



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification³ : C08L 33/26, C08K 5/05, 5/06	A1	(11) International Publication Number: WO 85/ 04890 (43) International Publication Date: 7 November 1985 (07.11.85)
(21) International Application Number: PCT/US85/00681 (22) International Filing Date: 15 April 1985 (15.04.85) (31) Priority Application Number: 600,879 (32) Priority Date: 16 April 1984 (16.04.84) (33) Priority Country: US (71) Applicant: THE DOW CHEMICAL COMPANY [US/US]; 2030 Dow Center, Abbott Road, Midland, MI 48640 (US). (72) Inventor: STANLEY, Jr., Frederick, W. ; 305 E. Meadowbrook, Midland, MI 48640 (US). (74) Agent: RUSSELL, H., David; The Dow Chemical Company, P.O. Box 1967, Midland, MI 48641-1967 (US).		(81) Designated States: BE (European patent), BR, DE (European patent), FR (European patent), GB (European patent), IT (European patent), JP, NL (European patent). Published <i>With international search report.</i>
(54) Title: WATER-IN-OIL EMULSIONS OF HYDROPHOBE ASSOCIATION POLYMERS AND A METHOD FOR THE PREPARATION THEREOF (57) Abstract A stable water-in-oil emulsion of a hydrophobe associative copolymer of a water-soluble monomer such as acrylamide and a hydrophobic monomer such as dodecyl methacrylate is formed by subjecting a water-in-oil emulsion of the corresponding monomers to copolymerization conditions in the presence of an oil-soluble initiator such as cumene hydroperoxide. Such copolymers associate in aqueous media containing salts such as sodium chloride to increase the viscosity of such media.		

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WATER-IN-OIL EMULSIONS OF
HYDROPHOBE ASSOCIATION POLYMERS
AND A METHOD FOR THE PREPARATION THEREOF

This invention relates to water-in-oil emulsions of hydrophobe association polymers and a method for the preparation thereof.

As taught in Encyclopedia of Polymer Science and Technology, Interscience Publishers, Vol. I, 192 (1964), it is known that the viscosity of an aqueous medium is increased by the addition of a water-soluble polymer. Such water-soluble polymers include polyacrylamide, acrylamide/acrylic acid copolymer, sodium polyacrylate, carboxymethyl cellulose, hydroxyethyl cellulose, methyl cellulose, polysaccharide as well as naturally occurring gums such as guar gum and chemically modified gums such as hydroxypropyl guar gum. As a result of this thickening capability, there are many existing, as well as potential, industrial applications for aqueous media thickened with such water-swellable polymers. As taught in US Re 28,474, it is often desirable to prepare such polymers in the form of water-in-oil emulsions which are then inverted into aqueous media at the time of use.

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Unfortunately, however, the aforementioned conventional water-soluble polymers suffer from many serious deficiencies or limitations in actual use in such industrial applications. For example, in many commercial applications, the polymers are exposed to shearing conditions which physically degrade them to lower molecular weight polymers thereby causing reduction of viscosity for the aqueous media containing them. Also, aqueous media containing the ionic water-soluble polymers exhibit substantial viscosity reduction when electrolytes are introduced into the media as is common in many applications, particularly in enhanced oil recovery. Finally, exposure of the aqueous media to high temperatures as is necessary for many applications normally causes a reduction in viscosity.

In attempts to overcome some of the aforementioned deficiencies of the conventional water-soluble polymers, it has been a common practice to cross-link the polymer in order to improve resistances to thermal as well as shear degradation. See, for example, US 3,247,171. Such attempts have generally not been successful. More recently, as taught in US 3,984,333, an aqueous medium has been thickened by dissolving a block copolymer having water-soluble blocks and water-insoluble blocks in the aqueous medium. While such block copolymers apparently exhibit reasonably good resistance to shear degradation, such polymers are difficult and often impractical to prepare. More importantly, such polymers do not exhibit significant tolerance of electrolytes normally present in the aqueous media to be thickened.

More recently, it has been discovered, as taught in US 4,432,881, to employ hydrophobe association

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copolymers of water-soluble ethylenically unsaturated monomers and hydrophobic ethylenically unsaturated copolymers in combination with nonionic surfactants in order to overcome many of the aforementioned deficiencies of the conventional water-soluble polymers and recently developed substitutes therefore. Unfortunately, such hydrophobe association polymers could not be readily made in the form of emulsions and thus were not as easily handled and utilized as is desired for many applications.

