means.

20 Packaged explosives are manufactured at fixed site manufacturing facilities and the cartridges of packaged explosives are transported to the blast site and hand loaded into predrilled blastholes. Bulk explosives are either manufactured at a manufacturing facility and transported in a specially designed truck to the mine or mixed on-site in manufacturing units located on trucks (called mobile manufacturing units or MMU's).

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The transport trucks and MMU's are provided with the mechanised means of loading bulk explosive into blastholes. The blasthole loading is usually carried out by either auguring, pouring, pumping or blow loading the bulk explosive into the blasthole, the loading method used depending on the physical characteristics of the type of bulk explosive used.
30 Loading by pumping is usually carried out by using a mechanical or pneumatic pump to push

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explosives compositions through a delivery hose into the blastholes. Blow loading of an explosive composition typically involves the use of compressed gas to blow the explosive through a delivery hose into blastholes and is a commonly used delivery method.

5 Both MMU's and fixed manufacturing facilities store relatively large quantities of chemical components which can be mixed together to form explosives compositions. For example, MMU's comprise several large storage containers for storing fuel oil, emulsion, particulate oxidiser salts, water and other explosive components. These components can be mixed in differing proportions to provide ANFO or various formulations of emulsion and
10 heavy ANFO.

The manufacturing processes carried out using MMU's and fixed manufacturing facilities can provide various explosives formulations having various physical characteristics by precise control of the component flow rate, temperature and other physical parameters
15 related to the manufacturing process.

One of the most important parameters in the manufacture, delivery and handling of emulsion explosives is the emulsion rheology. The rheology of the emulsion impacts on virtually every aspect of emulsion handling including the flow of the emulsion in pipes and
20 hoses; adhesion to the walls of the tanks and conduits of the manufacturing system; ease of pumping; retention in upholes and cracked ground; and retention of voidage at low density. For example, explosives compositions which are very dense and viscous can only be pneumatically or mechanically pumped through short loading hoses; they cannot be pumped through long hoses without the use of excessively high pumping pressures or the hoses block
25 up.

It has also been noted that a column of emulsion will fail to be retained in an uphole if there is adhesive failure between the emulsion column and the blasthole walls or a cohesive failure of the emulsion. These problems may be alleviated somewhat if the viscosity
30 (effective rigidity) of the emulsion is increased.

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While it is often desirable for an emulsion to exhibit a high viscosity in the blasthole, this is not optimal for transport, handling or loading the emulsion into blastholes, particularly when pumping. In other words, an explosive emulsion which has rheological characteristics which make the emulsion suitable for pumping through a loading hose, may not be suitable
5 for residence in a blasthole and vice versa.

In the past, many different techniques have been used to modify the rheology of explosives emulsions. Most of these approaches to rheology modification are based on chemical interactions such as the chemical crosslinking of components within the emulsion.
10 For example United States Patent 5,387,675 (Yeh) discloses the use of quaternary ammonium ether(s) of polyol(s) and polysaccharides as chemical thickeners in a range of products including explosives. United States Patent 5,145,535 describes the use of a cationic salt of CMC ether as a chemical thickener.

15 However, chemically-based rheology modification of emulsions generally suffers from the problems that the chemical reaction occurs at a relatively slow rate and is strongly temperature dependent and irreversible.

It has now been found that effective rheology modification of emulsions for emulsion
20 explosives can be provided using "associative thickeners" which are believed to rely on a physical interaction with components of the emulsion rather than chemical interactions.

Associative thickeners have been previously used in technologies such as the coating industry. For example United States Patent 5,521,235 (Redelius and Redelius) describes the
25 use of hydrophobically modified urethane ethoxylates as associative nonionic type thickeners in cationic type bitumen emulsion for rods, roofing and waterproofing to allow thicker coating layers to be formed. Canadian Patent 2079926 (Fistner) discloses an aqueous paint composition with high gloss for use on textiles, the paint comprising an associative thickener, preferably a polyurethane block copolymer or an alkali swellable acrylic polymer or an alkali
30 soluble acrylic polymer. Associative thickeners have also been used in thickening drilling



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muds, polishes, cleaners, personal care products such as cosmetics, food products and pharmaceuticals, hydraulic fluids and inks but not hitherto in explosives manufactured to control rheological characteristics.

5 We have now found that associative thickeners may be used in emulsions for use in explosive compositions, which associative thickeners provide for rapid and reversible changes in emulsion viscosity. Associative thickeners provide explosives emulsions having the desirable characteristics of (1) significant reduction in viscosity during pumping and (2) re-establishment of relatively high viscosity when pumping is terminated without damage to the
10 emulsion components. It is believed that the associative thickener provides a network of physical linkages throughout the emulsion which network can be reversibly broken down.

Accordingly the present invention provides an emulsion for use in emulsion explosives wherein said emulsion comprises an associated thickener.

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There is further provided an emulsion according to claim 1 wherein the emulsion has increased zero-shear viscosity relative to an emulsion absent the associative thickener and exhibits significant reduction in viscosity when subjected to applied shear force and reestablishes substantially the original viscosity when the applied shear force is removed.

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There is further provided a method of manufacturing an emulsion explosive composition comprising incorporating at least one associative thickener in an aqueous phase and subsequently emulsifying the aqueous phase in an oil phase to form a water-in-oil emulsion.

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There is further provided a method of manufacturing an emulsion explosive composition comprising incorporating at least one associative thickener in an oil phase and subsequently emulsifying an aqueous phase in the oil phase to form a water-in-oil emulsion.

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A wide variety of associative thickeners may be used in the present invention.

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Suitable associative thickeners may be selected in accordance with their compatibility with the emulsion explosive in which they are incorporated.

The associative thickener of the present invention may be polymeric or non-polymeric
5 and may act in either an aqueous or non-aqueous phase of the emulsion depending upon the chemical nature of the selected associative thickener.

