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(54) Emulsified water-based functional fluids thickened with water-soluble polymers containing hydrophobic groups

(57) An oil-in-water emulsified, preferably microemulsified, water-based functional fluid, e.g., metal working fluid, having improved rheological and/or anti-misting properties which contains polymer, oil, surfactant, and water. The polymer contains water soluble nonionic monomer species, e.g., acrylamide, water soluble anionic monomer species, e.g., Na acrylate, and water insoluble monomer species, e.g., N, N-dialkylacrylamide. The polymer acts as a thickener. The oil may be a mineral oil or a C_5 to C_{18}- alkane. The surfactant may be anionic or nonionic e.g. a metal organo sulfonate. In examples the polymeric thickener is a terpolymer of acrylamide, sodium acrylate and N-n-octyl acrylamide.

EMULSIFIED WATER-BASED FUNCTIONAL FLUIDS THICKENED WITH WATER-SOLUBLE POLYMERS CONTAINING HYDROPHOBIC GROUPS

Field of the Invention

This invention relates to:

(1) oil-in-water emulsified, preferably micro-emulsified water-based functional fluids thickened with certain water-soluble polymers derived from both water-soluble and water-insoluble monomers; and

(2) emulsified and emulsifiable systems with certain water based polymers, e.g., concentrates, which can form said water-based functional fluids.

Background of the Invention

The term "functional fluid" is used herein to refer to liquid systems which, very generally, can exercise a function, and primarily is used to refer to so-called working fluids, such as hydraulic fluids, metalworking fluids, glassworking fluids, quench fluids, rolling fluids and the like.

As a class, metalworking fluids can be characterized as capable of being utilized in one or more operations involving the manipulation of metals, including for example, rolling, forging, hot-pressing, blanking, bending, stamping, drawing, cutting, punching, spinning, quenching and the like.

Typical functions performed by a metalworking fluid in such operations include lubricating, enhancing the metal surface finish, increasing tool lifetime, cooling of the workpiece, flushing of debris away from the metal workpiece, and reducing energy requirements.

In addition, it is desirable that the metalworking fluids: are compatible with hard water, avoid staining of non-ferrous metals such as aluminum, copper or their alloys, exhibit good stability and long batch life, avoid excessive foam formation, avoid sediment or residues and inhibit melting.

Water-based functional fluids are not a new concept. However in recent times, the increasing cost and scarcity of petroleum has made it increasingly desirable to replace oil-based functional fluids with water-based functional fluids whenever possible. Other benefits can also flow from such replacements such as decreased fire hazard and environmental pollution problems, and a cleaner and safer workplace.

For example, one problem associated with oil-based metalworking functional fluids which has recently received attention is their effect on the upper respiratory tract of workers. Metalworking operations typically produce air-borne mists, fogs, and/or aerosols which carry materials found in the working fluid. Inhalation of such materials and/or bacteria growing in the same can lead to health problems. (*See* for example, Bennett, E. O. et al., "Occupational Airway Diseases in the Metalworking Industry", Tribology Vol. 18, No. 3 (June 1985)).

While water-based functional fluids may be viewed in general as being less hazardous to health than oil-based fluids, the misting thereof is still considered to be undesirable as well as uneconomical. Water-based mists are potential vectors for the spread of bacteria, and those mists derived from water based functional fluids can be irritating because they normally do not possess a neutral pH.

Consequently, it would be advantageous, from a health standpoint, to reduce misting as much as possible of even water-based fluids.

The replacement of oil-based functional fluids with water-based ones is not a simple task because it is difficult to modify the latter in their properties so as to perform to the same high degree as their oil-based counterparts.

For example, the oil in an oil-based functional fluid exhibits Newtonian behavior and a viscosity that is not only higher than water, but also fairly constant throughout the lifetime of fluid at prolonged high shear rates. Thus, one of the problems in formulating suitable water-based functional fluids has been to find a way to approximate the rheology of an oil-based system. This is sought to be achieved by the selection of thickening agents that provide the desired degree of thickening and at the same time are stable under high shear conditions.

The primary function of a thickener is to adjust the viscosity of the fluid to meet various technical requirements. Typical thickeners are polymeric materials.

The selection of a suitable thickener is complicated by the fact that water-based functional fluids can be formulated to present at least two distinctly different environments. These environments are characterized herein as solution and emulsion types.

In water-based solutions, the thickener is dissolved in water along with other additives needed to impart the desired characteristics to the fluid. Solution-type or synthetic fluids do not contain oil, but may or may not contain surfactant to aid in solubilizing the thickener. When surfactant is present, aggregates called micelles may form which can interact with the polymer to influence compatibility and fluid properties. Nevertheless, even where surfactants are employed, the thickener, in solution-type fluids, does not have to contend with oil-water interfacial boundary interactions of emulsion-type fluids.

Emulsion-type or semi-synthetic fluids, in contrast, contain oil (or non-polar equivalents), water, surfactant and whatever additional additives are needed to impart desired fluid properties. Consequently, the addition of a thickener thereto (depending on its physical properties) can impact on the characteristics of the emulsified system in a manner different than the way it does in a solution-type fluid because of the different interactions involved.

Undesirable interactions between surfactant and thickener in emulsion based systems can be exhibited as instability in the emulsion whereby phase separation occurs. Another undesirable interaction may result in gelation of a concentrate from which the final emulsion is derived. A gelled concentrate makes dilution to the final fluid difficult. In addition, the presence of surfactant may reduce the frictional resistance between polymeric chains and, thus, reduce the thickening effectiveness of the polymer.

The selection of a suitable thickener is further complicated by the variation in rheological properties which are induced thereby.

For example, in the case of many synthetically prepared polymer thickeners, the viscosity increasing action is rapidly reduced by such influences as high shear or extensional flow and/or heat. Furthermore, many polymer solutions exhibit, even at moderate thickener contents, strongly non-Newtonian flow phenomena, which manifests itself, in most cases, as a drastic reduction in viscosity as the shear rate increases and/or at higher temperatures in the system.

The reduction in viscosity in many instances becomes irreversible when the polymer chains are broken under high shear stress.

Thus, the most desirable thickeners impart adequate shear stability to the functional fluid, even at high shear loads, and quasi-Newtonian flow properties within a wide range of shear rates.

Another factor to be considered in the selection of a thickener is its thickening effectiveness per unit weight (i.e., thickening efficiency). As thickening efficiency increases, less thickener is needed to achieve a given effect, and the cost attributable to thickener is reduced. In addition, the less thickener used, the lower becomes the probability of adverse side effects induced by the thickener, such as instability and incompatibility with other fluid components.

Sensitivity to constituents which cause hardness (multi-valent metal ions) in water is still another property which affects thickener selection. Thus, for example, a fluid which exhibits high viscosity and desirable flow behavior in deionized water may revert to low viscosity and undesirable flow behavior in hard water because of thickener interactions. Hardness in the form of calcium and magnesium ions can also cause phase separation of emulsion-type fluids.

Many natural thickeners such as natural gums, resins, carbohydrates and cellulosics suffer from unacceptably high rates of biodegradability.

Finally, compatibility of the thickener with other additives present in the fluid needed to achieve fluid target properties is also of major concern.

As indicated above, water-based functional fluids may be of the solution- or emulsion-type. One of the advantages of emulsion-type water-based fluids over the solution type is that the existence of an oil phase broadens the scope of additives which can be incorporated into the fluid to include oil-soluble materials. This permits one to concentrate the oil soluble active ingredients for recycle. The oil phase may also impart improved lubricity and metal surface finish.

In contrast, active ingredients typically need to be water soluble or dispersible for solution-type fluids.

An emulsion may be defined as a formulation consisting of two immiscible liquids, usually water and oil, one of which is dispersed as small globules in the other. The formation and stabilization of an emulsion is made possible by the incorporation of a third substance, namely, the emulsifying agent also referred to broadly as a surfactant.

When the oil is dispersed as globules in water the emulsion is referred to as an oil-in-water emulsion (i.e., o/w).

Conversely, when the water is dispersed as globules in oil, the emulsion is referred to as a water-in-oil emulsion (i.e., w/o). Furthermore, in an o/w emulsion the oil is said to be in the internal, disperse, or discontinuous phase and the water is said to be in the external or continuous phase. The converse is true of a w/o emulsion.

The type of emulsion which is produced, o/w or w/o, depends primarily on the property of the emulsifying agent. This characteristic is referred to as the hydrophilic-lipophilic balance (HLB), i.e., the polar-nonpolar nature of the emulsifier. In fact, whether a surfactant is an emulsifier, wetting agent, detergent or solubilizing agent may be predicted from a knowledge of the hydrophile-lipophile balance.

In an emulsifying agent, such as sodium stearate $C_{17}H_{35}COONa$, the non-polar hydrocarbon chain, $C_{17}H_{35}$-, is the lipophilic or "oil-loving" group, whereas the carboxylate group, -COONa, is the hydrophilic or "water-loving" portion. The balance of the hydrophilic and lipophilic properties of an emulsifier (or combination of emulsifiers) strongly influences whether an o/w or w/o emulsion will result. In general, o/w emulsions are formed when the HLB of the emulsifier is within the range of about 13 to about 16 and w/o emulsions are formed when the range is about 4 to about 6. When the HLB ranges from about 7 to about 12, either W/O or O/W emulsions can be formed depending on the aqueous and oil phase compositions, oil:water ratio and temperature. This is also a range where microemulsions can form.

In practice, combinations of emulsifiers rather than single agents are most frequently used in the preparation of emulsions. Thus, it can be advantageous to have a predominantly hydrophilic emulsifier in the aqueous phase and a hydrophobic agent in the oil phase to form a complex film at the interface.

An important consideration with respect to emulsions is the stability of the finished product. The stability of any emulsion is characterized by the absence of coalescence of the internal phase, preferably the absence of creaming, and maintenance of elegance with respect to appearance (e.g. clarity and low turbidity), odor, color and other physical properties. Some industries define instability of an emulsion in terms only of agglomeration of the internal phase and its separation from the product. Creaming, resulting from flocculation and concentration of the globules of the internal phase, is also a form of instability; but is reversible. However, an emulsion is a dynamic system, and flocculation and resultant creaming represent potential steps toward complete coalescence of the internal phase. Furthermore, in the case of emulsion type water-based fluids, creaming can result in a lack of uniformity of additive distribution and, unless the formulation is thoroughly redispersed before use, the performance of the fluid may be inconsistent. Certainly the eye-appeal of an emulsion is affected by creaming, and it is therefore desirable to avoid this phenomenon. Another measure of emulsion stability is resistance to free-thaw cycles.

The breaking of an emulsion represents the highest degree of emulsion instability. When breaking occurs, simple mixing fails to resuspend the globules in a stable emulsified form, since the film surrounding the particles has been destroyed and the internal phase tends to coalesce.

The phase-volume or phase-weight ratio of an emulsion has a secondary influence on the stability of the product. This term refers to the relative volumes or weights, respectively, of water and oil in the emulsion. Generally, if one attempts to incorporate more than about 74 volume percent of oil in an o/w emulsion, the oil globules often coalesce and the emulsion breaks or inverts. In some stable emulsions, the value may be higher than 74 percent owing to the irregular shape and size of the globules.

A phenomenon important both in preparation and stabilization of emulsions is phase inversion; it can be an aid or a detriment in emulsion technology. Phase inversion involves a change in the type of emulsion from o/w to w/o or vice versa. When controlled properly during the preparation of an emulsion, phase inversion often results in a finer product, but when it gets out of hand during manufacturing or is brought about by other factors after the emulsion is formed, it can cause considerable trouble. For example, an o/w emulsion stabilized with sodium stearate can be inverted to the w/o type by adding calcium chloride to form calcium stearate. Inversion may also be produced by alterations in phase-volume or phase-weight ratio. In the manufacture of an emulsion, one can mix an o/w emulsifier with an oil and then add a small amount of water. Since the volume of the water is small compared with the oil, the water is dispersed by agitation in the oil even though the emulsifier preferentially forms an oil-in-water system. As more water is slowly added, the inversion point is gradually reached and the water and emulsifier envelop the oil as small globules to form the desired o/w emulsion.