10 The present invention is, in one aspect, a stable water-in-oil emulsion comprising (1) a continuous oil phase and dispersed therein (2) a discontinuous aqueous phase containing a hydrophobe associative copolymer of an ethylenically unsaturated, water-soluble
15 monomer (hereinafter called a water-soluble monomer) and an ethylenically unsaturated monomer having a hydrophobic moiety having at least 8 carbon atoms capable of associating with similar hydrophobic moieties or hydrophobic groups of a water-soluble surfactant (hereinafter this
20 monomer is called a hydrophobe monomer).

 In another aspect, the present invention is a disperse phase polymerization method for making the aforementioned stable water-in-oil emulsion which method comprises subjecting a water-in-oil emulsion containing a
25 water-soluble, ethylenically unsaturated monomer and an ethylenically unsaturated monomer having an associating hydrophobic moiety, to copolymerization conditions in the presence of an initiating amount of an oil-soluble, vinyl polymerization initiator. Surprisingly, by carrying out
30 the copolymerization in the presence of the oil-soluble initiator, the resulting copolymer exhibits greater hydrophobe associative characteristics than do copolymers

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prepared by disperse phase polymerization in the presence of the water-soluble initiators that are commonly employed in conventional disperse phase polymerization.

The copolymers prepared in the practice of this invention are useful in all applications which require aqueous media having increased viscosity such as for example, drilling mud formulations, fracturing fluids, liquid mobility control agents, aqueous solutions of inorganic salts, hydraulic fluids, lubricants, friction reducing agents, suspending agents, and aqueous suspensions of insoluble particulates such as paint formulations.

The emulsions of the present invention are stable water-in-oil emulsions wherein the dispersed phase is an aqueous phase having dispersed therein a hydrophobe associative copolymer, as defined herein, and the continuous oil phase is a water-immiscible inert organic liquid. The ratio of the aqueous phase to the oil phase is suitably any ratio that permits the formation of a water-in-oil emulsion. Preferably, however, based on the total weight of the water-in-oil emulsion, the disperse phase constitutes from 50 to 90, more preferably from 65 to 80, weight percent of the emulsion. The continuous oil phase preferably constitutes from 10 to 50, more preferably from 20 to 35, weight percent of the emulsion. While the amount of copolymer present in the emulsion is not particularly critical, it is preferably in the range from 10 to 60, most preferably from 20 to 50, weight percent based on the emulsions.

The hydrophobe associative copolymer is a copolymer of a water-soluble ethylenically unsaturated monomer and an ethylenically unsaturated monomer having a

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hydrophobe associative moiety. By "hydrophobe associative" is meant that, in aqueous media, the hydrophobic moieties of the polymer associate with each other or with hydrophobic moieties of another compound such as a surfactant present in the aqueous medium, thereby increasing the viscosity of the aqueous medium. Additionally, it is observed that this property of hydrophobic association is even further enhanced by the addition of a water-soluble electrolyte to the aqueous medium. This further enhancement (increase) of viscosity resulting from the addition of the electrolyte occurs in the absence of any precipitation or phase separation. In fact, the occurrence of such precipitation or phase separation upon addition of the electrolyte is not desirable in the practice of this invention.

The hydrophobe associative copolymer is predominantly hydrophilic in that it is soluble to a level of at least 0.1 weight percent in an aqueous medium consisting of 0.2 weight percent of sodium chloride and 0.01 weight percent of a water-soluble, nonionic surfactant, as defined hereinafter, all percentages being based on the aqueous medium. However, it contains sufficient hydrophobic moieties to increase the viscosity of an aqueous medium containing a suitable water-dispersible surfactant as defined hereinafter. Preferably, the concentration of hydrophobic groups in the polymer is such that, when 0.5 weight part of the polymer is dissolved in 100 weight parts of the aqueous medium containing at least 0.01 weight percent of the surfactant and at least one weight percent of sodium chloride, the Brookfield viscosity (as defined hereinbefore) of the aqueous medium is substantially higher than, e.g., at least twice, that of a similar aqueous medium except that the polymer is

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identical in all respects to the hydrophobe associative polymer except that it contains no hydrophobic groups. For example, if an aqueous solution containing one weight percent of a surfactant, one weight percent of sodium chloride and one weight percent of polyacrylamide (hydrophilic polymer) has a Brookfield viscosity of 10 cps (0.01 Pa·s), the aqueous solution containing one weight percent of the same surfactant, one weight percent of sodium chloride and one weight percent of a suitable hydrophilic/hydrophobic polyacrylamide, e.g., an acrylamide/dodecyl acrylate copolymer having a M_w equivalent to the polyacrylamide, will have a Brookfield viscosity of at least 20 cps (0.02 Pa·s).