The associative thickener may typically comprise a backbone or chain which is soluble in the organic, or alternatively the aqueous, phase of the emulsion. These associative
10 thickeners additionally comprises a number of moieties which are insoluble in the phase in which the backbone is soluble. These moieties are preferably dispersed along the backbone with insoluble moieties present within or as pendent or terminal groups on the chain.

The associative thickener may be a polymer soluble in either the aqueous or oil phase
15 and have insoluble moieties substituted thereto in substoichiometric amounts. Preferably the associative thickener comprises blocks of hydrophilic polymers or copolymer prepared with small amounts of hydrophobic comonomer. The hydrophilic polymer or copolymer is preferably prepared from monomers selected from the group consisting of vinylpyrrolidone, vinyl acetate, acrylamide, ethylene glycol, ethylene oxide, vinyl alcohol and propylene glycol
20 and their hydrophilic derivatives.

The hydrophobic monomer may be any monomer polymerisable with the hydrophilic monomer and which contains hydrophobic moieties. There are a wide variety of suitable hydrophobic monomers which will be known to those skilled in the art of associative
25 thickeners. Preferably the hydrophobic monomers selected from the group consisting of N-alkylacrylamides such as N-(4-ethylphenyl)acrylamide, N-(4-t-butylphenyl)acrylamide and the like. The associative thickener may be for example, a copolymer of acrylamide (a hydrophile) and N-4-(t-butyl)phenyl acrylamide (a hydrophobe) comprising less than 1 % mol % hydrophobic comonomer.





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The associative thickener may alternatively comprise blocks of hydrophobic copolymer prepared with small amounts of hydrophilic comonomer.

It will be apparent to those skilled in the art that molecules of this type can be synthesised by various methods. The two major synthetic routes to associative thickeners are through micellar copolymerisation or from the chemical modification of a water-soluble precursor polymer. The latter route has mainly been applied to cellulose derivatives, poly(acrylic acid) and ethoxylated urethane polymers. The micellar copolymerisation process involves essentially acrylamide-based copolymers. An additional synthetic route which utilises hydrophobic monomers with a built in surfactant character overcomes the need for the external surfactants used in the micellar technique.

Factors which influence the viscosifying ability of associative thickeners, in the absence of shear, are many and varied. Included in these are the molecular weight of the copolymer, the copolymer microstructure (hydrophobe content and hydrophobe distribution along the polymer chain), the hydrophobicity of the hydrophobe, the presence of charge either in the polymer backbone or on the pendant hydrophobic groups, the copolymer concentration, the presence of additives (e.g. salt or surfactant) and temperature. Depending on the relative influence of each of these factors and the copolymer chain flexibility, both interchain and intrachain associations may occur.

Preferably the emulsion suitable for use as an explosives emulsion is a water-in-oil or melt-in-oil emulsion or melt-in-fuel emulsion. Typically the associative thickener is dissolved in the aqueous or organic phase prior to emulsion formation. Typically the emulsion comprises 0.1% to 3% by weight of emulsion of associated thickener. More typically the associative thickener is present at a concentration of 0.2 to 2% by weight of emulsion. Suitable oxygen releasing salts for use in the aqueous phase of the emulsion of the present invention include the alkali and alkaline earth metal nitrates, chlorates and perchlorates, ammonium nitrate, ammonium chlorate, ammonium perchlorate and mixtures thereof. The preferred oxygen releasing salts include ammonium nitrate, sodium nitrate and calcium

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nitrate. More preferably the oxygen releasing salt comprises ammonium nitrate or a mixture of ammonium nitrate and sodium or calcium nitrates.

Typically the oxygen releasing salt component of the compositions of the present invention comprise from 45 to 95 % w/w and preferably from 60 to 90 % w/w of the total emulsion composition. In compositions wherein the oxygen releasing salt comprises a mixture of ammonium nitrate and sodium nitrate the preferred composition range for such a blend is from 5 to 80 parts of sodium nitrate for every 100 parts of ammonium nitrate. Therefore, in the preferred composition the oxygen releasing salt component comprises from 45 to 90 % w/w (of the total emulsion composition), ammonium nitrate or mixtures of from 0 to 40 % w/w, sodium or calcium nitrates and from 50 to 90 % w/w ammonium nitrate.

Typically the amount of water employed in the compositions of the present invention is in the range of from 0 to 30 % w/w of the total emulsion composition. Preferably the amount employed is from 4 to 25 % w/w and more preferably from 6 to 20 % w/w.

The water immiscible organic phase of the emulsion composition of the present invention comprises the continuous "oil" phase of the emulsion composition and is the fuel.

Suitable organic fuels include aliphatic, alicyclic and aromatic compounds and mixtures thereof which are in the liquid state at the formulation temperature. Suitable organic fuels may be chosen from fuel oil, diesel oil, distillate, furnace oil, kerosene, naphtha, waxes such as microcrystalline wax, paraffin wax and slack wax, paraffin oils, benzene, toluene, xylenes, asphaltic materials, polymeric oils such as the low molecular weight polymers of olefines, animal oils, vegetable oils, fish oils and other mineral, hydrocarbon or fatty oils and mixtures thereof. Preferred organic fuels are liquid hydrocarbons generally referred to as petroleum distillates such as gasoline, kerosene, fuel oils and paraffin oils.

Typically the organic fuel or continuous phase of the emulsion comprises from 2 to 15 % w/w and preferably 3 to 10 % w/w of the total composition.