One alternative to preparing an o/w emulsion through inversion is to add the oil to an aqueous solution of the emulsifying agent. In this way, the external phase, water, is always in excess and the ratio of the volumes of the water and oil is always such as to favor the formation of an o/w emulsion.

Finally, emulsion type water-based functional fluids are categorized herein as being a macroemulsion emulsion (i.e. course or milky emulsion) or a microemulsion. Whether a system is designated a macro- or microemulsion depends on the globule size of the internal phase. Microemulsions, variously referred to as micellar solutions, soluble oils, or swollen micelles, are thermodynamically stable and are typically characterized as being clear, bright and transparent (and, hence, apparently homogeneous and microdispersed), whereas macroemulsions are thermodynamically unstable, visibly turbid and two phase. These characteristics are due to the balance of forces at the oil-water interface and the fact that the particle (i.e., micro-droplet) in a microemulsion is typically smaller than the wave-length of visible light. Although clear to the eye, the presence of the microemulsion particles can be detected by neutron or light-scattering techniques.

As used herein, the term "microemulsion" is used in its broadest sense to encompass thermodynamically stable mixtures of one or more surfactants or co-surfactants and at least 2 immiscible liquids, e.g., water and oil, which can appear faintly turbid or opalescent as well as (and preferably) completely clear. Microemulsions can be characterized by excellent ambient temperature storage stability and an average particle size of about less than 0.1 micron. In contrast, macroemulsions are turbid in appearance (e.g., cow's milk) and possess an average particle size of at least about 0.1 micron.

Microemulsions generally exhibit enhanced long-term stability relative to macroemulsions, i.e., they remain as initially formulated without separating into macroscopically observable, multiple phases, longer than do macroemulsions.

In addition, systems (e.g., concentrates) adapted to form microemulsions exhibit rapid dilutability, e.g., merely adding water will disperse the system to a stable state. Such systems possess low interfacial tension and typically appear as transparent and translucent solutions which enhances their aesthetic appeal. In addition, microemulsions increase the range of specific gravity which can be possessed by the oil employed therein. A microemulsion also increases the uniformity of delivery of the functional additives to the workpiece, and because of its stability facilitates recirculation of such functional additives.

Microemulsions are typically formed by selecting a combination of low (e.g., 4-10) and high (e.g., 11-16) HLB surfactants and adjusting their ratio (e.g., balancing) to accommodate the water and oil phase, the temperature and compositional parameters such as aqueous phase salinity, and oil phase alkane carbon number, with a view toward ultimately achieving a single-phase system.

More specifically, microemulsion phase behavior can be characterized by equilibrating mixtures of surfactants, oil and water, preferably with equal volumes of oil and water followed by measuring the volumes of microemulsion and excess oil and/or aqueous phases. Measurements are taken as a function of surfactant HLB, temperature, or aqueous and oil phase compositional parameters.

Equilibrated microemulsified systems consisting of oil, water, and surfactants can be characterized as existing as one of four types, namely: (1) Single phase; (2) Two phases with the lower microemulsion phase in equilibrium with excess oil; (3) Two phases with the upper microemulsion phase in equilibrium with excess water; and (4) Three phases with the middle microemulsion phase in equilibrium with both excess oil and water.

Upper (u), middle (m), and lower (l) phase microemulsions exist at relatively low surfactant concentrations.

The transition of the microemulsion type in the direction along the path from upper to middle to lower is called a hydrophilic shift since it progressively involves the absorption of water and rejection of oil. In this simplified model, hydrophilic shift can result from increasing HLB of the surfactant, changes in temperature, and increasing alkane carbon number in the oil.

The reverse transition, in the direction along the path from lower to middle to upper is called a lipophilic shift and involves the absorption of oil and rejection of water. A lipophilic shift can result from decreasing HLB, changes in temperature, and increasing aqueous salinity.

Parameters which cause a hydrophilic shift can be offset by those causing a lipophilic shift. Surfactant structure expressed as an HLB can thus be used to compensate for changes in conditions.

Typically, the ultimate goal of the formulator is to produce a stable, single-phase system whether balanced or not. One way of achieving this goal is to start with a "simplified system" defined herein to consist of surfactant, and equal volumes of oil, and zero salinity water at room temperature. From this simplified system, one obtains information about the particular average HLB needed to balance the emulsion.

Balanced microemulsions occur, when water and oil uptakes by the microemulsion phase are approximately equal. In a balanced microemulsion, the microemulsion phase contains most of the surfactant, and the microemulsion phase may exist alone (single phase) or in equilibrium with excess oil and/or water phases. The overall average HLB of the surfactant system employed (as described hereinafter) which achieves a balanced microemulsion is referred to herein as the Balanced-HLB.

Determination of the Balanced-HLB of a simplified system assists the formulator in evaluating the direction of changes which may be needed to formulate more complex systems. These changes may be required to compensate for disturbances in the HLB balance induced by alterations to the compositional parameters of the system relative to the simplified system.

For example, in complex microemulsified systems, e.g. those containing one or more additives additional to those present in the simplified system, the aforedescribed shifts can be induced by interactions between the additives and the components of the simplified system, e.g., surfactant-additive interactions. Such interactions can cause the effective HLB of the surfactant system to be different from the pre-established HLB listed for the surfactant in the literature. Consequently, the Balanced-HLB of the complex microemulsified system may no longer correspond to the Balanced-HLB derived from the simplified system. When this occurs, adjustments can be made to the system, e.g. to the surfactant system, through trial and error until the microemulsion phase again contains equal volumes of oil and water. Such adjustments are often referred to collectively as "rebalancing" of the system and can result in a new Balanced-HLB for the rebalanced complex system relative to the balanced simplified system.

The concept of a balanced microemulsion, whether for simple or complex systems, is useful to the formulator in designing single-phase microemulsions even where the amounts of oil and water employed in the final emulsified fluid are not equal (e.g. where it is desirable to have low o/w phase ratios). For example, a balanced microemulsion identifies the saturation volume of oil and water which can be maintained in the microemulsified phase for a system having a selected composition. Thus, when the amount of oil to be present in the final microemulsion is selected to be significantly below the oil saturation volume of the balanced microemulsion, the formulator can adjust the o/w phase ratio to produce a single phase system by (1) controlling the amount of final water in the system to be at or below the water saturation volume of the corresponding balanced microemulsion; (2) adjusting the average HLB of the surfactant to increase the microemulsified phase water saturation volume, relative to the saturation volume of the corresponding balanced microemulsion; (3) adding more surfactant to increase the water saturation volume of the microemulsified phase, relative to the saturation volume of the corresponding balanced microemulsion, although this can be disadvantageous from an economic standpoint because surfactants are expensive; and (4) perform combinations of any of steps 1 to 3.

Accordingly, it will be observed from the above, that if one can achieve a balanced microemulsion, whether consisting of a single microemulsified phase, or multiple phases including a microemulsified phase, one can easily produce a single phase microemulsified system, even if the final product is not balanced, i.e. the final product contains unequal amounts of oil and water in the microemulsified phase.

Another utility of the balanced microemulsion concept is that it permits the formulator to control whether a macroemulsion or a microemulsion will form. For example, a macroemulsion will not form when the volumes of oil and water employed in a system are at or below the corresponding oil and water saturation volumes of the balanced microemulsion. Conversely, a macroemulsion will form when any of the oil and/or water volumes employed in the system are above the corresponding saturation volumes of the balanced microemulsion.

Further background discussions of microemulsified systems are provided in "Model for Microemulsions" by Robbins, M. L. and Bock, J., Journal of Colloid and Interface Science, Vol. 124, No. 2, P. 462-85 (August 1988);

"Effect of Solvent on Microemulsion Phase Behavior", by Graff; J. L., Bock, J., and Robbins, M.L., ACS Symposium Series No. 371, P. 163-89 (1988); "Theory For the Phase Behavior of Microemulsions" by Robbins, M.L., Micellization, Solubilization, and Microemulsions, vol. 2, P. 713-53 (1977); and U.S. Patent No. 4,764,285, the disclosures of which are incorporated herein by reference.

Selecting a suitable polymeric thickener for use in conjunction with microemulsified water-based functional fluids has the added difficulty of increased probability for more pronounced surfactant-thickener interactions. These interactions can lead to phase incompatibility and ultimately to separation.

In view of the above, there has been a continuing search for new emulsion type-based functional fluids having improved rheological, anti-misting, physical and chemical stability and dilutability properties. The present invention was developed in response to this search.

U.S. Patent No. 4,694,046 discloses high molecular weight, water-soluble polymers containing both water-soluble and water-insoluble monomers. The water-soluble monomers are acrylamide (AM) and a salt of acrylic acid (H), and the water-insoluble monomer is a higher alkyl acrylamide (R). Hence, these polymers are conveniently referred to as HRAM. The charged groups of the acrylic acid salt monomer are incorporated into these polymers by direct polymerization of the alkali metal acrylate, by post-hydrolysis of some of the acrylamide monomers with an alkali metal hydroxide, or by neutralizing acrylic acid monomer with base. Since the charge of monomer species incorporated into the backbone of the polymer is negative, HRAM polymers are also referred to as being anionic polymers. HRAM polymers described in this patent constitute a species of polymer employed as the thickener in the presently claimed invention. However, the utility described for these polymers in the subject patent is as a thickener in aqueous solutions. No utility for oil-in-water emulsified systems is disclosed. One of the techniques described in this patent for preparing the HRAM polymers involves the use of a water-continuous microemulsion to disperse the oil-soluble monomer in a solution of the water-soluble monomers in accordance with U.S. Patent No. 4,521,580. In addition, numerous other techniques are described which do not involve the use of microemulsions. None of the examples employ the microemulsion technique, and no specific details are disclosed except as otherwise incorporated by reference through the '580 patent.

U.S. Patent No. 4,521,580, as indicated above, discloses a microemulsion process for preparing acrylamide-alkylacrylamide copolymers also commonly referred to as RAM copolymers for convenience. Such polymers are illustrated by a structural formula at column 4, lines 25 et seq. This structural formula does not include anionically charged monomers either in the preparation or in the final polymer. Consequently, this patent does not disclose the preparation of HRAM polymers using the microemulsion technique. At column 4, lines 5 et seq. the oil:surfactant ratio is disclosed to range from 4:1 to 1:4. In example 1, an acrylamide/dodecylacrylamide polymer is prepared using the microemulsion technique. None of the examples employ oil for the disperse phase, but use hexadecane instead. While the monomers start out in microemulsion form, the resulting product mixture is said to become slightly hazy and slightly foamy. In addition, the final polymer is always removed and recovered from the emulsion for dissolution in water. Accordingly, there is no suggestion that HRAM polymers, if made by the microemulsion technique, would remain emulsified when formed. In addition, there is no suggestion in this reference to manipulate conditions to maintain a microemulsion of RAM nor HRAM, since the polymer is always recovered for eventual dissolution in water. The failure to disclose utility in and of itself of a microemulsion of the polymers described in the '580 patent is, therefore, carried over into the '046 patent discussed above.

U.S. Patent No. 4,673,716 discloses an alternative process for preparing HRAM polymers using complete solubilization of the water-insoluble monomer into an aqueous solution of the water-soluble monomers. The use of these polymers in oil-in-water emulsions is not described. (See also U.S. Patent No. 4,694,058).

U.S. Patent No. 4,612,332 discloses the use of HRAM polymers in a surfactant-free stable aqueous foam. The use of these polymers in oil-in-water emulsions is not disclosed.

U.S. Patent No. 4,734,205 discloses the use of a hydrophobic functionalized polymer, which includes HRAM, in conjunction with a cationic polymer to break oil-in-water emulsions. Hydrophobic functionalized polymer enhances the formation of floc particles allowing the emulsified oil to coalesce into a separate oil layer. No use of the HRAM polymers in an oil-in-water emulsion is disclosed.