Exemplary preferred copolymers include copolymers of from 90 to 99.995, more preferably from 98 to 99.995, most preferably from 99 to 99.9, mole percent of one or more water-soluble monomers with from 0.005 to 10, more preferably from 0.005 to 2, most preferably from 0.1 to 1, mole percent of one or more hydrophobic monomers. For these polymers, it is found that preferred amounts of hydrophobic monomers will vary with the molecular weight of the polymer. For example, a hydrophilic/hydrophobic polymer having a weight average molecular weight near 200,000, preferably contains from 1 to 2 mole percent of hydrophobic monomer. Alternatively, the hydrophilic/hydrophobic polymer having a weight average molecular weight of 2 million preferably contains from 0.05 to 0.25 mole percent of hydrophobic monomer.

In general, the molecular weight of the hydrophobe associative copolymer is low enough such that an aqueous medium containing 0.1 weight percent of the polymer can be subjected to a degree of shear on the order of

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10,000 sec^{-1} without causing the polymer to degrade significantly. Moreover, the polymer has a molecular weight such that, when 0.5 weight part of the polymer and 0.5 weight part of the surfactant are dissolved in 100 weight parts of water, the Brookfield viscosity of the water is increased to at least 2 centipoises (0.002 Pa·s) (as measured using a Brookfield LVT viscometer equipped with a UL adaptor and operated at 6 rpm and 25°C). While polymers having very high molecular weight, e.g., weight average molecular weight (M_w) greater than 5 million, can be suitably employed, such polymers tend to degrade when subjected to high shear, e.g., in excess of 10,000 sec^{-1} . Accordingly such polymers are less preferred for some applications. Preferably, the hydrophilic/hydrophobic polymers used in this invention have weight average molecular weights (M_w) as determined by the intrinsic viscosity method described in the examples in the range from 200,000 to 5 million, most preferably from 800,000 to 2.5 million.

Water-soluble monomers suitably employed in the hydrophobe associative copolymers include those which are sufficiently water-soluble to form at least a 10 weight percent solution when dissolved in water and readily undergo addition polymerization to form polymers which are water-soluble. Exemplary water-soluble monomers include ethylenically unsaturated amides such as acrylamide, methacrylamide and fumaramide and their N-substituted derivatives such as 2-acrylamido-2-methylpropane sulfonic acid (AMPS), N-(dimethylaminomethyl)acrylamide as well as N-(trimethylammoniummethyl)acrylamide chloride and N-(trimethylammoniumpropyl)methacrylamide chloride; ethylenically unsaturated carboxylic acids such as acrylic acid, methacrylic acid, itaconic acid and fumaric acid;

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and other ethylenically unsaturated quaternary ammonium compounds such as vinylbenzyl trimethyl ammonium chloride, sulfoalkyl esters of unsaturated carboxylic acids such as 2-sulfoethyl methacrylate, aminoalkyl esters of unsaturated carboxylic acids such as 2-aminoethyl methacrylate, vinyl amines such as vinyl pyridine and vinyl morpholine, diallyl amines and diallyl ammonium compounds such as diallyl dimethyl ammonium chloride, vinyl heterocyclic amides such as vinyl pyrrolidone, vinylaryl sulfonates such as vinylbenzyl sulfonate as well as the salts of the foregoing monomers. Of the foregoing water-soluble monomers, acrylamide and combinations of acrylamide and acrylic acid, including salts of acrylic acid such as sodium acrylate or ammonium acrylate, are preferred. Acrylamide and combinations thereof with up to 75 mole percent of acrylic acid or salt thereof, based on total water-soluble monomer, are more preferred. Most preferred are polymers wherein the water-soluble monomer is a mixture of acrylamide with from 5 to 50 mole percent, especially from 5 to 30 mole percent of acrylic acid or salt thereof.

Suitable hydrophobic monomers include those which are (1) water-insoluble, i.e., less than 0.2 weight part of the hydrophobic monomer will dissolve in 100 weight parts water and (2) ethylenically unsaturated compounds having hydrophobe associative groups (herein-called hydrophobic moieties).