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The emulsifier of the emulsion composition of the present invention may comprise emulsifiers chosen from the wide range of emulsifiers known in the art from the preparation of emulsion explosive compositions. It is particularly preferred that the emulsifier used in the emulsion composition of the present invention is one of the well known emulsifiers based on the reaction products of poly[alk(en)yl] succinic anhydrides and alkylamines, including the polyisobutylene succinic anhydride (PiBSA) derivatives of alkanolamines. Other suitable emulsifiers for use in the emulsion of the present invention include alcohol alkoxylates phenol alkoxylates, poly(oxyalkylene)glycols, poly(oxyalkylene)fatty acid esters, amine alkoxylates, fatty acid esters of sorbitol and glycerol, fatty acid salts, sorbitan esters, poly(oxyalkylene) sorbitan esters, fatty amine alkoxylates, poly(oxyalkylene)glycol esters, fatty acid amines, fatty acid amide alkoxylates, fatty amines, quaternary amines, alkyloxazolines, alkenyloxazolines, imidazolines, alkylsulphonates, alkylarylsulphonates, alkylsulphosuccinates, alkylarylsulphonates, alkylsulphosuccinates, alkylphosphates, alkenylphosphates, phosphate esters, lecithin, copolymers of poly(oxyalkylene)glycols and poly(12-hydroxystearic)acid and mixtures thereof.

Typically the emulsifier of the emulsion comprises up to 5 % w/w of the emulsion. Higher proportions of the emulsifying agent may be used and may serve as supplemental fuel for the composition but in general it is not necessary to add more than 5 % w/w of emulsifying agent to achieve the desired effect. Stable emulsions can be formed using relatively low levels of emulsifier and for reasons of economy it is preferable to keep the amount of emulsifying agent used to the minimum required to form the emulsion. The preferred level of emulsifying agent used is in the range of from 0.1 to 3.0 % w/w of the water-in-oil emulsion.

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If desired, other optional fuel materials, hereinafter referred to as secondary fuels may be incorporated into the emulsion in addition to the water immiscible organic fuel phase. Examples of such secondary fuels include finely divided solids and water miscible organic liquids which can be used to partially replace water as a solvent for the oxygen releasing salts or to extend the aqueous solvent for the oxygen releasing salts. Examples of such secondary

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fuels include finely divided solids and water miscible organic liquids which can be used to partially replace water as a solvent for the oxygen releasing salts or to extend the aqueous solvent for the oxygen releasing salts. Examples of solid secondary fuels include finely divided materials such as sulphur, aluminium, urea and carbonaceous materials such as
5 gilsonite, comminuted coke or charcoal, carbon black, resin acids such as abietic acid, sugars such as glucose or dextrose and vegetable products such as starch, nut meal, grain meal and wood pulp. Examples of water miscible organic liquids include alcohols such as methanol, glycols such as ethylene glycol, amides such as formamide and urea and amines such as methylamine.

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Typically the optional secondary fuel component of the composition of the present invention comprises from 0 to 30 % w/w of the total composition.

The water-in-oil emulsion composition may be prepared by a number of different
15 methods. One preferred method of manufacture includes: dissolving said oxygen releasing salts in water at a temperature above the crystallization point of the salt solution, preferably at a temperature in the range from 20 to 110 °C to give an aqueous salt solution; combining an aqueous salt solution, a water immiscible organic phase, and an emulsifier with rapid mixing to form a water-in-oil emulsion; and mixing until the emulsion is uniform.

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It lies within the invention that there may also be incorporated into the emulsion other substances or mixtures of substances which are oxygen releasing salts or which are themselves suitable as explosive materials. For example the emulsion may be mixed with prilled or particulate ammonium nitrate or ammonium nitrate/fuel oil mixtures.

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Other optional additives may be added to the emulsion explosive compositions hereinbefore described including non-associative thickening agents or chemical thickening agents such as zinc chromate or a dichromate either as a separate entity or as a component of a conventional redox system such as for example, a mixture of potassium dichromate and
30 potassium antimony tartrate.



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Without wishing to be bound by theory, it is believed that the associative thickener increases the zero-shear viscosity by the non-soluble moieties of different associative thickener molecules associating together in the solvent, giving localised points of linkage between the soluble backbones of the molecules. These associations are believed to give rise to an
5 extensive three-dimensional structure of the associative thickener molecules in the solvent, the 3-dimensional structure acting to hinder solvent flow and therefore raise the emulsion viscosity.

The points of association are not permanent as they are only formed through relatively
10 weak physical forces. Under the influence of applied shearing force, the points of association can be disrupted and the emulsion can flow normally. However the disruption only subsists while the shearing force is applied. If the shearing force is removed the points of association can rapidly be re-formed, re-establishing the 3-dimensional network.

15 It is believed that the driving force for formation of the associations has a primarily thermodynamic basis. For example, where the associative thickener constitutes a hydrophobically modified water-soluble polymer, the driving force for the associations is a large entropic increase (accompanied by a small enthalpic change) arising from the breakdown of the ordered structure of water molecules around the hydrophobes as they are removed from
20 solution. This aggregation is therefore favoured due to the large decrease in the free energy resulting from a net decrease in the number of hydrophobe-water contacts. The aggregation in aqueous solution of the hydrophobic groups on the polymer chains thus results in intermolecular associations, forming physical linkages between the chains. These linkages produce polymolecular structures with a high hydrodynamic volume and consequently,
25 enhanced viscosification properties.

Advantageously, the incorporation of an associative thickener into an emulsion for use in an emulsion explosive composition provides a marked viscosifying effect, especially for emulsions having a dispersed phase with a small average droplet size. We have found that
30 the apparent viscosity of such an emulsion may display an increase of 150% or more. We

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observed that the apparent viscosity, when measured as a function of shear rate, demonstrated an apparent viscosity far greater than for emulsions unmodified by associative thickeners over relatively low shear rates. The apparent viscosity of the emulsions comprising an associative thickener coincided with the apparent viscosities of an unmodified emulsion at higher shear rates. This clearly shows that emulsions comprising associative thickeners may be pumped, augured or otherwise transported as readily as standard emulsions yet may exhibit apparent viscosities far greater than for standard emulsions at low or zero shear such as when loaded in a bore hole.