U.S. Patent No. 4,432,881 discloses an aqueous liquid medium having increased low shear viscosity prepared by dispersing into the aqueous medium 1) a water-soluble polymer having pendant hydrophobic groups; and 2) a water-dispersible surfactant. The water-soluble polymer acts as a thickener. The surfactant-polymer combination can be employed in an aqueous media having increased viscosity such as drilling mud formulations, fracturing fluids, liquid mobility control agents, aqueous solutions of inorganic salts, hydraulic fluids, lubricants, friction reducing agents, suspending agents, aqueous suspensions of insoluble particulates such as paint formulations and the like.

(Column 2, lines 60 et seq.) The preferred utility is enhanced oil recovery. Numerous hydrophobic monomer containing polymers are disclosed including HRAM (Column 6, lines 48 et seq.). However, the system described in this patent is of the solution-type not of the emulsion-type.

U.S. Patent No. 4,814,096 discloses an aqueous liquid medium having increased low shear viscosity and utility as a mobility control agent in enhanced oil recovery prepared by dispersing into the aqueous medium 1) a hydrophilic/hydrophobic polymer having hydrophobic groups; and 2) a water-dispersible surfactant. This patent is a continuation-in-part of the above-described 4,432,881 patent and claims an enhanced oil recovery process using the polymers disclosed in the '881 patent. No utility in oil-in-water emulsions is disclosed.

U.S. Patent No. 4,395,524 discloses non-ionic and anionic water-soluble addition copolymers of acrylamide and N-substituted acrylamides as flow improvers in and as absorbents from aqueous systems, particularly multi-phase latex systems. Other additional vinyl monomers can be incorporated into the copolymer which are hydrophilic such as acrylic acid. While hydrolysis of initially hydrophobic monomers to produce hydrophilic monomers is contemplated (Column 6, lines 50 et seq.), the resulting hydrolyzed products are not disclosed to include anionic monomer metal or ammonium salts either in the monomer system or in the final polymer. Thus, while example 10 discloses RAM terpolymers, specific HRAM polymers are not disclosed. Oil-in-water emulsions are not disclosed.

U.S. Patent No. 4,802,914 discloses a process for agglomerating mineral oil concentrate utilizing dispersions of polymer binders or dry polymer binders. Most preferred polymers are water-soluble poly(acrylamide) based polymers. While use of these polymers is contemplated in water-in-oil emulsion systems and dispersion in oil systems, no use is disclosed in oil-in-water systems (See, Column 14, lines 8 et seq.). Several polymers represented by various structural formulas are disclosed throughout the patent. However, as will be observed therefrom, none of these monomers correspond to the hydrophobic alkyl acrylamide monomer of the present invention. While an alkyl acrylamido monomer is disclosed at column 8, line 20, it is not hydrophobic since the R_{14} and R_{15} groups attached to the nitrogen atom are either hydrogen or methyl. (See also, U.S. Patent No. 4,767,449, which is a continuation-in-part of a common parent of the '914 patent discussed above.)

U.S. Patent No. 4,853,447 discloses copolymer derived from copolymerizing an acrylamide monomer and a cationic monomer. At column 8, lines 65 et seq., use of these copolymers as rheological control additives, well control and workover fluids, cutting fluids, completion fluids, anti-misting additives, drag reducing agents and the like is disclosed.

U.S. Patent No. 4,520,182 discloses acrylamide-alkylacrylamide copolymers as water-soluble viscosifiers. These RAM-type copolymers do not contain anionic monomer groups.

U.S. Patent No. 4,668,410 discloses aqueous functional fluids containing a copolymer derived from (a) ethylenically unsaturated carboxylic acids (e.g., acrylic acids); (b) surface-active unsaturated ester which contains repeating ethyleneoxy units; and (c) methacrylic acid or esters or acrylic acid esters of aliphatic C_1 - C_{18} alcohols. Optional monomers include ethylenically unsaturated comonomers such as vinyl esters, e.g., vinyl acetate; polyethylenically unsaturated compounds such as divinyl benzene; and molecular weight regulators such as dodecyl mercaptan. Neither acrylate monomer salts nor dialkyl acrylamido hydrophobic monomers are disclosed. Oil-in-water microemulsion concentrates are described at column 7, lines 35 et seq. (See also, U.S. Patent No. 4,769,167, which is a continuation-in-part of the above-identified '410 patent.)

U.S. Patent No. 4,806,256 discloses water-based hydraulic fluids in oil-in-water emulsified or non-emulsified form, thickened with an ionic viscoelastic surfactant. Such surfactants are not polymeric.

The Handbook of Coatings Additives, by L. J. Calbo, published by Marcel Dekker, Inc. (1987), at pages 67, 76-78, 83, 85, 87, 89 and 117 discloses the use of associative polymer thickeners in paints.

An article by D. N. Schulz, et al., entitled "Hydrocarbon Associating Polymers as Anti-Misting and Drag-Reducing Agents", printed in ACS Polymer Science and Eng. Preprints, Vol. 61, P. 57 (1989), discloses that oil soluble associating polymers not only increase a hydrocarbon's solvent shear and elongational viscosity, but also enhance its anti-misting and drag-reducing properties. In addition, a functional relationship between elongational viscosities as measured by a tubeless siphon apparatus and anti-misting properties is disclosed.

The rheological properties of hydrophobically associating polymers, such as HRAM, in aqueous solutions is disclosed in "Structure and Properties of Hydrophobically Associating Polymers" by Bock, J., Siano, D., Valint Jr., P., and Pace, S., ACS Advances in Chemistry Series: Polymers in Aqueous Media, No.. 22, P. 411-23 (1989).

U.S. Patent No. 4,911,736 discloses oil-in-water emulsions containing an interpolymer of (1) 97-99 wt. % of a water soluble acid monomer or salt thereof, e.g., acrylic acid, and (2) from 1 to 3 wt. % of a polymerizable ester monomer derived from a C_{10}-C_{30} alkanol. The polymer acts as an emulsifier and emulsion stabilizer. The emulsions are disclosed to be useful in oil spill management, pipeline transportation of heavy crude and cleaning of oil contaminated vessels.

U.S. Patent No. 4,882,077 discloses an oil-in-water emulsified metal working fluid containing paraffinic oil, an ester derived from a C_6 to C_{20} mono or dibasic acid and C_6 to C_{20} alcohols, emulsifier and water.

U.S. Patent No. 4,915,859 discloses polymer containing water-in-oil microemulsions which invert when added to an aqueous solution in the presence of an inverting agent or physical stress. The inversion causes dissolution of the polymer into water. The polymer is a vinyl additive polymer.

Aqueous-based functional fluids are disclosed in U.S. Patent Nos. 4,313,836; 4,447,348; 4,468,339; 4,598,026; 4,659,488; and 4,661,275.

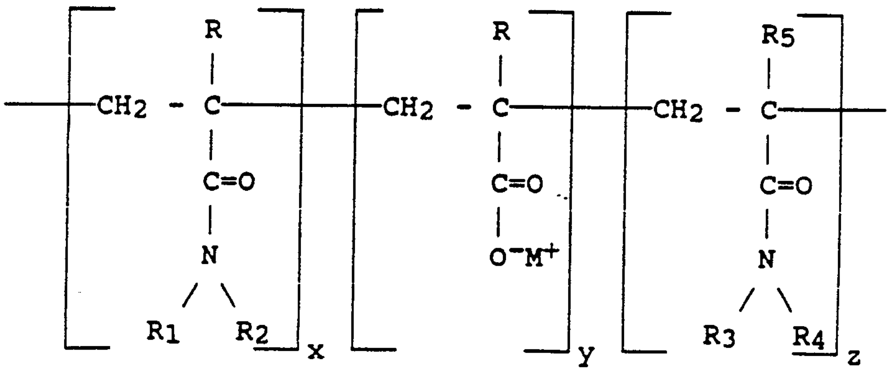
Summary of the Invention

It has been found that certain polymers of the type described herein when incorporated into oil-in-water emulsions particularly microemulsions, produce strong polymer-surfactant interactions. Such interactions have the dual effect of stabilizing the emulsion over a wide range of conditions and enhancing the emulsion's shear and extensional viscosity. The tendency of the emulsion fluid to break up into droplets when subjected to a shear field is minimized, thereby suppressing misting of the emulsion. This property renders the emulsion particularly suited for use in metalworking operations.

In addition, whereas emulsions containing polyacrylamides having varying amounts of water-soluble anionic monomer exhibit viscosity loss compared to aqueous solutions of the polymer, the addition of hydrophobic groups to such polyacrylamides results in such strong polymer-surfactant interaction in the emulsion that the viscosity of the emulsion can be enhanced several orders of magnitude at low shear rates. The resultant viscosity of such emulsions is higher than either that of an aqueous solution containing the same amount of polymer, or an emulsion otherwise the same except for the absence of the polymer.

Accordingly, in one aspect of the present invention there is provided an oil-in-water emulsion having an aqueous continuous phase and a base oil disperse phase comprising:

> (A) polymer having water soluble nonionic monomer species, water soluble anionic monomer species and water insoluble monomer species present within the structure thereof at a respective mole ratio in the polymer of from about 1:0.030:0.0025 to about 1:0.40:0.080 and said polymer having at least about 60 mole % of the total monomer species present within the structure thereof represented by the formula:



$$-\left[CH_2-\overset{R}{\underset{\underset{N(R_1)R_2}{C=O}}{C}}\right]_x-\left[CH_2-\overset{R}{\underset{\underset{O^-M^+}{C=O}}{C}}\right]_y-\left[CH_2-\overset{R_5}{\underset{\underset{N(R_3)R_4}{C=O}}{C}}\right]_z- \qquad (I)$$

(II) nonionic water soluble monomer

(III) anionic water soluble monomer

(IV) water-insoluble monomer

wherein in Formula I, monomer species II is water soluble nonionic, species III is water soluble anionic, and species IV is water insoluble and wherein R independently can represent hydrogen or unsubstituted or polar hydrocarbyl substituted methyl, R_1 and R_2 can independently represent unsubstituted or polar hydrocarbyl substituted C_1 to C_3 alkyl, provided that the number of carbons represented by $R_1 + R_2$ is not greater than 4, when R_1 and R_2 are unsubstituted; R_3 and R_4 independently can represent hydrogen, alkyl, cycloalkyl, aryl, alkaryl and aralkyl, provided the number of carbons represented by $R_3 + R_4$ is at least 6; R_5 can represent hydrogen or alkyl; M is a cation selected from at least one member of the group consisting of Groups IA, IB, IIA, IIB of the periodic chart and ammonium and polar hydrocarbyl substituted ammonium; x, y and z are numbers which represent a mole ratio of monomer species II:III:IV within said polymer of from about 1:0.030:0.0025 to about 1:0.40:0.080;

(B) base oil;

(C) at least one surfactant; and

(D) water

said polymer being present in the aqueous phase in an amount sufficient to increase the shear viscosity at 24°C of the emulsion relative to the emulsion absent the polymer; and said base oil, surfactant, and water being present in amounts sufficient to produce an oil-in-water emulsion.

In another aspect of the present invention there is provided emulsified water-based functional fluid, and concentrate adapted to form the emulsified water-based functional fluid by dilution of the concentrate with water at a dilution weight ratio of added water:concentrate of from about 10:90 to about 99:1. The fluid and concentrate contain the above-described polymer wherein the presence of the anionic water soluble monomer is optional, surfactant, and base oil and optionally (for the concentrate) water in amounts effective to improve the rheological properties of the final fluid as well as to cause the concentrate to form an emulsion, preferably a microemulsion when subjected to said dilution.

In still another aspect of the present invention there is provided a method for improving at least one of the rheological or anti-mist properties of a water-based functional fluid by causing the fluid to form an oil-in-water emulsion containing the above-described polymer in the aqueous phase thereof.

In a still further embodiment of the present invention there is provided a method for forming a concentrate containing the above-described polymers adapted to form an oil-in-water emulsified water-based functional fluid when diluted with water.