The hydrophobic moieties preferably have at least 8 carbon atoms and are most preferably pendant organic groups having hydrophobicities comparable to one of the following: aliphatic hydrocarbon groups having at least four carbons such as C_4 to C_{20} alkyls and cycloalkyls; polynuclear aromatic hydrocarbon groups such as

naphthyls; alkylaryls wherein alkyl has one or more carbons, preferably 4 to 8 carbons; haloalkyls of 4 or more carbons, preferably perfluoroalkyls; polyalkyleneoxy groups wherein alkylene is propylene or higher alkylene and there is at least 1 alkyleneoxy unit per hydrophobic moiety. Exemplary hydrophobic monomers include the higher alkyl esters of α, β -ethylenically unsaturated carboxylic acids such as dodecyl acrylate, dodecyl methacrylate, tridecyl acrylate, tridecyl methacrylate, tetradecyl acrylate, tetradecyl methacrylate, octadecyl acrylate, octadecyl methacrylate, ethyl half ester of maleic anhydride, diethyl maleate, and other alkyl esters derived from the reactions of alkanols having from 4 to 20, preferably from 8 to 20, carbon atoms with ethylenically unsaturated carboxylic acids such as acrylic acid, methacrylic acid, maleic anhydride, fumaric acid, itaconic acid and aconitic acid; alkylaryl esters of ethylenically unsaturated carboxylic acids such as nonyl- α -phenyl acrylate, nonyl- α -phenyl methacrylate, dodecyl- α -phenyl acrylate and dodecyl- α -phenyl methacrylate; N-alkyl, ethylenically unsaturated amides such as N-octadecyl acrylamide, N-octadecyl methacrylamide, N,N-dioctyl acrylamide and similar derivatives thereof; α -olefins such as octene-1, decene-1, dodecene-1 and hexadecene-1; vinyl alkylates wherein alkyl has at least 8 carbons such as vinyl laurate and vinyl stearate; vinyl alkyl ethers such as dodecyl vinyl ether and hexadecyl vinyl ether; N-vinyl amides such as N-vinyl lauramide and N-vinyl stearamide; and ar-alkylstyrenes such as t-butyl styrene. Of the foregoing hydrophobic monomers, the alkyl esters of acrylic acid, methacrylic acid, N-alkyl acrylamides and N-alkyl methacrylamides wherein alkyl has from 8 to 20 carbon atoms, and the alkyl styrenes wherein alkyl has from 4 to 8 carbons such as t-butyl, are preferred. The alkyl methacrylates wherein

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alkyl has from 10 to 20 carbon atoms and t-butyl styrene are more preferred. Dodecyl methacrylate and N-dodecyl methacrylamide are the most preferred where hydrolysis is not a problem. In applications wherein hydrolysis is a problem such as in caustic floods, t-butyl styrene is most preferred.

Emulsions of the aforementioned hydrophobe-associative copolymers are advantageously prepared by copolymerizing the water-soluble monomers with hydrophobic monomers dispersed in a water-in-oil emulsion. The conditions and procedures employed are generally those described in US 3,284,393; US 3,624,019; and US 3,734,873, except that an oil-soluble initiator is employed. Employing such conditions and procedures, an aqueous solution of water-soluble monomer(s) is first dispersed in the inert hydrophobic organic liquid containing the hydrophobic monomer and a sufficient amount of a water-in-oil emulsifying agent to form a water-in-oil emulsion.

The water-immiscible oil phase of the emulsion generally comprises at least one inert hydrophobic liquid. Usually such liquid is an organic liquid such as a liquid hydrocarbon or substituted hydrocarbon. Preferred organic liquids are the halogenated hydrocarbons such as perchloroethylene, methylene chloride and the like as well as liquid hydrocarbon having from 4 to 15 carbons per molecule including aromatic and aliphatic hydrocarbons and mixtures thereof, e.g., benzene, xylene, toluene, mineral oils, liquid paraffins such as kerosene, naphtha and the like. Of the foregoing organic liquids, the hydrocarbons are the more preferred, with aliphatic hydrocarbons being most preferred.