10 When the associative thickener is incorporated into the dispersed phase of the emulsion, the droplets have been observed to be significantly harder to deform although at relatively high shear rates, the resistance to deformation is overcome. In a preferred embodiment of the present invention, the associative thickener is incorporated into the dispersed aqueous phase of a water-in-oil emulsion.

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We have observed that in a number of the emulsions prepared incorporating an associative thickener demonstrate increased stability with respect to an unmodified emulsion. We have also observed that the average droplet size and droplet distribution is similar to and exhibits similar general behaviour to standard emulsions over time.

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Dynamic shear studies of emulsions comprising the associative thickener demonstrate elastic character in the emulsions over a wider range of frequencies and strains than would be expected in unmodified emulsions.

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Advantageously, the emulsions incorporating the associative thickener demonstrate less rheopectic behaviour than would be expected with unmodified emulsions.

Throughout this specification and the claims which follow, unless the context requires otherwise, the word "comprise", and variations such as "comprises" and "comprising", will be understood to imply the inclusion of a stated integer or step or group of integers or steps

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but not the exclusion of any other integer or step or group of integers or steps.

The invention is now demonstrated by but in no way limited to the following examples;

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Example 1

In this example, a copolymer of acrylamide and N-(4-t-butylphenyl) acrylamide was used as an associative thickener. The associative thickener was synthesised using an aqueous micellar free radical polymerisation route. The resultant copolymer contained no more than 10 1 % mol. of the hydrophobic monomer.

The effect of ammonium nitrate and sodium chloride on the solution properties of the associative thickener were investigated. The concentration of associative thickener was 0.50 % w/w with ammonium nitrate levels ranging from 10 % w/w to 60 % w/w. The shear rate 15 range was varied from 0.00186 S^{-1} to 1470 S^{-1} with a constant delay time of 5 sec and an integration time of 5 sec using a Bohlin VOR rheometer. The samples were examined as a function of shear rate and also as a function of shear time at a constant rate.

The results are shown in Figures 1 to 3. Figure 1 shows the apparent viscosity at 25°C 20 as a function of shear rate (sweep up and down) for 0.50 % w/w aqueous associative thickener solutions containing various levels of ammonium nitrate. The arrows indicate the direction of sweep. Figure 2 shows the apparent viscosity at 25°C at a constant shear rate of 0.583 S^{-1} as a function of shear time for 0.50 % w/w aqueous associative thickener solutions containing various levels of ammonium nitrate. Figure 3 shows the apparent viscosity at 25 25 $^{\circ}\text{C}$ at a shear rate of 0.583 S^{-1} as a function of the ammonium nitrate concentration for 0.50 % w/w aqueous associative thickener solutions.

The results indicated that in aqueous ammonium nitrate solution the associative thickener offered significant enhancement of the viscosity but that under the influence of shear 30 the associative thickener led to shear thinning, achieving viscosities closer to that of pure

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water at high shear rates (that is greater than 100/s). Time dependent effects were also seen, with the associative thickener exhibiting rheopexy (increased viscosity as a function of shear time) at low shear rates and thixotropy (decreased viscosity as a function of shear time) at higher shear rates.

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Example 2

In this example, a copolymer of acrylamide and N-(4-t-butylphenyl) acrylamide was used as an associative thickener.

10 The effect of sodium chloride on the solution properties of the associative thickener were investigated. The concentration of associative thickener of 0.50% w/w and 1.50% w/w with sodium chloride levels ranging from 5 % w/w to 25 % w/w. The shear rate range was varied from 0.00186 S^{-1} to 1470 S^{-1} with a constant delay time of 5 sec and an integration time of 5 sec using a Bohlin VOR rheometer. The samples were examined as a function of
15 shear rate and also as a function of shear time at a constant rate.

The results are shown in Figures 4 to 6. Figure 4 shows the apparent viscosity at 25 °C as a function of shear rate (sweep up and down) for 0.50 % w/w aqueous associative thickener solutions containing various levels of sodium chloride. The arrows indicate the
20 direction of sweep. Figure 5 shows the apparent viscosity at 25 °C at a constant shear rate of 0.583 l/s as a function of shear time for 0.50 % w/w aqueous associative thickener solutions containing various levels of sodium chloride. Figure 6 shows the apparent viscosity at 25 °C at a shear rate of 0.583 S^{-1} as a function of the sodium chloride concentration for 0.50 % w/w aqueous associative thickener solutions.

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The results indicated that in aqueous NaCl solution the copolymers offered significant enhancement of the viscosity but that under the influence of shear they showed shear thinning, achieving viscosities closer to that of pure water at high shear rates (that is greater than 100/s). Time dependent effects were also seen, with the copolymer exhibiting rheopexy
30 (increased viscosity as a function of shear time) at low shear rates and thixotropy (decreased

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viscosity as a function of shear time) at higher shear rates.

Example 3

Preparation of a Water-in-Oil Emulsion

5 A water-in-oil emulsion of the following composition was prepared for use in the example; Oxidiser Solution - 91.5 % w/w

 ammonium nitrate (78.9 % w/w)

 water (20.7 % w/w)

 buffer (0.4 % w/w)

10 Fuel Phase - 9 % w/w

 hydrocarbon oil/emulsifier mix (9% w/w).

 The emulsifier was an uncondensed amide form of the reaction product of an alkanolamine and poly(isobutylene)succinic anhydride (PiBSA). The emulsion was prepared
15 by dissolving ammonium nitrate in the water at elevated temperature (98°C) then adjusting the pH of the oxidiser solution so formed to 4.2. The fuel phase was then prepared by mixing the emulsifier with the hydrocarbon oil. The oxidiser phase was then added in a slow stream to the fuel phase at 98°C with rapid stirring to form a homogeneous water-in-oil emulsion.

20 Emulsion of this formulation was suitable for use in forming an explosives emulsion.

 A first portion of the water-in-oil emulsion was set aside as a control sample. The associative thickener of Example 1 was incorporated at a concentration of 1.5 % w/w into the aqueous phase of a second test sample of the emulsion.