Description of Preferred Embodiments

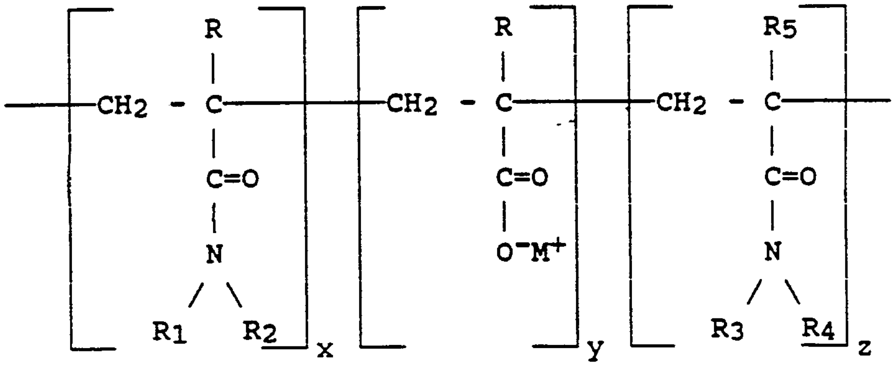
The present invention is directed to various emulsified or emulsifiable combinations and/or compositions of (A) water soluble polymer thickener comprised of at least two, preferably at least three types of monomers, namely, (i) water soluble nonionic monomer, (ii) optional water-soluble anionic monomer, and (iii) water insoluble monomer; (B) base oil; (C) surfactant; and (D) water. Such combinations can be employed as water-based functional fluids, as described hereinabove, alone or in combination with other additives.

As used herein, the term "water soluble", when applied to a polymerizable monomer, is intended to include those hydrophilic monomers which are sufficiently water soluble such that at least 1 gm. thereof will dissolve in 1 liter of water at 24°C.

As used herein, the term "water insoluble", when applied to a polymerizable monomer, is intended to include those hydrophobic monomers which are sufficiently water insoluble that less than 1 gm. will dissolve in 1 liter of water at 24°C. The term "water soluble" when applied to polymers is meant that they contain typically at least 75, preferably at least 85, and most preferably at least 95 mole % of water-soluble monomer in the structure thereof.

(A) The Water Soluble Polymer Thickener

The water soluble polymer thickener of the present invention can be represented as being comprised of polymerized monomer species comprised of non-ionic water soluble, water insoluble, and optionally and preferably anionic water soluble. Such polymerized monomer species can be represented by the following structural formula:



$$-\left[CH_2-\overset{\substack{R\\|}}{\underset{\substack{|\\C=O\\|\\N\\R_1\quad R_2}}{C}}-\right]_x\left[CH_2-\overset{\substack{R\\|}}{\underset{\substack{|\\C=O\\|\\O^-M^+}}{C}}-\right]_y\left[CH_2-\overset{\substack{R_5\\|}}{\underset{\substack{|\\C=O\\|\\N\\R_3\quad R_4}}{C}}-\right]_z- \qquad (I)$$

(II) nonionic water soluble monomer

(III) anionic water soluble monomer

(IV) water-insoluble monomer

wherein each R independently can be hydrogen or unsubstituted, or polar hydrocarbyl substituted, methyl; R_1 and R_2 can independently represent hydrogen or unsubstituted or polar hydrocarbyl substituted, alkyl, typically C_1 to C_3, preferably C_1 to C_2, most preferably C_1, alkyl. Typically the total number of carbons in $R_1 + R_2$ will not be greater than about 4, preferably not greater than about 2 when R_1 and R_2 are unsubstituted.

Because the identity of various groups, i.e., R, R_1 and R_2 will affect the water solubility of the various polymerizable monomer species, it is contemplated that R, R_1 and R_2 may contain polar groups as substituents or internally located therewithin. The balance between the polar and non-polar portions of R_1 and R_2 will therefore ultimately determine the water solubility of the polymerizable monomer species.

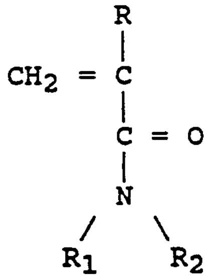
Accordingly, as used in this specification and claims, the phrase "polar hydrocarbyl substituted" is meant to include hydrocarbyl groups which contain at least one pendant or internal polar group containing species selected from the group consisting of hydroxy, oxy, alkoxy, polyalkoxy, polyalkoxyalkyl, thio, oxyalkylene, carboxyalkylene, hydroxyalkyl, provided the ratio of polar species to non-polar (e.g., alkyl) species collectively present is sufficient to render the corresponding polymerizable monomer species water soluble as defined herein. Typically the polar hydrocarbyl groups contain about 1 to 4 carbons per polar group.

Thus, the above description of R_1 and R_2 when existing as unsubstituted alkyl is intended to illustrate the approximate limits of water solubility in the polymerizable monomer when not compensated with hydrophylic polar groups.

R_3 and R_4 collectively represent an organic hydrophobe, i.e., together they must contain at least 6, preferably at least 7, and most preferably at least 8 carbons. Subject to this proviso, R_3 and R_4 independently can represent hydrogen, alkyl, typically C_1 to C_{22}, preferably C_4 to C_{20}, most preferably C_6 to C_{18}, straight or branched alkyl, cycloalkyl, typically C_4 to C_{10}, preferably C_5 to C_8, most preferably C_5 to C_6 cycloalkyl, aryl, typically C_6 to C_{14} aryl, alkaryl and aralkyl wherein the alkyl and aryl portions thereof are as described above. R_5 can represent hydrogen or alkyl, typically C_1 to C_{10}, preferably C_1 to C_5 alkyl, e.g., methyl. M is at least one cation of a metal or nitrogen selected from the group consisting of Groups IA (e.g., Na^+, K^+, Li^+, Rb^+, Cs^+), IIA (e.g., Mg, Ca, Sr, Ba), IB (Cu, Ag, Au), IIB (Zn, Cd, Hg) of the periodic chart, ammonium, and polar hydrocarbyl substituted or unsubstituted ammonium, e.g., ethanol ammonium; and x, y and z are numbers which represent the respective mole proportion between each of monomer species II, III, and IV in the polymer when expressed in the mole ratio x:y:z as described hereinafter in greater detail.

It is to be understood that Formula I is not intended to depict any particular sequence of monomer species in the polymer, since the polymer is typically prepared by radical polymerization resulting in a random copolymer. Moreover, such polymers are typically terminated with hydrogen atoms.

The water-soluble nonionic monomer species can be derived from a variety of monomers. Thus, for example, the polymerizable monomer, from which monomer species II of Formula I can be derived, can be represented by the formula:



(II')

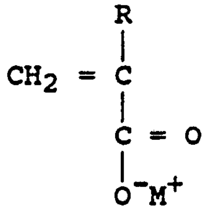
wherein R, R_1, and R_2 are as described in connection with Formula I.

Representative examples of suitable water soluble nonionic polymerizable monomers include ethylenically unsaturated amides such as acrylamide, methacrylamide and their N-substituted derivatives such as N-methyl acrylamide, N,N-dimethyl acrylamide, N-ethylmethacrylamide, N,N-dimethyl methacrylamide. The preferred water soluble nonionic monomer is acrylamide.

In lieu of starting with the monomer depicted by Formula II', one can start with, for example, acrylic and/or methacrylic acids in the polymerization reaction mixture, and then react the resulting polymerized acids with ammonia or pertinent hydrocarbyl amine to form suitable amide species.

The water soluble anionic monomer species III of Formula I can also be derived from a number of different sources.

Thus, for example, an anionic monomer represented by the formula:



$$CH_2 = C(R)-C(=O)-O^-M^+$$

(III')

wherein R, and M are as described in connection with Formula I, can be directly copolymerized with monomer species II' and IV' to yield the anionically charged species in the resulting polymer.

A suitable alternative to the monomer of Formula III' includes acrylic and/or methacrylic acids provided the resulting pendant free acid groups in the polymer are neutralized in accordance with appropriate base.

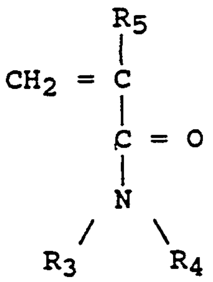
A second alternative to producing the anionic monomer species III in Formula I is to hydrolyze and neutralize, with appropriate metal base or ammonium hydroxide, a certain portion of amide groups present on, for example, monomer species II in the polymer. The degree of hydrolysis and neutralization is sufficient to yield the appropriate proportion of Species III in the polymer as represented by y in Formula I as described herein. Techniques for post-treatment are described in U.S. Patent No. 4,694,046, e.g., Examples 2 to 8, the disclosure of which is herein incorporated by reference.

A third alternative to producing the anionic monomer species is to hydrolyze and neutralize in the polymer, ester, e.g., acrylate or methacrylate, containing species derived from a C_1 to C_3 alcohol.

The preferred anionic monomer species III of Formula I is the sodium or ammonium salt of acrylic or methacrylic acid.

The water insoluble monomer species IV of Formula I can be derived from monomers similar to those described in connection with monomer II′ with the exception that the N-alkylamide groups incorporated into the polymer are hydrophobic.

Such monomer species can be represented by the formula:



$$CH_2=C(R_5)-C(=O)-N(R_3)(R_4)$$

(IV′)

where R_5, R_3, and R_4 are as described in Formula I.

Representative examples of suitable water insoluble monomers include N-octylacrylamide, N-t-octylacrylamide, N,N-dioctylacrylamide, N-decylacrylamide, N-N-didecylacrylamide, N-octyl-N-decylacrylamide, N-dodecylacrylamide, N,N-di-dodecylacrylamide, N-tetradecylacrylamide, N,N-ditetra-decylacrylamide, N-octadecylacrylamide, N,N-diocta-decylacrylamide, N-docosylacrylamide, as well as the cor-responding methacrylamides of the above acrylamides, and mixtures thereof.

The preferred water insoluble monomer is N-octylacrylamide.

The mole ratio of the water-soluble nonionic (II) water-soluble anionic (III) water insoluble monomer species (IV) in the polymer thickener (e.g., the values of x, y and z of Formula I in the ratio x:y:z) controls, both the emulsion stability, and the rheology of the system.

The polymer thickeners of the present invention can be generally classified into two types, namely (1) those that contain only water soluble nonionic and water insoluble monomer species (referred to herein for convenience as RAM type Polymers, i.e. Y in Formula I is 0); and (2) those polymers which contain anionic water soluble species in addition to the monomer species found in RAM-type polymers. The second category of polymer thickeners which also contain anionic water soluble monomer species is referred to herein for convenience as HRAM type polymers. It has been found that RAM type polymers tend to cause an HLB shift (e.g., lipophilic shift) in the HLB of previously balanced surfactant/oil/water microemulsified systems. As a consequence, the addition of the RAM polymer thickener can unbalance a previously balanced microemulsion causing phase separation.

It has been further found that the resulting unbalanced microemulsion can be rebalanced by adjusting the HLB of the surfactants employed (e.g., selecting new surfactants or adjusting the ratio of surfactants) and/or by adjusting the polymer structure, e.g., by incorporating water soluble anionic monomer species into the RAM polymer thereby converting the same to an HRAM type polymer.

While one can employ RAM type polymers and still achieve a balanced microemulsion, such polymers have been found to be more sensitive to changes in the x:z monomer ratio of Formula I in terms of the impact of such changes on the degree of HLB shift. This sensitivity is significantly reduced by employing HRAM type polymers. The presence of even small amounts of the water soluble anionic monomer species in the HRAM polymer is believed to significantly reduce the effectiveness of the water insoluble (hydrophobic) monomer at causing HLB shift. This permits one to employ a greater range of hydrophobic monomer content in the polymer than would otherwise be desirable in RAM type polymers.

In addition, while HRAM polymers can also cause an HLB shift, the x:y:z ratio of Formula I can be more easily controlled for a given surfactant/oil/water system such that no, or minimal, readjustment of the surfactant HLB ratio is needed to achieve a balanced microemulsion.

Moreover, increasing the amount of anionic species within the polymer of the present invention increases the intra-molecular repulsion between such groups, thereby stretching the polymer, i.e., increases its hydrodynamic size, and ultimately increases the viscosity of the emulsion to a greater extent than RAM type polymers.