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Emulsifiers suitably employed for purposes of emulsifying the aqueous phase in the oil phase are those emulsifiers that promote the formation and stabilization of water-in-oil emulsions. Normally such emulsifiers have a hydrophilic-lipophilic balance (HLB) in the range from 2 to 9, most preferably from 3 to 6. Preferably, the emulsifying agent is sorbitan monooleate, the reaction product of oleic acid with isopropanolamide or a mixture thereof. Other suitable emulsifying agents include, for example, hexadecyl sodium phthalate, decyl sodium phthalate, octadecyl sodium phthalate, sorbitan monooleate, sorbitan stearate, glycerine mono- or distearate and combinations of such emulsifying agents. Generally, the emulsifier is used in amounts sufficient to provide the desired water-in-oil emulsion. This amount is normally in the range from 0.1 to 20, preferably from 3 to 5, weight percent based on the weight of monomer.

Prior to polymerization, an oil-soluble free-radical generating initiator is added to the emulsion. By an "oil-soluble" catalyst is meant one which is sufficiently soluble in the oil phase of the emulsion that an initiating amount, preferably from 0.01 to 90, most preferably from 0.1 to 90, weight percent of the catalyst based on the oil phase will dissolve in the oil phase. Examples of preferred oil-soluble initiators include diisopropyl peroxydicarbonate, 4-(t-butylperoxylperoxycarbonyl)-3-hexyl-6-[7-(t-butylperoxycarbonyl)heptyl]-cyclohexene (4-TBPCH), cumene hydroperoxide and t-butyl peroxyneodecanoate, with 4-TBPCH and cumene hydroperoxide being most preferred. Examples of suitable, but less preferred initiators include t-butyl hydroperoxide and benzoyl peroxide. The oil-soluble initiator is added in a catalytic amount, preferably from 0.001 to 10, most

preferably from 0.01 to 1, weight percent based on total monomers. In addition to the aforementioned ingredients, the emulsion polymerization recipe optionally includes, for example, chain transfer agents, chelating agents,
5 buffers, and salts.

The resulting stable water-in-oil emulsion of monomer(s) is then heated under free-radical forming conditions in order to copolymerize the monomers to form a water-in-oil emulsion of the hydrophobe associative
10 polymer.

The temperature of copolymerization is any temperature which is sufficient to cause the initiator to form free radicals, preferably from 10°C to 90°C, most preferably from 20°C to 60°C. The copolymerization is
15 typically carried out under an inert atmosphere such as a nitrogen atmosphere.

When ready for use, the resulting emulsions are readily inverted into an aqueous phase by adding a water-soluble surfactant such as described in US 3,624,019.
20 Preferably, this inverting surfactant is a nonionic water-dispersible surfactant having hydrophobe moieties capable of associating in an aqueous medium with the hydrophobic groups of the hydrophobe associative copolymer, thereby causing a significant increase in viscosity of
25 the aqueous medium under the conditions described in U.S. Patent 4,432,881. Examples of water-dispersible surfactants preferred for this purpose include alkyl polyethyleneoxy compounds represented by the formula, $RO(EO)_n-H$, wherein R is C_8-C_{18} alkyl, EO is ethyleneoxy and n is a number
30 from 1 to 10. Other suitable nonionic surfactants are described in McCutcheon's, Detergents and Emulsifiers,

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North American Edition, 1980 Annual. Of the foregoing surfactants, the ethoxylated alkyl phenol and ethyloxylated fatty alcohols are more preferred. Usually, the ratio of the surfactant to hydrophobe associative copolymer is one that produces a viscosity at least twice that of a solution containing only the polymer. Preferably, the weight ratio of the copolymer to surfactant is from 20:1 to 0.5:1, most preferably from 10:1 to 1:1.

The amount of hydrophobic associative composition, i.e., the combination of hydrophobe associative copolymer and surfactant, in the aqueous medium being used is sufficient to provide the desired increase in viscosity of the aqueous medium. Preferably, such amounts of agent range from 0.01 to 1.5 weight percent, most preferably from 0.05 to 1 weight percent, based on the aqueous medium.

In addition to the hydrophobe associative copolymer and water-dispersible surfactant, the hydrophobic associative composition may also contain or be used in combination with a non-polymeric, water-soluble electrolyte including salts of monovalent and divalent cations such as, for example, ammonium, alkali metal and alkaline earth metal chlorides, bromides, nitrates, sulfates, carbonates, and acetates; monobasic and di- and tribasic acids such as, for example, hydrochloric acid, sulfuric acid, phosphoric acid and oxalic acid; and monovalent bases such as, for example, sodium hydroxide and potassium hydroxide. Such electrolytes may be present in the aqueous media as in the case of brines and other aqueous media containing water-soluble salts of various metals and other water-soluble electrolytes. Such aqueous media often contain from 0.01 to 20 weight percent of

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salts of alkali metals and alkaline earth metals. These electrolytes generally reduce the critical micelle concentration of the surfactant when added to an aqueous medium containing the surfactant. Thus, such electrolytes
5 enhance hydrophobic association between the hydrophobe associative copolymer and the water-dispersible surfactant.