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 A comparison of the test sample with the control sample showed that the associative thickener enhanced the zero shear viscosity of the test sample. Furthermore the test sample exhibited shear thinning as a function of applied shear rate, the test sample having the same viscosities as the control sample at higher shear rates. Upon relaxation of the shear force, the
30 test sample immediately regained high zero shear viscosity .

Example 4

The following chemicals were used in the preparation of the samples used in this example:

- * E25/66T (emulsifier, ex Orica Australia)
- 5 * Paraffin Oil (ex Orica Australia)
- * Sodium Chloride (98+ %, Aldrich Chemical Company, Inc.)
- * Water (Millipore "Milli-Q" Grade)

All chemicals were used as supplied without further purification.

- 10 The continuous phase (oil phase) for the comparative emulsions was prepared using 30% w/w E26/66T and 70% w/w paraffin oil, while the dispersed phase (aqueous phase) was a 25% w/w sodium chloride solution. All emulsions were prepared at ambient temperature from continuous and dispersed phases at this temperature.

- 15 A Sunbeam Beatermix JM-040 five-speed electronic hand mixer with a whisk-type stirrer was employed in the preparation of the emulsions. The speed setting used was dependent on the droplet size required for the emulsion.

- 20 The highly concentrated emulsions were prepared as follows: 94g of aqueous phase was slowly added to 6g of constantly mixing oil phase over a 5 minute time period. Emulsification and refinement was then continued for a further specified period of time, with the emulsion vessel being moved in a circular motion during this time to ensure complete dispersion of the aqueous phase in the oil phase.

- 25 Emulsions of approximately 6 μ m average droplet size were prepared using the highest speed setting (Speed 5) and a refinement time of 5 minutes.

An emulsion of approximately 12 μ m average droplet size was prepared using the lowest speed setting (Speed 1) and a refinement time of 2.5 minutes.

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An emulsion of approximately 18 μm average droplet size was prepared using the lowest speed setting (Speed 1) and a refinement time of 45 seconds.

These emulsions will hereon be referred to as Emulsion S6, Emulsion S12 and
5 Emulsion S18 respectively.

The acrylamide/N-(4-butylphenyl)acrylamide copolymer used to thicken the internal phase of the emulsions was obtained from a free-radical copolymerisation in an aqueous micellar medium. This polymerisation technique produces a copolymer with an essentially
10 block-like structure, with hydrophobic regions being dispersed along the hydrophilic polymer backbone. It is believed that the copolymer is polydisperse in nature, with polymer chain compositions ranging from hydrophobe rich to pure acrylamide.

The copolymer/salt solution was prepared by dissolving 1.5% w/w of copolymer in
15 a 25% w/w sodium chloride solution using gentle magnetic stirring at ambient temperature.

The thickened emulsions were prepared using essentially the same method as for standard emulsions. However, due to the increased viscosity of the dispersed phase, small amounts of the copolymer/salt solution were continuously added to the oil phase in the
20 emulsion vessel until all of the dispersed phase had been added. This occurred over a 5 minute period.

All emulsions were prepared using the highest speed setting (Speed 5) on the mixer.

Thickened emulsions of approximately 6 μm , 12 μm and 18 μm were prepared using
25 refinement times of 40 minutes, 10 minutes and 4 minutes 45 seconds respectively. They will hereon be referred to as Emulsion T6, Emulsion T12 and Emulsion T18 respectively.

The measuring system utilised in all measurements was a Bohlin VOR rheometer with a stainless steel concentric cylinder (C14) geometry consisting of a cup of diameter 15.4 mm
30 and a bob of diameter 14.0 mm. The base of the bob was conical with cone angle 150°, the

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purpose of which was to minimise any end effects on the flow of the sample.

The 86.6 g.cm torsion bar was used for all shear time, shear rate sweep and flow/relaxation measurements, together with the oscillatory measurements of Emulsion T6.

- 5 The oscillatory measurements on the remaining emulsions employed the 18 g.cm torsion bar. Each was selected to ensure maximum sensitivity.

The available method of measurement enabled the shearing of the emulsion sample at each particular shear rate for a specified time, prior to the measurement at that shear rate
10 being taken. This initial period of pre-shear is known as the *delay time*. Taking the measurement at a particular shear rate involved averaging a number of instantaneous torque readings taken over a specified time period to produce the reported data value. This period of measurement is known as the *integration time*.

- 15 The torque signal was zeroed manually prior to the start of each measurement.

All measurements were performed at a temperature of 25°C.

The apparent viscosity as a function of time was recorded in what will be referred to
20 as "shear time" measurements. For these measurements, the sample was continuously sheared at a single fixed shear rate and data collected at fixed intervals. A shear rate of 0.581 S^{-1} , together with a delay time of 5 seconds and an integration time of 5 seconds, was used in each measurement.

- 25 The initial shear time measurement on each emulsion was performed within 15 minutes of manufacture and the apparent viscosity was monitored over a 5000 second time period. This measurement gave an indication of the structure formation and relaxation of the emulsions immediately after manufacture.

- 30 The apparent viscosity of each emulsion was then monitored over time (days), with

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one shear time measurement being taken at the beginning of the day of interest, with the duration of the measurement being 500 seconds.

Shear rate sweeps were performed over the full shear rate range of 0.00186 S^{-1} to 1470 S^{-1} . Two types of shear rate sweep measurements were conducted.

The first involved the sequential step-wise increase of shear rate to high shear rates followed by the sequential step-wise decrease of shear rate back to low shear rates. These will be referred to as "Up-Down" shear rate sweep measurements. An integration time of 5 seconds was employed for all measurements, while delay times of 5, 30, 60, 180 and 600 seconds were used for each emulsion. These measurements gave an indication of the destructuration and restructuration times for the emulsions.