Conversely, the absence of a hydrophobic monomer species in a polymer containing water soluble non-ionic and anionic monomer species (e.g., HPAM-type polymer) weakens the polymer interaction with surfactants and oil to the extent that water is extracted from the emulsion and part of the surfactant and oil creams to the surface. Since the polymer is too hydrophilic to interact with the surfactant, it phase separates with its associated water. Including hydrophobic monomer species in the polymer decreases the hydrophilicity of the polymer and alters the polymer-water and polymer-surfactant interactions, whereby extraction of water from the emulsion is decreased and emulsion stability increased.

Accordingly, while any amount of each monomer type may be incorporated into the polymer thickener which is effective to achieve viscosity enhancement, it is contemplated that such effective amounts constitute a mole ratio of monomer species II:III:IV in said polymer, e.g., represented by x:y:z respectively in Formula I, of typically from about 1:0:.0020 to about 1:0.40:0.080.

For RAM type polymers, it is contemplated that such effective amounts constitute a mole ratio of monomer species II:IV (monomer species III being absent) in said polymer e.g., represented by x:z (with y being 0) respectively in Formula I, of typically from about 1:0.0020 to about 1:0.080, preferably from about 1:0.0020 to about 1:0.030 and most preferably from about 1:0.0025 to about 1:0.020.

For HRAM type polymers it is contemplated that such effective amounts constitute a mole ratio of monomer species II:III:IV in said polymer, e.g., represented by x:y:z respectively in Formula I, of typically from about 1:0.030:0.0025 to about 1:0.40:0.080, preferably from about 1:0.05:0.0030 to about 1:0.25:0.030, and most preferably from about 1:0.10:0.0050 to about 1:0.20:0.020.

In addition to the three monomer species II, III and IV of Formula I in the polymer, various amounts of other monomers can be included in the polymer as replacements therefor, which fall within one of the above described monomer types.

Thus, typically not greater than about 70, preferably not greater than about 50 mole % of the water soluble nonionic monomer species II can be replaced with other water soluble nonionic monomer species such as those derived from monomers which include amides having similar $(R_1)(R_2)N$- groups described in connection with Formula I but based on such ethylenically unsaturated acids such as itaconic, fumaric, maleic and crotonic; vinyl heterocyclic amides such as vinyl pyrrolidone, vinyl amines or amides such as vinylpyrridine and vinyl morpholine; sulfoalkylesters of the aforedescribed unsaturated acids such as 2-sulfoethyl methacrylate; amino alkyl esters of the aforedescribed unsaturated acids, such a 2-aminoethyl methacrylate; vinyl aryl sulfonate esters such as vinyl benzyl sulfonate; vinyl esters such as vinyl acetate; vinyl ethers such as vinyl ethylether; lower (C_1 to C_4) alkyl full or half esters of ethylenically unsaturated acrylic, methacrylic, itaconic, fumaric, maleic and crotonic acids as well as the free acids per se.

Similarly, typically not greater than about 50, preferably not greater than about 30 mole % of the water soluble anionic monomer species III of Formula I in the polymer can be replaced with other water soluble anionic Group IA, IB, IIA and IIB metal and substituted or unsubstituted hydrocarbyl ammonium and ammonium salt species derived from such water insoluble ethylenically unsaturated acids as itaconic, fumaric, maleic, and crotonic, and salts of: 2-acrylamide-2-methyl proponic sulfonic acids (AMPS)®, vinyl arylsulfonic acids such as vinylbenzyl sulfonate, and styrene sulfonate.

Finally, typically not greater than about 50, preferably not greater than about 30 mole % of the water insoluble monomer species IV of Formula I can be replaced in the polymer with other water insoluble monomer species derived from water insoluble higher (e.g., C_8 - C_{20}) 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, as well as the alkyl half esters and diesters of other alkyl esters derived from the reactions of higher alkanols having from 8 to 20 carbon atoms with ethylenically unsaturated carboxylic acids such as fumaric acid, itaconic acid and crotonic acid, alkylaryl esters of ethylenically unsaturated carboxylic acids such as nonyl-α-phenyl methacrylate, dodecyl-α-phenyl acrylate and dodecyl-α-phenyl methacrylate; N- or N,N-C_6-C_{12} alkyl or dialkyl amides derived from such ethylenically unsaturated acids as itaconic, fumaric, maleic and crotonic, such as N,N-dioctyl maleamide; α-olefins such as octene-1, decene-1, dodecene-1 and hexadecene-1; vinyl alkylates wherein the alkyl portion 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 alkylstyrenes such as t-butyl styrene.

However, while the mole ratio of each general type of monomer species, i.e., water soluble nonionic:water soluble anionic:water insoluble monomer in the final polymer corresponds to the mole ratios represented by x:y:z, the sum of the mole percents of the specific monomer species II + III + IV of Formula I in the final polymer will be typically at least about 60, preferably at least about 70, and most preferably at least about 80 (e.g., 90-100) mole % of the total monomer species in the polymer.

Preferably the water soluble polymer is a terpolymer consisting only of the monomers depicted in Formula I.

The weight average molecular weight of the water soluble polymer thickeners of the present invention is sufficiently high such that when an o/w emulsion is prepared containing the polymer (typically at least 0.1 weight percent of the polymer), the shear viscosity (as determined by the Contraves Rheometer LS-30) of the emulsion is increased (typically at least by about 10% at 24°C relative to the viscosity of the emulsion without the polymer at the same temperature. The weight average molecular weight of the polymer is preferably also sufficiently low enough such that said polymer-containing emulsion can be subjected to a degree of shear of greater than 1000 sec^{-1} without causing significant irreversible shear degradation, e.g., less than about 10,000,000. In general as the molecular weight of the polymer is increased, the viscosity at low shear rates increases substantially. However, at higher shear rates, the molecular weight effect on viscosity observed at low shear rates is much less.

Thus, while any viscosity effective molecular weight of the polymer can be employed, it is contemplated that such effective weight average molecular weights will vary typically from about 100,000 to about 10,000,000, preferably from about 200,000 to about 8,000,000, and most preferably from about 500,000 to about 5,000,000.

Polymer composition is determined by a variety of classical analytical techniques which include elemental analysis and NMR. The carboxyl content of the polymers is determined by potentiometric titration following conversion to the acid form with an ion-exchange column. If the water-insoluble hydrophobic group content in the polymer is too low to allow quantification by conventional analytical techniques, the amount of water-insoluble hydrophobic monomer added to the reactor can be assumed to be completely incorporated into the polymer. This assumption can be verified by extracting unreacted monomer, if any, in a suitable hydrocarbon solvent, quantifying the extracted monomer by gas chromatography, and adjusting the mole % of polymerized monomer to account for unreacted monomer.

The weight average molecular weights of the polymers is determined by either a classical laser light-scattering (LLS) technique or by a sedimentation-LLS technique. A multiangle LLS apparatus (Dawn model B, Wyatt Technology) is used to determine the scattered light intensity at 15 angles simultaneously. Molecular weights are determined by performing a Zimm analysis of the data, preferably with the software supplied by the manufacturer. For further discussion, see, the Bock et al. article "Structure and Properties of Hydrophobically Associating Polymers" cited above, ACS Advances in Chemistry Series: Polymers in Aqueous Media, No. 22, p. 411-23 (1989), the disclosure of which is herein incorporated by reference.

The aforementioned polymer thickeners are advantageously prepared by any conventional polymerization technique, such as by the use of a water-continuous microemulsion to disperse the oil soluble monomer in a solution of water-soluble monomers. This technique is disclosed in U.S. Patent Nos. 4,694,046 and 4,521,580 the disclosures of which are herein incorporated by reference.

An alternative and preferred technique is the micellar solution technique whereby oil soluble monomers are dispersed using an aqueous micellar solution of water soluble monomers. These techniques are described in U.S. Patent No. 4,694,046 and 4,528,348, the disclosures of which are herein incorporated by reference.

(B) Base Oil

The base oil is not a particularly critical aspect for the end use of the present invention since the oil primarily serves as a nonpolar organic liquid which can be dispersed in water to form an emulsion having water as the continuous phase. However, the specific oil type or composition does affect the formulation of surfactants employed to achieve suitable emulsion stability or to form microemulsions. In short, the base oil employed will influence what constitutes the Balanced-HLB of the system and the surfactant HLB is adjusted accordingly. Methods for balancing surfactants to accommodate the Balanced-HLB are disclosed in "Emulsions:

Theory and Practice", Becker, P., ACS Monograph No. 162, Reinhold (1965), the disclosure of which is herein incorporated by reference. The base oil can optionally serve as a vehicle for nonpolar additives in the emulsion.

For purposes of the following description, the term "base oil" is understood to encompass light hydrocarbon or hydrocarbon mixtures which are preferably substantially inert and can form o/w emulsions with water. Such oils will typically have a viscosity of about 40 to about 200 Saybolt Universal Seconds (SUS) at 100°F. By "substantially inert" is meant that oil will not autogeneously chemically react with other fluid additives in a manner that will alter the function intended to be performed by said additives.

Thus, base oils suitable for use in preparing compositions of the present invention include those conventionally employed as crankcase lubricating oils for spark-ignited and compression-ignited internal combustion engines, such as automobile and truck engines, marine and railroad diesel engines, power transmitting fluids, e.g., ATF gear lubricants, industrial oils, pump oils and the like.

Representative liquids suitable for use as the base oil include natural and synthetic oils, e.g., the solvent neutrals, white oils, naphthenic oils, etc. the linear and branched alkanes and haloalkanes of ten to eighteen carbons, polyhalo- and perhaloalkanes of up to about six carbons, the cycloalkanes of five or more carbons, the corresponding alkyl-and/or halo-substituted cycloalkanes, the aryl hydrocarbons, the lower alkylaryl hydrocarbons, and the haloaryl hydrocarbons.

Specific examples include Stoddard Solvent, decane, isooctane, undecane, tetradecane, cyclopentane, cyclohexane, isopropylcyclohexane, 1,4-dimethylcyclohexane, cyclooctane, benzene, toluene, xylene, ethyl benzene, tert-butyl-benzene, halobenzenes especially mono- and polychlorobenzenes such as chlorobenzene per se and 3,4-dichlorotoluene, 1,2-difluoro-tetrachloroethane, dichlorofluoromethane, 1,2-dibromotetrafluoroethane, trichlorofluoromethane, 1-chloropentane, 1,3-dichlorohexane.

Also useful as base oils are the low molecular weight, liquid polymers, generally classified as oligomers, which include the dimers, tetramers, pentamers, etc. Illustrative of this large class of materials are such liquids as the propylene tetramers, isobutylene dimers, and the like.

Natural oils are preferred. Natural base oils include mineral lubricating oils which may vary widely as to their crude source, e.g., whether paraffinic, naphthenic, mixed paraffinic-naphthenic, and the like; as well as to their formation, e.g., distillation range, straight run or cracked, hydrofined, solvent extracted and the like.

More specifically, the natural lubricating oil base stocks which can be used in the compositions of this invention may be liquid petroleum oils, straight mineral lubricating oil, solvent treated, acid treated or distillates derived from paraffinic, naphthenic, asphaltic, or mixed base crudes, or, if desired, various blended oils may be employed as well as residuals, particularly those from which asphaltic constituents have been removed. Oils of appropriate viscosity derived from coal or shale are also useful base oils.

Synthetic base oils include hydrocarbon oils and halo-substituted hydrocarbon oils such as polymerized and interpolymerized olefins [e.g., polybutylenes, polypropylenes, propylene-isobutylene copolymers, chlorinated polybutylenes, poly(1-hexenes), poly(1-octenes), poly(1-

decenes)]; alkylbenzenes [e.g., dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di(2-ethylhexyl)benzenes]; polyphenyls (e.g., biphenyls, terphenyls, alkylated polyphenyls); and alkylated diphenyl ethers and alkylated diphenyl sulfides and the derivatives, analogs and homologs thereof.

Alkylene oxide polymers and interpolymers and derivatives thereof where the terminal hydroxyl groups have been modified by esterification, etherification, etc., constitute another class of known synthetic lubricating oils. These are exemplified by polyoxyalkylene polymers prepared by polymerization of ethylene oxide or propylene oxide, the alkyl and aryl ethers of these polyoxyalkylene polymers e.g., methyl-polyisopropylene glycol ether having an average molecular weight of 1000, diphenyl ether of polyethylene glycol having a molecular weight of 500-1000, diethyl ether of polypropylene glycol having a molecular weight of 1000-1500); and mono- and polycarboxylic esters thereof, for example, the acetic acid esters, mixed C_3-C_8 fatty acid esters and C_{13} Oxo acid diester of tetraethylene glycol.