In addition to the hydrophobic associative composition and electrolyte (salt), the aqueous medium may contain a variety of other ingredients common to
10 mobility control fluids, fracturing fluids, drilling muds, or other additives depending upon the intended use of the aqueous medium. The aqueous medium may also contain various additives such as, for example, anti-oxidants and antimicrobials, stabilizers, and fillers.

15 In general, the hydrophobe associative compositions described herein are useful in the same applications and under the same conditions as disclosed for the hydrophobe associative compositions described in U.S. patent 4,432,881.

20 The following examples are given to illustrate the invention and should not be construed as limiting its scope. Unless otherwise indicated, all parts and percentages are by weight.

A. Emulsion Preparation

25 Example 1

A water-in-oil emulsion of an acrylamide/dodecyl methacrylate copolymer is prepared by first dispersing 112.5 g of acrylamide and 0.09 g of the pentasodium salt

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of diethylenetriaminepentaacetic acid in 166.5 g of water to form the aqueous phase. The oil phase is made by dissolving 2.25 g of sorbitan monooleate, 3.3 g of isopropanolamide of oleic acid, and 12 g of dodecyl methacrylate in 103.2 g of Isopar[®] M (a liquid hydrocarbon). The aqueous phase is then added to the oil phase in a Waring blender operating at its highest speed. The resulting water-in-oil emulsion is transferred to a 500-ml resin pot equipped with an agitator and a N₂ purge tube. After the pot is purged with nitrogen for one hour, 1 g of a 10 percent solution of diisopropyl peroxydicarbonate in Isopar[®] M, a preferred oil-soluble initiator is added to the emulsion at 20°C while continuing the nitrogen purge and agitation of the emulsion. The temperature of the emulsion rises to 50°C in 20 minutes and is maintained in the range of 40°C-50°C during the remainder of the polymerization (i.e., about 4 hours). The resulting water-in-oil emulsion of acrylamide/dodecyl methacrylate copolymer (32.5 percent polymer solids) is recovered from the resin pot.

Example 2

Following the procedure of Example 1, a water-in-oil emulsion containing the monomers used in Example 1 is prepared and purged with N₂ for one hour. To the emulsion at 24°C is added 1 ml of a 10 percent solution of 4-(t-butylperoxylperoxycarbonyl)-3-hexyl-6-[7-(t-butylperoxycarbonyl)heptyl]cyclohexene in Isopar[®] M, and a nitrogen stream containing 0.1 percent SO₂ is bubbled into the emulsion thereby providing a preferred oil-soluble redox initiator. The temperature rises to 50°C in 10 minutes and is maintained in the range of 40°C-50°C during the remainder of the copolymerization (i.e., about 4 hours).

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Example 3

A water-in-oil emulsion of acrylamide/dodecyl methacrylate copolymer is made following the procedure of Example 1 except that 1 ml of an aqueous solution of t-butyl hydroperoxide (0.36 g in 10 ml of water) is employed as suitable oil-soluble (>50 percent) initiator which is also slightly (1-5 percent) soluble in water. The polymerization is initiated by bubbling a stream of nitrogen containing 0.1 percent SO₂ through the emulsion at 20°C. The temperature of the emulsion increased to 45°C in 10 minutes and is maintained at 45°C for the remainder of the copolymerization (i.e., about 4 hours). The resulting water-in-oil emulsion containing 32.5 percent copolymer solids is recovered.

15 Example C (Comparison example)

A water-in-oil emulsion of an acrylamide/dodecyl methacrylate is made following the procedure of Example 1 except that 2 ml of an aqueous solution of 2,2'-azobis(amidinopropane)hydrochloride (0.56 g in 10 ml of H₂O) is employed as a water-soluble, oil-insoluble initiator and is added to the aqueous phase prior to forming the emulsion. The emulsion is heated to 35°C and maintained in the range of 40°C-50°C until polymerization is completed (i.e., about 4 hours).