In addition, for Emulsion S6 only "Down-Up" experiments, in which the shear rate was sequentially decreased then increased in a step-wise fashion, were also conducted, enabling the comparison of Up-Down and Down-Up measurements. These measurements were conducted over five shear rate ranges, namely 0.00186 S^{-1} to 0.116 S^{-1} , 1.16 S^{-1} , 11.6 S^{-1} , 116 S^{-1} and 1160 S^{-1} respectively. These measurements gave an indication of the shear rate range over which most destructuration of the emulsion occurs.

The second type of shear rate sweep measurement, which will be referred to as a "shear rate sweep under continuous measurement", involved the gradual increase and decrease of the shear rate over the shear rate range, with instantaneous readings recorded throughout. In contrast to the previous shear rate sweeps, these measurements did not require delay and integration times to be specified by the user. These measurements were conducted in each of the three rheometer gears, namely Gear 0 (18.2 S^{-1} to 1460 S^{-1}), Gear 1 (0.182 S^{-1} to 14.6 S^{-1}) and Gear 2 (0.00182 S^{-1} to 0.146 S^{-1}). The selected sweep time was 600 seconds, with the entire measurement involving an increase in shear rate over 600 seconds followed by a decrease in shear rate over a further 600 seconds (1200 seconds in total).

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Flow/relaxation, or stress relaxation, experiments involve shearing the emulsion at a specified shear rate for a specified period of time, thus applying an accumulated strain to the emulsion, and monitoring the decay of the torque on the bob for a specified period of time following the cessation of shear. The measurement gave information about the recovery of the emulsion after shear.

The flow/relaxation behaviour of Emulsion S6 was studied most thoroughly. For this emulsion, shear rates of 0.116 S^{-1} , 0.581 S^{-1} , 1.16 S^{-1} , 4.61 S^{-1} , 11.6 S^{-1} , 46 S^{-1} , 116 S^{-1} , 461 S^{-1} and 1160 S^{-1} were employed together with shear times of 30 seconds and 600 seconds. The relaxation was monitored for 100 seconds. The relaxation curves were then normalised by dividing all shear stresses in each curve by the value of the first shear stress recorded, allowing further comparison of relaxation behaviour.

For remaining emulsions, shear rates of 0.116 S^{-1} , 1.16 S^{-1} , 11.6 S^{-1} and 116 S^{-1} with shear times of 30 seconds and 600 seconds were used. The relaxation was monitored over a 200 second time period and normalised curves were also produced.

Two types of oscillatory measurements were conducted.

The first, known as an "Oscillation Test", measured various dynamic variables, including G' (storage modulus), G'' (loss modulus) and phase angle δ , over a frequency range of 0.004 Hz to 20Hz. Amplitudes of 10%, 20%, 30% and 40%, corresponding to strains of 0.0206, 0.0412, 0.0618 and 0.0823 respectively, were employed for these measurements. Oscillation of the sample occurred only during measurement at each frequency.

The second type of measurement, known as a "Strain Sweep", measured the dynamic variables over a range of strains, namely 0.000206 to 0.206 (0.1% to 100% amplitude). Frequencies of 0.1 Hz, 1 Hz, 10 Hz and 20 Hz were employed.

Results were interpreted using plots of $\tan \delta$ as a function of frequency and strain

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respectively. This is due to the fact that $\tan \delta = G''/G'$. Thus $\tan \delta > 1$ indicates that the emulsion is behaving predominantly as a viscous or liquid material, which $\tan \delta < 1$ indicates elastic or solid-like behaviour. Finally, $\tan \delta = 1$ marks the transition from "flow" to "oscillation" of the emulsion.

5

Three further points should be noted for all measurements. Firstly, with the exception of the initial shear time measurements, rheological measurements were not commenced until one day after the manufacture of the emulsion. This length of time enabled a state of equilibrium to be attained. Secondly, any data point with a torque range of less than 1.0%
10 was considered to be unreliable and was therefore omitted from the data presented. Finally, a new emulsion sample was used for each measurement, so that results could be directly compared without having to account for shear history of the sample.

Droplet sizing of each emulsion was performed using a Malvern Masterizer and a
15 magnetically stirred cell. The general procedure for analysing an emulsion was as follows. The cell was filled with paraffin oil and a background reading taken. A small sample of emulsion was collected on the end of a Pasteur pipette. The magnetic stirrer was then switched on and emulsion added to the paraffin oil by shaking the pipette in the oil until a sufficient concentration had been obtained. After allowing the sample to stir for a short time
20 (around 10 seconds), the stirrer was switched off and a measurement immediately taken.

For freshly manufactured emulsions, further measurements were taken in five minute intervals for a 2.5 hour time period so that the stability of the droplets could be monitored. On subsequent days, measurements were taken in five minute intervals over a 15 minute time
25 period, allowing the average droplet size of the emulsions to be monitored over time.

The droplet size distributions of these emulsions are shown in Figure 7, while their average droplet sizes (on the day of manufacture) and apparent viscosities (as measured on the second day, at which time it is thought than an equilibrium droplet packing, and thus a
30 stable apparent viscosity is attained) are listed in Table 1.

TABLE 1
Average droplet size and apparent viscosities for standard and thickened emulsions of various droplet size

5	Emulsion	Average Droplet Size (μm)	Apparent Viscosity (Pa.s)
	S6	6.18	180
	S12	11.04	90
	S18	17.72	65
	T6	6.09	500
10	T12	11.19	200
	T18	18.24	125

As can be seen from the data, the average droplet size and droplet size distributions of Emulsions S6 and T6 are very closely matched. Thus any differences in rheological behaviour as discussed below may be attributed predominantly to the incorporation of the associative thickener into the dispersed phase droplets. For Emulsions S12 and T12, however, while possessing similar average droplet sizes, it can be seen in Figure 7 that the droplet size distributions of these two emulsions are significantly different, with the thickened emulsion displaying a wider distribution. Similarly, Emulsions S18 and T18 exhibit similar average droplet size but significantly different droplet size distributions. Thus, for these latter emulsions, any observed differences in the rheological behaviour of the corresponding pairs of standard and thickened emulsions may be partly due to this difference in droplet size distribution, in addition to the incorporation of associative thickener into the internal phase droplets.