Another suitable class of synthetic lubricating oils comprises the esters of dicarboxylic acids (e.g., phthalic acid, succinic acid, alkyl succinic acids and alkenyl succinic acids, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkyl malonic acids, alkenyl malonic acids) with a variety of alcohols (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, diethylene glycol monoether, propylene glycol). Specific examples of these esters include dibutyl adipate, di(2-ethylhexyl) sebacate, di-n-hexyl fumarate, dioctylsebacate, diisoctyl azelate, diisodecyl azelate, dioctyl phthalate, didecyl phthalate, dieicosyl sebacate, the 2-ethylhexyl diester of linoleic acid dimer, and the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of ethyl-hexanoic acid.

Esters useful as synthetic oils also include those made from C_5 to C_{12} monocarboxylic acids and polyols and polyol ethers such as neopentyl glycol, trimethylolpropane, pentraerythritol, dipentaerythritol and tripentaerythritol.

Silicon-based oils such as the polyalkyl-, polyaryl-, polyalkoxy-, or polyaryloxysiloxane oils and silicate oils comprise another useful class of synthetic oils. They include tetraethyl silicate, tetraisopropyl silicate, tetra-(2-ethylhexyl)silicate, tetra-(4-methyl-2-ethylhexyl)silicate, tetra-(p-tert-butylphenyl)silicate, hexa-(4-methyl-2-pentoxy)disiloxane, poly(methyl)siloxanes and poly(methylphenyl)siloxanes. Other synthetic lubricating oils include liquid esters of phosphorus-containing acids (e.g., tricresyl phosphate, trioctyl phosphate, diethyl ester of decylphosphonic acid) and polymeric tetrahydrofurans.

Unrefined, refined and rerefined oils can be used as the base oil according to the present invention. Unrefined oils are those obtained directly from a natural or synthetic source without further purification treatment. For example, a shale oil obtained directly from retorting operations, a petroleum oil obtained directly from distillation and used without further treatment would be an unrefined oil. Syncrude obtained from tar sands is another example of unrefined oil. Refined oils are similar to the unrefined oils except they have been further treated in one or more purification steps to improve one or more properties. Many such purification techniques, such as distillation, solvent extraction, acid or base extraction, filtration and percolation are known to those skilled in the art. Rerefined oils are obtained by processes similar to those used to obtain refined oils applied to refined oils which have been already used in service. Such rerefined oils are also known as reclaimed or reprocessed oils and often are additionally processed by techniques for removal of spent additives and oil breakdown products.

The preferred base oils include the linear and branched C_{10} - C_{18} alkanes, mineral oil and refined petroleum oils.

(C) Surfactant

The surfactants useful for preparing emulsified water-based functional fluid of the present invention are those surface active agents which will stably disperse (preferably as a single phase microemulsion) the base oil in an aqueous medium containing an effective amount of the aforementioned water-soluble thickener of Component-A.

Accordingly, such surfactants can be nonionic, anionic, cationic, or amphoteric, with the nonionic and anionic type of surfactants being preferred.

Preferred surfactants have an average HLB in the range of typically from about 7 to about 16, preferably from about 8 to about 14, and most preferably from about 9 to about 12. HLBs in the range of 9 to 12 are preferred for microemulsions.

Moreover, the desired effect, e.g., viscosity response, emulsion stability, and emulsion type, for a given set of conditions can be achieved by adding a single surfactant having the desired HLB value, or by adding a mixture of surfactants having different HLB values which combine on a weight average basis to provide the desired average HLB value according to the equation:

$$\text{Average HLB} = \frac{[(WtS_1)(HLB\ S_1) + (WtS_2)(HLB\ S_2)]}{WtS_1 + WtS_2} \qquad \text{(Eq. 1)}$$

Wherein: WtS_1 = Weight of First Surfactant in Surfactant Mixture.

WtS_2 = Weight of Second Surfactant in Surfactant Mixture.

$HLB\ S_1$ = HLB of First Surfactant.

$HLB\ S_2$ = HLB of Second Surfactant.

Equation 1 deals only with a 2-surfactant mixture. However, as would be obvious to one skilled in the art, Equation 1 can be modified to determine the average HLB of 3 or more surfactants if necessary.

While the HLB of a single surfactant system is technically not an average value, the term "average HLB" is intended herein to refer to the HLB of a single surfactant in a one surfactant system as well as the weighted average HLB of surfactant mixtures, and is not intended to imply that a mixture of surfactants is being used.

Typically, when a single surfactant having the desired HLB is not available, a primarily oil soluble surfactant (e.g., a lipophilic surfactant having an HLB between about 4 and about 10) is blended with a primarily water soluble surfactant (e.g., a hydrophilic surfactant having an HLB between about 8 and about 20) at various ratios on a weight average basis to impart the desired average HLB (e.g., Balanced-HLB) to the resultant surfactant mixture.

Many such surfactants of each type are known to the art. *See*, for example, McCutcheon's "Emulsifiers & Detergents", 1981, North American Edition, published by McCutcheon Division, MC Publishing Co., Glen Rock, N.J., U.S.A., which is hereby incorporated by reference for its disclosures in this regard.

Among the nonionic surfactant types are the alkyl or alkaryl polyethyleneoxy compounds represented by the formula:

$$R_6O(EO)_n\text{-}H \qquad (V)$$

wherein R_6 is C_8 - C_{26} alkyl or alkaryl, EO is ethyleneoxy or propyleneoxy or mixtures thereof (to give copolymers) and n is a number from 1 to 50. Nonionic surfactants also include the reaction products of ethylene oxide or mixtures of ethylene oxide and higher alkylene oxide with active hydrogen compounds such as phenols, alcohols, carboxylic acids and amines, e.g., ethoxylated dodecyl alcohol, propylene glycol mono butylether, and alkylphenoxyethyleneoxy ethanols. Ethylene oxide/propylene oxide block copolymers are also useful nonionic surfactants. Glycerol esters and sugar esters such as the sorbitol esters of alkyl carboxylic acids and their ethoxylated derivatives are also known to be nonionic surfactants. A typical nonionic surfactant class useful with the present invention are the alkylene oxide-treated alkyl phenols such as the ethylene oxide alkyl phenol condensates sold by the Rohm & Haas Company. A specific example is Triton X-100 which contains an average of 9-10 ethylene oxide units per molecule, has an HLB value of about 13.5 and a molecular weight of about 628. Many other suitable nonionic surfactants are known; see, for example, the aforementioned McCutcheon's as well as the treatise "Non-ionic Surfactants" edited by Martin J. Schick, M. Dekker Co., New York, 1967, which is hereby incorporated by reference for its disclosures in this regard.

As noted above, cationic, anionic and amphoteric surfactants can also be used. Generally, these are all hydrophilic surfactants. Anionic surfactants contain negatively charged polar groups while cationic surfactants contain positively charged polar groups. Amphoteric surfactants contain both types of polar groups in the same molecule. A general survey of useful surfactants is found in Kirk-Othmer Encyclopedia of Chemical Technology, Second Edition, Volume 19, page 507 et seq. (1969, John Wiley and Son, New York) and the aforementioned compilation published under the name of McCutcheon's. These references are both hereby incorporated by reference for their disclosures relating to cationic, amphoteric and anionic surfactants.

Among the useful anionic surfactant types are substituted polyethyleneoxy compounds represented by the formula:

$$R_6O-(EO)_n-X \qquad (VI)$$

wherein R_6, EO, and n are as defined in connection with Formula V, and X is SO_3H or CO_2H or PO_3H_2 and mixtures; salts of long chain carboxylates (also known as carboxylate soaps) such as potassium oleate, sodium laurate, potassium stearate, potassium caprolate, sodium palmitate and the like; metal-organo sulfonates wherein the metal can be as described in connection with M of Formula I, e.g., alkaryl sulfonates, such as alkali or alkaline earth metal C_8 - C_{30}, preferably C_{10} - C_{25} alkyl-benzene or xylene-sulfonates including tetracosenyl benzene sulfonate, sodium nonylbenzene sulfonate and potassium dodecylbenzene sulfonate (<u>See</u>, USP 4,140,642, the disclosure of which is herein incorporated by reference); alkali metal alkyl sulfates such as sodium dodecyl sulfate and alkali metal dialkyl sulfosuccinates such as sodium dihexyl sulfosuccinate and sodium dioctyl sulfosuccinate; salts of resin acids such as abietic acid and dihydroabietic acid, salts of hydrocarbyl substituted succinic anhydride, e.g., potassium polyisobutenyl succinate, and alkyl phosphate esters, e.g., dodecyl hydrogen phosphate.

Useful cationic surfactants include alkyl ammonium or quaternary ammonium salts, e.g., dodecyl ammonium hydrochloride, dodecyl trimethyl quaternary ammonium chloride and the like, and ethoxylated fatty amines. Other suitable cationic surfactants are described in McCutcheon's, supra. Also included in the aforementioned surfactants are oligomeric and polymerizable surfactants described at pages 319-322 of Blackley, *Emulsion Polymerization Theory and Practice*, John Wiley and Sons (1975). Examples of such oligomers include ammonium and alkali metal salts of functionalized oligomers sold by Uniroyal Chemical under the trade name "Polywet" and copolymers of acrylonitrile and acrylic acid having molecular weights less than 2000 which are prepared in the presence of chain terminating agents such as n-octyl mercaptan. Examples of polymerizable surfactants include sodium salts of 9- and 10-(acrylylamido)stearic acid and the like.

Amphoteric surfactants include the imidazoline types, e.g., fatty acid - aminoethylethanolamine or ethylene diamine condensates and similar types.

Various cationic, anionic and amphoteric surfactants are available from the industry, particularly from such companies as Exxon Chemical, Tomah Products, Mazer, Lonza, Rohm & Haas, Union Carbide Corporation. Further information about anionic and cationic surfactants also can be found in U.S. Patent No. 3,933,660 and the texts "Anionic Surfactants", Parts II and III, edited by W. M. Linfield, published by Marcel Dekker, Inc., New York, 1976 and "Cationic Surfactants", edited by E. Jungermann, Marcel Dekker, Inc., New York, 1976. All of these references are incorporated by reference for their disclosures in regard to surfactants.

Of the foregoing surfactants, the anionic and nonionic, and mixtures thereof are preferred.

The most preferred surfactants are alkali metal alkyl:benzene, toluene or xylene sulfonates and mixtures thereof with ethoxylated alkanols or alkyl phenols.

In general, the type of application and the requirements characteristic of the application will determine the type and amount of surfactant employed to give the desired viscosity response yet still achieve emulsion stability. For example, if the end use of the fluid formulation employs a macro o/w emulsion, lower amounts of surfactant are needed, whereas the formation and maintenance of a microemulsion typically involves a somewhat higher amount of surfactant, subject to the constraints relating to the saturation volumes of oil and water derived from balanced microemulsions discussed earlier.

(D) Water

The water employed in the emulsified water-based functional fluids of the present invention preferably is distilled or deionized. While some degree of hardness is acceptable, the desirable water for use herein will contain typically less than about 400 ppm, preferably less than about 100 (e.g., 50-0) ppm $CaCO_3$ equivalents.

Water hardness can be classified into two types, namely, (1) bicarbonate (temporary) and (2) noncarbonate (permanent). Water containing Ca, Mg, ferrous (Fe), and other multiply charged cations along with bicarbonate, sulfate, and other such anions is called hard water because of its action on soaps. When soap is added to hard water it forms precipitates with these salts.

Thus, hardness can reduce surfactant efficiency by reducing its solubility in water. This can lead to emulsion instability and phase separation.

Generally, the emulsified water-based functional fluid composition of the present invention comprises an effective amount of water, base oil and surfactant to provide an emulsion, preferably a microemulsion, and most preferably a single-phase microemulsion, of the base oil (Component - B) dispersed in a continuous aqueous phase which contains the water soluble polymer thickener (Component - A), and surfactant (Component - C) which maybe in either phase depending on its type.