25 B. Polymer Evaluation

To more clearly observe the association effects and remove any interferences of the emulsifiers, polymers are precipitated from the emulsions using methanol. The procedure is as follows: 100 g of emulsion is added to 500 ml of methanol in a Waring blender. After stirring

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for 1 minute, the resulting suspension is filtered.
After filtration the sample is resuspended in 500 ml of
MeOH and filtered two additional times. The copolymer is
air dried overnight. Infrared analyses of the copolymer
5 shows it to be free of emulsifying surfactants.

To test for association, the copolymer solu-
tions are made up in 3 percent NaCl containing various
levels of a hydrophobe associative surfactant. The pro-
cedure is as follows: To 100 g of a 0.75 percent solu-
10 tion of polymer in 3 percent solution of sodium chloride
in water is added 0, 20, 40, 60, 80 and 100 percent of an
ethoxylated aliphatic alcohol based on copolymer. Sub-
sequently, an aqueous solution of sodium lauryl sulfate
is added to the resulting solutions. The solutions are
15 shaken until the copolymer dissolves. The viscosities of
the solutions are then measured using a Brookfield LVT
SC4 viscometer at 25°C. A 18/13 spindle is used at 6
rpm. The data is shown in Table I.

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TABLE I

	Sample No.	Copolymer ¹	% NaLS ²	% TDA-6 ³	Viscosity ⁴ cps	(Pa·s)
5	1	Ex. 1	0.075	0	insoluble	
	2	Ex. 1	0.075	20	900	(0.900)
	3	Ex. 1	0.075	40	1200	(1.200)
	4	Ex. 1	0.075	60	1200	(1.200)
	5	Ex. 1	0.075	80	1400	(1.400)
	6	Ex. 1	0.075	100	1600	(1.600)
10	7	Ex. 2	0.075	0	insoluble	
	8	Ex. 2	0.075	20	300	(0.300)
	9	Ex. 2	0.075	40	600	(0.600)
	10	Ex. 2	0.075	60	1500	(1.500)
	11	Ex. 2	0.075	80	not measured	
15	12	Ex. 2	0.075	100	3500	(3.500)
	13	Ex. 3	0.075	0	insoluble	
	14	Ex. 3	0.075	20	100	(0.100)
	15	Ex. 3	0.075	40	110	(0.110)
	16	Ex. 3	0.075	60	120	(0.120)
20	17	Ex. 3	0.075	80	250	(0.250)
	18	Ex. 3	0.075	100	340	(0.340)
	19*	Ex. C	0.075	0	325	(0.325)
	20*	Ex. C	0.075	20	280	(0.280)
	21*	Ex. C	0.075	40	250	(0.250)
25	22*	Ex. C	0.075	60	350	(0.350)
	23*	Ex. C	0.075	80	400	(0.400)
	24*	Ex. C	0.075	100	410	(0.410)

*Not an example of the invention.

30 ¹Copolymer as described in the named example at 0.75 percent concentration based on the aqueous medium (including 3% NaCl) being tested for viscosity.

35 ²NaLS - an aqueous solution of 10% sodium lauryl sulfate in water is added to the aqueous medium to provide the concentration indicated which is based on the weight of the aqueous medium being tested for viscosity.

40 ³TDA-6 - ethoxylated tridecyl ether added as 100% active composition to provide the indicated concentration based on the aqueous medium being tested for viscosity.

45 ⁴Brookfield viscosity in centipoise using a Brookfield LVT SC4 viscometer operating a 18/13 spindle at 6 rpm and 25°C.

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Only the copolymer made with the water-soluble initiator (Example C) is soluble in 3 percent salt solution. The rest are either partially or completely water-insoluble. However, as TDA-6 surfactant is added

5 the viscosity of these solutions (Examples 1-3) increases dramatically while the copolymer made with a water-soluble initiator changed only slightly. Also the copolymers made with completely oil-soluble initiators (Examples 1

10 made with TBHP which is partially soluble in both the oil and aqueous phases. The increase in viscosity with surfactant addition is typical behavior of association polymers as the surfactant associates with the hydrophobic groups to solubilize the polymer.

1. A stable water-in-oil emulsion comprising (1) a continuous oil phase and dispersed therein (2) a discontinuous aqueous phase containing a hydrophobe associative copolymer of an ethylenically unsaturated water-soluble monomer and an ethylenically unsaturated monomer having a hydrophobic moiety having at least 8 carbon atoms capable of associating with a similar hydrophobic moieties or hydrophobic groups of a water-soluble surfactant.