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Table 1 clearly shows that incorporation of associative thickener into the internal phase droplets of an emulsion has a marked viscosifying effect, especially for the emulsions of approximately 6 μm average droplet size.

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The standard and thickened emulsions display similar behaviour under steady shear flow, with both sets of emulsions exhibiting shear thinning and thixotropic behaviour in their apparent viscosities as a function of shear rate. In addition, the emulsions of larger average droplet size, both thickened and unthickened, display some rheopectic behaviour, especially
5 when long delay times are employed.

The apparent viscosities of Emulsions S6 and T6 as a function of shear rate are given in Figure 8. The displayed curves were obtained using a 60 second delay time and 5 second integration time and is representative of the curves produced using all five delay times for
10 each of the three emulsion droplet sizes. The figure clearly illustrates that the sweep up curve for the thickened emulsion lies above that of the standard emulsion for the majority of the shear rate sweep up, with the curves merging at the highest shear rates. This behaviour is believed to be attributed to the relative deformability of the droplets of the standard and thickened emulsions. The fact that the sweep up curve of the emulsion containing associative
15 thickener lies above that of the standard emulsion indicates that the droplets of the thickened emulsions have increased resistance to deformation. Thus the apparent viscosity of the thickened emulsions remain higher than for the standard emulsions during the shear rate sweep up, since the thickened emulsion has less tendency to flow as a result of the decreased deformability of the emulsion droplets. This increase in resistance to deformation of the
20 droplets of the thickened emulsions would be expected, since these droplets are of greater apparent viscosity due to the incorporation of associative thickener and are, therefore, effectively "harder" and subsequently more difficult to deform, than the droplets of the standard emulsions. At high shear rates however, this increased resistance to deformation is overcome, and the droplets of the thickened emulsions are distorted to a similar extent to that
25 of the standard emulsions. Consequently, the sweep up curves coincide at high shear rates. In addition, Figure 8 shows that the thickened emulsion displays increased hysteresis relative to that of the standard emulsions. Indeed, this observation is generally observed for each of the emulsions of different average droplet size for all delay times employed. This suggests that, once deformed, the emulsion droplets containing associative thickener regain their
30 original shape and packing less rapidly than the droplets of the standard emulsions, that is,

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the thickened emulsions display increased resistance to the reformation of structure following destructure at high shear.

The shear stress as a function of time following cessation of 30 seconds of shear at a shear rate of 1.16 s^{-1} is shown for each of the standard and thickened emulsions in Figure 9. As can be seen from Figure 9, the initial shear stresses observed for the thickened emulsions are greater than those attained by the corresponding standard emulsions. This behaviour is believed to imply that the thickened emulsions tend to display increased elastic behaviour relative to the standard emulsions. This tendency is further supported by comparing the plateau values of the shear stress maintained by each of the emulsions. For example, Figure 9 shows that the stress maintained by each of the thickened emulsions is greater than that of the corresponding standard emulsions. Indeed, this was the case for all of the shear rates employed in this study, with the trend being more apparent at the lower applied shear rates. In addition, the normalised curves show that the relaxation of the thickened emulsions is significantly slower than that of the standard emulsions, as evidenced by the gradients of the curves of the standard emulsions being greater than those of the thickened emulsions. This is believed to indicate that the shear stress is dissipated more quickly for the standard emulsions or, in other words, that the thickened emulsions are more capable of maintaining the accumulated strain. In addition, this suggests that the thickened emulsions "solidify" at increased strains, which again shows that the thickened emulsions are able to store more energy than the standard emulsions. These observations, by definition, again indicate the increased elastic behaviour of the thickened relative to the standard emulsions.

The standard and thickened emulsions generally show very similar behaviour under dynamic shear flow. Both sets of emulsions display significant Maxwellian behaviour, with consideration of $\tan \delta$ as a function of frequency at several amplitudes revealing that the transition from flow to oscillatory behaviour for the emulsions occurs at higher frequency for increasing amplitude.

Tan δ as a function of frequency at 30% amplitude is shown in Figure 10 for all

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emulsions prepared in this study. It can be clearly seen from the figure that the frequency at which the transition from predominantly viscous to primarily elastic behaviour occurs is significantly decreased for the thickened relative to the corresponding standard emulsions. This was the case for all amplitudes studied. In fact, for the thickened emulsions, the value
5 of $\tan \delta$ remains below unity over the entire frequency range studied in many cases, that is, the thickened emulsions display predominantly elastic behaviour over the whole frequency range. These observations clearly illustrate the increased elastic component of the rheological behaviour of thickened emulsions relative to that of the standard emulsions.

10 Similarly, consideration of $\tan \delta$ as a function of strain for a number of different frequencies reveals that, for both sets of emulsions, the transition from predominantly elastic to primarily viscous behaviour occurs at higher strain for increasing applied frequency.

Tan δ as a function of strain at a frequency of 0.1 Hz is shown in Figure 11 for
15 Emulsions S6, S12, T6 and T12. It can be clearly seen from the figure that the aforementioned transition point occurs at higher strains for the thickened relative to the standard emulsions. This appears to be the general trend for all pairs of corresponding emulsions at all frequencies studied. These observations again imply that the thickened emulsions show increased elastic behaviour relative to that of the standard emulsions.

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While the invention has been explained in relation to its deferred embodiments it is to be understood that various modifications thereof will become apparent to those skilled in the art upon reading the specification. Therefore, it is to be understood that the invention disclosed herein is intended to cover such modifications as fall within the scope of the
25 appended claims.