Thus, while any effective amount of water can be employed in the final fluid composition, it is contemplated that such effective amounts will range typically from about 50 to about 99, preferably from about 70 to about 98, and most preferably from about 80 to about 97 weight percent, based on the fluid weight.

Similarly, while any effective amount of base oil can be employed in the final fluid composition, it is contemplated that such effective amounts will be sufficient to achieve, a phase weight or volume ratio, i.e., weight or volume ratio of base oil:water in the final fluid of typically from about 1:1000 to about 1:10, preferably from about 1:500 to about 1:15, and most preferably from about 1:400 to about 1:20.

Component-A (polymer thickener) is employed in the final fluid in an amount effective to cause at least some increase in the shear viscosity at 24°C of the emulsified fluid relative to the viscosity of the fluid with no polymer.

Typically, Component-A effective amounts will be sufficient to cause a shear viscosity increase at 24°C, as determined by the Contraves Rheometer LS-30, relative to the emulsified fluid without Component-A. Desirably, such viscosity increase will be typically at least 5, preferably at least 10, and most preferably at least 50%.

Where anti-mist properties are sought to be imparted to the fluid, effective amounts of polymer can be expressed as that needed to yield an Extensional Viscosity Equivalent (EVE) of typically from about 0.1 to about 20, preferably from about 0.2 to about 15, and most preferably from about 0.5 to about 10 cm.

The EVE test is particularly useful in predicting whether a particular polymer can achieve virtually total mist suppression and at what polymer concentration. This can be achieved by developing calibration curves which plot polymer concentration versus EVE. It has been established in the Chao et al. article (cited below) that a linear relationship exists between EVE and total mist suppression. Moreover, below a certain polymer concentration the EVE will be about 0. The polymer concentration at which this occurs is referred to herein as the Experimental End Point (EEP). It has been found that dividing the EEP concentration by 10 yields the approximate polymer concentration at which total mist suppression begins. This concentration is referred to herein as the Total Mist Suppression Commencement Point (TMSCP). The EVE associated with the TMSCP is determined by interpolation of the EVE/polymer concentration linear plot below the Experimental End Point. If less than total mist suppression is acceptable, one can further interpolate the EVE and polymer concentrations below the TMSCP to a point which correlates with acceptable observed partial mist suppression.

The above described EVE ranges include, at the low ends thereof, those determined from the above interpolation technique.

The "Extensional Viscosity Equivalent" of an emulsified water-based functional fluid as used herein is intended to refer to the height in centimeters to which a liquid column of the fluid can be pulled, without breaking, from a container containing the fluid by touching a 3.8 cm long x 20 gauge syringe (flat tip) needle (0.023 in. I.D.) (connected to a vacuum pump) to the surface of the liquid, maintaining a vacuum above the polymer solution (at a temperature of about 25° C.), and moving the needle and fluid apart at 5 mm/second (+/- 1 mm/sec.) (e.g., by lowering the fluid container while keeping the needle point fixed, or by raising the needle above the fluid surface) to siphon the fluid. A measure is taken of the distance separating the fluid surface in the container and the needle point when the siphon breaks. The greater the distance separating the needle tip and the bulk fluid surface at the point at which the siphon breaks, the longer the tubeless siphon liquid column at the break point and, hence, the greater the stringiness of the fluid. The break height of a tubeless siphon is related to the extensional viscosity of a fluid and can be correlated with the anti-mist properties of the fluid, i.e., the greater the E.V.E., the better the anti-mist properties of the fluid. The vacuum used should be sufficient to maintain a substantially constant velocity of fluid flow through the needle. Generally, a vacuum of about - 40 kPa will be employed. For more information, see K. K. K. Chao and M. C. Williams, *J. Rheology*, 27 (5) 451-474 (1983).

An alternative method for evaluating anti-mist properties (and hence effective amounts of thickener) is the Atomizer Spray Technique. For this procedure, an atomizer spray bottle equipped with a pump to pressurize the contents of the bottle is employed. One suitable bottle for this procedure identified as the Mini-Air Sprayer, can be obtained from Consolidated Plastics Co., Twinsburg, Ohio.

A control emulsion sample (no thickener) is charged to the sprayer, which is then pressured to a recorded level sufficient to eject the sample in the form of a spray. The control sample is then sprayed directly at a large absorbent paper, e.g., filter paper, mounted at a recorded distance from the sprayer, e.g., about 1 foot for a recorded period of time (e.g., 10 secs.). The droplets of the spray will then wet the filter paper. A circle is then immediately drawn around the outer boundaries of wet spots marked by the droplets such that the circle encloses at least 95 % of the wet spot area. The area enclosed by the circle is then calculated and designated Area 1.

The above procedure is then repeated (after washing the sprayer) using the same control sample to which has been added a measured amount of thickener. The sprayer is pressurized to the same degree as employed for control sample alone, and fresh filter paper is mounted at the same distance from the sprayer as employed in the control run. The spray time is the same as employed for the control. The area of the resulting circle generated by the test sample and drawn in accordance with the above control run procedure is designated Area 2. The ratio of Area-1/Area-2 is designated herein as the mist ratio.

Effective anti-mist amounts of Component-A thickener will yield mist ratios of typically from about 1.5 to about 150, preferably from about 2 to about 100 and most preferably from about 5 to about 50.

It is contemplated that such effective anti-mist amounts of Component-A thickener will be typically at less than 0.1, preferably less than 0.05, and most preferably less than 0.02 wt. %, based on the total fluid weight.

In view of the above, while any effective viscosity enhancing amount of Component-A can be employed in the emulsified water-based functional fluid it is contemplated that such effective amounts will range typically from about .001 to about 1.0, preferably from about 0.005 to about 0.5, and most preferably from about 0.01 to about 0.3 weight %, based on the emulsion fluid composition weight.

The amount of Component-C (surfactant) employed in the emulsified water-based functional fluid is effective to achieve an o/w emulsion of base oil in water. Preferably the amount of Component-C is sufficient to yield a single phase microemulsion, and preferably also sufficient to interact with Component-A (Thickener) to give enhanced shear and extensional viscosity (i.e. anti-mist) properties.

Accordingly, while any effective amount of Component-C surfactant can be employed, it is contemplated that such effective amounts for a microemulsion will range typically from about 0.1 to about 10, preferably from about 0.2 to about 5, and most preferably from about 0.5 to about 3 weight %, based on the weight of the fluid composition.

Similarly, effective Component-C amounts for a macroemulsion will range typically from about 0.06 to about 8, preferably from about 0.11 to about 4, and most preferably from about 0.3 to about 2.4 weight %, based on the fluid composition weight.

It is also desirable that the surfactant amount be related to the amount of base oil (Component-B) in order to maintain emulsion stability.

Accordingly, Component-C (surfactant) is desirably employed in an emulsified functional fluid of the present invention in an amount sufficient to yield a weight ratio of Component-B:Component-C of typically not greater than about 20:1, preferably not greater than about 10:1, and most preferably not greater than about 5:1.

The present invention is also directed to concentrates which are also emulsions or can be made into emulsions by the addition of water. Whether the concentrate will exist as an emulsion depends in part on the oil:water phase weight or volume ratio employed for the concentrate. The concentrate may contain water in amounts of from about 5 up to about 90% of the concentrate total weight to ensure concentrate homogeneity and dilutability with additional water. Also, for matters of convenience, concentrates are typically formulated with the desired final amount of oil, surfactant and additives, so that final fluids can be made by addition of water.

The concentrates of the present invention will contain typically not greater than 90, preferably not greater than 50, and most preferably not greater than 25 weight percent of the water normally present in the final emulsified functional fluid.

Thus, the concentrates of this invention can be converted to emulsified water-based (i.e., aqueous) functional fluids by dilution with water. This dilution is usually done by standard mixing techniques, usually at room or slightly elevated temperatures, e.g., below 100°C. This is often a convenient procedure since the concentrate can be shipped to the point of use before the additional water is added. Thus, the cost of shipping a substantial amount of the water in the final water-based functional fluid is saved. Only the water necessary to formulate the concentrate (which is determined primarily by phase stability, dilutability, ease of handling and convenience factors), need be shipped.

Generally, the emulsified water-based fluids of the present invention are made by diluting the aforedescribed concentrates with water, wherein the ratio of added water:concentrate is in the range of about 10:90 to about 99:1 by weight.

The concentrates and emulsified water-based functional fluids can optionally include other conventional additives commonly employed in water-based functional fluids. These other additives include functional additives, corrosion-inhibitors, rust inhibitors, lubricity agents, bactericides, dyes, water-softeners, odor masking agents, anti-foam agents, pH buffers, coupling agents to compatibilize oil or water soluble additives, and the like, as well as additional surfactants over and above those indicated as Component (C).

The term "functional additives" as used herein is intended to define typically oil-soluble, water-insoluble additives which function in conventional oil-based systems such as E.P. agents, anti-wear agents, load-carrying agents, friction modifiers, and lubricity agents, etc. as described hereinafter. They can also function as anti-slip agents, film formers. As is well known, such additives can function in two or more of the above-mentioned ways. For example, E.P. agents often function as load-carrying agents. The term "oil-soluble, water-insoluble functional additive" refers to a functional additive which is not soluble in water above a level of about 1 gram per 100 milliliters of water at 25° C., but is soluble in base oil to the extent of at least one gram per liter at 25° C.

These functional additives can also include certain solid lubricants such as graphite, molybdenum disulfide and polytetrafluoroethylene and related solid polymers, wax, e.g., paraffin wax, microcrystalline wax, polyethylene, and oxidized polyethylene.

The functional additives can also include frictional polymer formers. Briefly, these are potential polymer forming materials which are dispersed in a liquid carrier (e.g., oil) at low concentration and which polymerize at rubbing or contacting surfaces to form protective polymeric films on the surfaces. The polymerizations are believed to result from the heat generated by the rubbing and, possibly, from catalytic and/or chemical action of the freshly exposed surface. A specific example of such materials is dilinoleic acid and ethylene glycol combinations which can form a polyester frictional polymer film. These materials are known to the art and descriptions of them are found, for example, in the journal "Wear", Volume 26, pages 369-392, the disclosure of which is hereby incorporated by reference for its discussions of frictional polymer formers.

The functional additives also include known metal or amine salts of organo sulfur, phosphorus, boron or carboxylic acids which are the same as or of the same type as used in oil-based fluids. Typically such salts are of carboxylic acids of 1 to 22 carbon atoms including both aromatic and aliphatic acids; sulfur acids such as alkyl and aromatic sulfonic acids and the like; phosphorus acids such as phosphoric acid, phosphorus acid, phosphinic acid, acid phosphate esters and analogous sulfur homologs such as the thiophosphoric and dithiophosphoric acid and related acid esters; boron acids include boric acid, acid borates and the like. Useful functional additives also include metal dithiocarbamates such as molybdenum and antimony dithiocarbamates; as well as phosphates and phosphites; borate amine salts, chlorinated waxes; molybdenum phosphates, chlorinated waxes and sodium nitrite or nitrate.

Many such functional additives are known to the art. For example, descriptions of additives useful in conventional oil-based systems and in the aqueous-based systems of this invention are found in "Advances in Petroleum Chemistry and Refining", Volume 8, Edited by John J. McKetta, Interscience Publishers, New York, 1963, pages 31-38 inclusive; Kirk-Othmer "Encyclopedia of Chemical Technology", Volume 12, Second Edition, Interscience Publishers, New York, 1967, page 575 et seq.; "Lubricant Additives" by M. W. Ranney, Noyes Data Corporation, Park Ridge, N.J., U.S.A., 1973; and "Lubricant Additives" by C. V. Smalheer and R. K. Smith, The Lezius-Hiles Co., Cleveland, Ohio, U.S.A. These references are hereby incorporated by reference for their disclosures of functional additives useful in the systems of this invention.