2. The emulsion of Claim 1 wherein the copolymer is a copolymer of from 40 to 99.9 mole percent of acrylamide, from 0 to 50 mole percent of acrylic acid and from 0.1 to 10 mole percent of an alkyl methacrylate or acrylate wherein alkyl has from 8 to 12 carbon atoms, or an aralkyl styrene wherein alkyl has from 4 to 8 carbons, said copolymer having a weight average molecular weight in the range from 800,000 to 2.5 million.

3. The emulsion of Claim 2 wherein the oil phase is a normally liquid aliphatic hydrocarbon.

4. An aqueous composition comprising the emulsion of Claim 1 and an inverting amount of a nonionic

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water-dispersible surfactant having hydrophobic moieties capable of associating with the hydrophobic moieties of the copolymer of the emulsion.

5. The composition of Claim 4 wherein the nonionic surfactant is an ethoxylated aliphatic alcohol or an alkyl polyethyleneoxy glycol monoether or alkylaryl polyethyleneoxy glycol monoether wherein alkyl has from 8 to 20 carbon atoms and from 1 to 20 ethyleneoxy groups per polymer molecule.

6. The composition of Claim 5 which contains an amount of a water-soluble non-polymeric electrolyte sufficient to increase the viscosity of the composition.

7. The composition of Claim 9 wherein the electrolyte is a salt of alkali metal or alkaline earth metal or a combination of two or more of such salts.

8. A disperse phase polymerization method which comprises subjecting a water-in-oil emulsion containing a water-soluble, ethylenically unsaturated monomer and an ethylenically unsaturated monomer having an associating hydrophobic moiety, to copolymerization conditions in the presence of an initiating amount of an oil-soluble, vinyl polymerization initiator thereby forming the emulsion of Claim 1.

9. The method of Claim 8 wherein the oil-soluble initiator is diisopropyl peroxydicarbonate, 4-(t-butylperoxylperoxycarbonyl)-3-hexyl-6-[7-(t-butylperoxycarbonyl)heptyl]cyclohexene, cumene hydroperoxide or t-butylperoxyneodecanoate.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US85/00681

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁵		
According to International Patent Classification (IPC) or to both National Classification and IPC INT. CL. C08L 33/26; C08K 5/05; C08K 5/06 U.S. CL. 524/804, 827, 831		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁴		
Classification System	Classification Symbols	
U.S.	524/804, 827, 831	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁶		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴		
Category [*]	Citation of Document, ¹⁶ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No. ¹⁸
A	US, A, 3,247,171 (WALKER ET AL) 19 APRIL 1966	1-9
A	US, A, 3,284,393 (VANDERHOFF ET AL) 08 NOVEMBER 1966	1-9
A	US, A, 3,624,019 (ANDERSON ET AL) 30 NOVEMBER 1971	1-9
A	US, A, 3,734,873 (ANDERSON ET AL) 22 MAY 1973	1-9
A	US, A, 3,984,333 (VAN de KRAATS ET AL) 05 OCTOBER 1976	1-9
A	US, A, 3,998,777 (CONNELLY ET AL) 21 DECEMBER 1976	1-9
A	US, A, 4,090,992 (SCANLEY) 23 MAY 1978	1-9
A	US, A, 4,147,681 (LIM ET AL) 03 APRIL 1979	1-9
A	US, A, 4,180,637 (EVANI ET AL) 25 DECEMBER 1979	1-9
A	US, A, 4,200,720 (EVANI ET AL) 29 APRIL 1980	1-9
A	US, A, 4,330,450 (LIPOWSKI ET AL) 18 MAY 1982	1-9
<p>[*] Special categories of cited documents: ¹⁵</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search ¹	Date of Mailing of this International Search Report ²	
14 MAY 1985	04 JUN 1985	
International Searching Authority ¹	Signature of Authorized Officer ²⁰	
ISA/US	RONALD W. GRIFFIN	

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, ¹⁶ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No ¹⁸
A	US, A, 4,432,881 (EVANI ET AL) 21 FEBRUARY 1984	1-9
A	US, A, 4,435,528 (DOMINA) 06 MARCH 1984	1-9
T	US, A, 4,452,940 (ROSEN) 05 JUNE 1984	1-9
A	EP, A, 0074660 (FAN ET AL) 23 MARCH 1983	1-9