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The claims defining the invention are as follows;



1. An emulsion suitable for use in the manufacture of emulsion explosives, wherein said
5 emulsion comprises at least one associative thickener.
2. An emulsion according to claim 1 wherein the associative thickener comprises a chain of
hydrophilic material soluble in the aqueous phase of the emulsion, and hydrophobic moieties
insoluble in the aqueous phase which moieties are dispersed along said chain or are present
10 as terminal groups.
3. An emulsion according to claim 1 wherein the associative thickener comprises blocks of
hydrophilic co-polymer prepared with small amounts of hydrophobic comonomer.
- 15 4. An emulsion according to claim 3 wherein the hydrophilic copolymer is prepared from
monomers selected from the group consisting of vinylpyrrolidone, vinyl acetate, acrylamide,
ethylene glycol, ethylene oxide, vinyl alcohol and propylene glycol and their hydrophilic
derivatives.
- 20 5. An emulsion according to claim 4 wherein the hydrophobic comonomer is selected from
the group consisting of N-alkylacrylamides such as N-(4-ethylphenyl)acrylamide, N-(4-t-
butylphenyl) acrylamide.
6. An emulsion according to claim 1 wherein the associative thickener is a copolymer of
25 acrylamide and N-4-(t-butyl)phenyl acrylamide comprising less than 1 % mol % hydrophobic
comonomer.
7. An emulsion according to claim 1 wherein the associative thickener comprises blocks of
hydrophobic co-polymer prepared with small amounts of hydrophilic comonomer.



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8. An emulsion according to claim 1 wherein the emulsion has increased zero-shear viscosity relative to an emulsion absent the associative thickener and exhibits significant reduction in viscosity when subjected to applied shear force and reestablishes substantially the original viscosity when the applied shear force is removed.

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9. An emulsion explosive composition comprising an emulsion wherein said emulsion comprises at least one associative thickener.

10. An emulsion explosive according to claim 9 wherein the associative thickener comprises a chain of hydrophilic material soluble in the aqueous phase of the emulsion, and hydrophobic moieties insoluble in the aqueous phase which moieties are dispersed along said chain or are present as terminal groups.

11. An emulsion explosive according to claim 9 wherein the associative thickener comprises blocks of hydrophilic co-polymer prepared with small amounts of hydrophobic comonomer.

12. An emulsion explosive according to claim 11 wherein the hydrophilic copolymer is prepared from monomers selected from the group consisting of vinylpyrrolidone, vinyl acetate, acrylamide, ethylene glycol, ethylene oxide, vinyl alcohol and propylene glycol and their hydrophilic derivatives.

13. An emulsion explosive according to claim 12 wherein the hydrophobic comonomer is selected from the group consisting of N-alkylacrylamides such as N-(4-ethylphenyl)acrylamide, N-(4-t-butylphenyl) acrylamide.

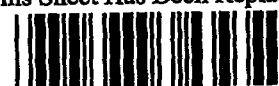
14. An emulsion explosive according to claim 9 wherein the associative thickener is a copolymer of acrylamide and N-4-(t-butyl)phenyl acrylamide comprising less than 1 % mol % hydrophobic comonomer.

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15. An emulsion explosive according to claim 9 wherein the associative thickener comprises blocks of hydrophobic co-polymer prepared with small amounts of hydrophilic comonomer.
16. An emulsion explosive according to claim 9 wherein the emulsion has increased zero-shear viscosity relative to an emulsion absent the associative thickener and exhibits significant reduction in viscosity when subjected to applied shear force and reestablishes substantially the original viscosity when the applied shear force is removed.
17. A method of manufacturing an emulsion explosive composition comprising incorporating at least one associative thickener in an aqueous phase and subsequently emulsifying the aqueous phase in an oil phase to form a water-in-oil emulsion.
18. A method of manufacturing an emulsion explosive composition according to claim 17 wherein the associative thickener comprises a chain of hydrophilic material soluble in the aqueous phase of the emulsion, and hydrophobic moieties insoluble in the insoluble phase which moieties are dispersed along said chain or are present as terminal groups.
19. A method of manufacturing an emulsion explosive composition according to claim 17 wherein the associative thickener comprises blocks of hydrophilic co-polymer prepared with small amounts of hydrophobic comonomer.
20. A method of manufacturing an emulsion explosive composition according to claim 19 wherein the hydrophilic copolymer is prepared from monomers selected from the group consisting of acrylamide, styrene, vinylpyrrolidone, vinyl acetate and acrylamide and its derivatives, poly(ethylene glycol), ethylene oxide, vinyl alcohol and propylene glycol and its derivatives.
21. A method of manufacturing an emulsion explosive composition according to claim 20 wherein the hydrophobic comonomer is selected from the group consisting of N-alkylacrylamides such as N-(4-ethylphenyl)acrylamide, N-(4-t-butylphenyl) acrylamide.



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22. A method of manufacturing an emulsion explosive composition according to claim 17 wherein the associative thickener is a copolymer of acrylamide and N-4-(t-butyl)phenyl acrylamide comprising less than 1 % mol % hydrophobic comonomer.

5 23. A method of manufacturing an emulsion explosive composition according to claim 17 wherein the emulsion has increased zero-shear viscosity relative to an emulsion absent the associative thickener and exhibits significant reduction in viscosity when subjected to applied shear force and reestablishes substantially the original viscosity when the applied shear force is removed.

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24. A method of manufacturing an emulsion explosive composition comprising incorporating at least one associative thickener in an oil phase and subsequently emulsifying an aqueous phase in the oil phase to form a water-in-oil emulsion.

15 25. A method of manufacturing an emulsion explosive composition according to claim 24 wherein the associative thickener comprises blocks of hydrophobic co-polymer prepared with small amounts of hydrophilic comonomer.

20 26. A method of manufacturing an emulsion explosive composition according to claim 24 wherein the emulsion has increased zero-shear viscosity relative to an emulsion absent the associative thickener and exhibits significant reduction in viscosity when subjected to applied shear force and reestablishes substantially the original viscosity when the applied shear force is removed.