In certain of the typical fluids of the present invention, the functional additive is a sulfur or chlorosulfur E.P. agent, known to be useful in oil-base systems. Such materials include chlorinated aliphatic hydrocarbons, such as chlorinated wax; organic sulfides and polysulfides, such as benzyl-disulfide, bis-(chlorobenzyl)disulfide, dibutyl tetrasulfide, sulfurized methyl ester of oleic acid, sulfurized alkylphenol, sulfurized dipentene, sulfurized terpene, and sulfurized Diels-Alder adducts; phosphosulfurized hydrocarbons, such as the reaction product of phosphorus sulfide with turpentine or methyl oleate; phosphorus esters such as the dihydrocarbon and trihydrocarbon phosphites and phosphates, e.g., dibutyl phosphite, diheptyl phosphite, dicyclohexyl phosphite, pentylphenyl phosphite, dipentylphenyl phosphite, tridecyl phosphite, distearyl phosphite and polypropylene substituted phenol phosphite (as well as the corresponding phosphates); metal thiocarbamates, such as zinc dioctyldithiocarbamate and barium heptylphenol dithiocarbamate; and Group II metal salts of phosphorodithioic acid, such as zinc dicyclohexyl phosphorodithioate, and the zinc salts of a phosphorodithioic acid.

The functional additive can also be anti-chatter or anti-squawk agents. Examples of the former are the amide metal dithiophosphate combinations such as disclosed in West German Pat. No. 1,109,302; amine salt-azomethene combinations such as disclosed in British Patent Specification No. 893,977; or amine dithiophosphate such as disclosed in U.S. Pat. No. 3,002,014. Examples of anti-squawk agents are N-acyl-sarcosines and derivatives thereof such as disclosed in U.S. Pat. Nos. 3,156,652 and 3,156,653; sulfurized fatty acids and esters thereof such as disclosed in U.S. Pat. Nos. 2,913,415 and 2,982,734; and esters of dimerized fatty acids such as disclosed in U.S. Pat. No. 3,039,967. The above-cited patents are incorporated herein by reference for their disclosure as pertinent to anti-chatter and anti-squawk agents useful as a functional additive in the aqueous systems of the present invention.

Mixtures of two or more of any of the aforedescribed functional additives can also be used. Preferably, the functional additives are pre-blended simultaneously or sequentially, with the base oil before contact with water-soluble components of the fluid or concentrate.

Typically, a functionally effective amount of the functional additive is present in the fluids of this invention. For example, if the functional additive is intended to serve primarily as a load-carrying agent, it is present in a load-carrying amount.

The water-based functional fluids of this invention often contain at least one inhibitor for corrosion of metals. These inhibitors can prevent corrosion of either ferrous or non-ferrous metals (e.g., copper, bronze, brass, titanium, aluminum and the like) or both. The inhibitor can be organic or inorganic in nature. Usually it is sufficiently soluble in water to provide a satisfactory inhibiting action though it can function as a corrosion inhibitor without dissolving in water, and it need not be water-soluble. Many suitable inorganic inhibitors useful in the aqueous systems of the present invention are known to those skilled in the art. Included are those described in "Protective Coatings for Metals" by Burns and Bradley, Reinhold Publishing Corporation, Second Edition, Chapter 13, pages 596-605. This disclosure relative to inhibitors is incorporated herein by reference.

Specific examples of useful inorganic inhibitors include alkali metal nitrites, sodium di- and tripolyphosphate, potassium and dipotassium phosphate, alkali metal borate and mixtures of the same.

Many suitable organic inhibitors are known to those of skill in the art. Specific examples include hydrocarbyl amine and hydroxy-substituted hydrocarbyl amine neutralized or amidated (i.e., reacted to form amide) acid compounds, such as neutralized boric acid, neutralized or amidated citric and/or tartaric acid, amine neutralized phosphates and hydrocarbyl phosphate esters, neutralized or amidated fatty acids (e.g., those having about 8 to about 22 carbon atoms, e.g., tall oil fatty acids), neutralized aromatic carboxylic acids (e.g., 4-tertbutyl benzoic acid), neutralized naphthenic acids and neutralized hydrocarbyl sulfonates. Mixed salt esters of alkylated succinimides are also useful. Particularly useful amines include the alkanol amines such as ethanol amine, diethanol amine, triethanol amine and the corresponding propanol amines, benzotriazoles, benzimidazoles and their derivatives, e.g., 1-diethanolamine methylbenzotriazole are also preferred (See, U.S. Patent No. 4,177,155 the disclosure relative to inhibitors is herein incorporated by reference). Mixtures of two or more of any of the aforedescribed corrosion inhibitors can also be used. The corrosion inhibitor is usually present in concentrations in which they are effective in inhibiting corrosion of metals with which the aqueous composition comes in contact.

The water-based functional fluids of the present invention can contain anti-rust agents. Suitable anti-rust agents include mixtures derived from the reaction product of fatty acids (e.g., C_8 - C_{22}), boric acid and hydroxy amines, e.g., diethanolamine which contain borated fatty amides and borate hydroxy amine esters; borate esters of hydroxy alkyl amines such as diethanolamine (See, U.S. Patent No. 3,642,652); aryl sulfonamido carboxylic acids, their amine salts and mixtures of the same with borated esters of diethanolamine (See, U.S. Patent No. 4,297,236) and monovalent metal or amine salts of sulfonic acid, polybasic acids (e.g., tall oil fatty acids) and alkanolamides (See, U.S. Patent No. 4,395,286). The above identified patents are incorporated herein for their disclosure of anti-rust agents.

The water-based functional fluids of the present invention (particularly those that are used in cutting or shaping of metal) can also contain at least one polyol with inverse solubility in water. Such polyols are those that become less soluble as the temperature of the water increases. They thus can function as surface lubricity agents during cutting or working operations since, as the liquid is heated as a result of friction between a metal workpiece and worktool, the polyol of inverse solubility "plates out" on the surface of the workpiece, thus improving its lubricity characteristics.

Other lubricity agents include long chain alcohols, e.g., C_{12} to C_{16} alcohols, long chain fatty acids, e.g., C_{12} to C_{22} acids such as oleic acid, and salts or esters thereof, e.g., alkanolamine soaps, or esters such as butyl stearates which also serve as extreme pressure agents (See, U.S. Patent No. 4,027,512, the disclosure of which is herein incorporated by reference as to lubricity agents).

The water-based functional fluids of the present invention can also include at least one bactericide. Such bactericides are well known to those of skill in the art and specific examples can be found in the aforementioned McCutcheon publication in the section entitled "Functional Materials" under the heading "Antimicrobials" on pages 9-20 thereof. This disclosure is hereby incorporated by reference as it relates to suitable bactericide for use in the fluids of this invention. Generally, these bactericides are water-soluble, at least to the extent to allow them to function as bactericide. Representative examples of suitable bactericides include 2,4,5-trichlorophenol, sodium salts of 2,2′-dihydroxy-5,5′-dichlorodiphenyl methane and orthophenyl phenol.

The fluids of the present invention can also include such other materials as dyes, e.g., an acid green dye; water softeners, e.g., ethylene diamine tetraacetate sodium salt or nitrilo triacetic acid short chain fatty acids and alkanol amines; odor masking agents, e.g., citronella, oil of lemon, and the like; and anti-foamants, such as the well-known silicone anti-foamant agents. The fluids of this invention may also include an anti-freeze additive where it is desired to use the composition at a low temperature. Materials such as ethylene glycol and analogous polyoxyalkylene polyols can be used as anti-freeze agents. The amount used will depend on the degree of anti-freeze protection desired and will be known to those of ordinary skill in the art.

Among the many diverse coupling agents which can be employed in combination with the above-described surface active agents are the aliphatic and aromatic glycols and ethers derived therefrom. The aliphatic glycols may be polyalkylene glycols, preferably those in which the alkylene radical is a lower alkylene radical having from 1 to about 10 carbon atoms. Such alkylene glycols are illustrated by ethylene glycol, trimethylene glycol, 1,2-butylene glycol, 2,3-butylene glycol, tetramethylene glycol, hexamethylene glycol, or the like. Specific examples of the ethers include monophenyl ether of ethylene glycol, mono-(heptylphenyl)-ether of triethylene glycol, mono-alpha-octyl-beta-naphthyl ether of tetrapropylene glycol, mono-(polyisobutene[molecular weight of 1000]substituted phenyl)ether of octapropylene glycol, and mono-(o,p-dibutylphenyl)ether of polybutylene glycol, mono-(heptylphenyl)ether of trimethylene glycol and mono-(3,5-dioctylphenyl)ether of tetra-trimethylene glycol, etc. The mono-aryl ethers are obtained by the condensation of a phenolic compound such as an alkylated phenol or naphthyl with one or more moles of an epoxide such as ethylene oxide, propylene oxide, trimethylene oxide, or 2,3-hexylene oxide. The condensation is promoted by a basic catalyst such as an alkali or alkaline earth metal hydroxide, alcoholate, or phenate. The temperature at which the condensation is carried out may be varied within wide ranges such as from room temperature to about 250°C. Ordinarily it is preferably 50° - 150° C. More than one mole of the epoxide may condense with the phenolic compound so that the product may contain in its molecular structure one or more of the radicals derived from the epoxide. A polar-substituted alkylene oxide such as epichlorohydrin or epibromohydrin likewise is useful to prepare the mono-aryl ether product and such product likewise is a useful surface active agent for stably suspending or dispersing water insoluble salts of this invention in aqueous fluids. Likewise useful coupling agents are the mono- and dialkyl ethers of the aliphatic glycols in which the alkyl radical is, e.g., ethyl, butyl, octyl, nonyl, dodecyl, behenyl, etc e.g., ethylene glycol monobutyl ether, diethylene glycol monobutyl ether. The fatty acid esters of the mono-aryl or mono-alkyl ethers of aliphatic glycols also are useful. The fatty acids include e.g., acetic, oleic acid, stearic acid, iso-stearic acid, linolenic acid, linoleic as well as commercial acid mixtures such as are obtained by the hydrolysis of tall oils, etc. Specific examples are diethylene glycol monobutyl ether acetate, the oleate of mono-(heptylphenyl)ether of tetraethylene glycol and the acetate of mono-(polypropene [having molecular weight of 1000]-substituted phenyl)ether of tri-propylene glycol.

A pH buffering agent is useful in maintaining the pH level of the emulsion above 7, preferably above 8. Suitable pH buffering agents are well known and include, but are not limited, to various amines such as ethanolamines, diethanolamines, triethanolamines, borate amines, and alkali or alkaline earth metal hydroxides or carbonates.

As indicated above, the water-based functional fluids of the present invention can contain additional surfactants over and above those indicated as Component (C). These additional surfactants are typically selected to be useful in enhancing the dispersibility of the above indicated other additives, particularly the functional additives. Any one or more of the surfactants indicated above as Component (C) can be used. These surfactants, when used, are generally employed in effective amounts to enhance the dispersion of the above-indicated additives in the emulsified fluids of the invention.

It should also be noted that many of the ingredients described above for use in making the fluids of this invention are industrial products which exhibit or confer more than one property on such systems. Thus, a single ingredient can provide several functions thereby eliminating or reducing the need for some other additional ingredient.

Representative effective amounts of the above classes of additives in the final fluid are summarized below:

Additive Type	wt. % Broad	Preferred
Functional additive	.001-5	.01-1
Corrosion inhibitor	0.002-0.025	0.004-0.015
Rust inhibitor	0.1-1.5	0.2-0.75
Lubricity agent	0.2-0.75	0.04-0.5
Bactericide	0.02-0.15	0.04-0.1
Water softener	0.002-0.05	0.01-0.25
Odor masking	0.002-0.25	0.0004-0.01
Anti-foam	0.001-0.05	0.002-0.005
Coupling agent	0.01-0.5	0.04-0.25

The following examples are given as specific illustrations of the claimed invention. It should be understood, however, that the invention is not limited to the specific details set forth in the examples. All parts and percentages in the examples as well as in the remainder of the specification are by weight unless otherwise specified.

Example 1

Synthesis of HRAM-1 Polymer

An HRAM terpolymer of acrylamide, sodium acrylate and N-*n* octyl acrylamide was synthesized using the micellar polymerization technique. In a 5 liter glass reactor equipped with stainless steel baffles, turbine impellers and nitrogen sparger, 75.0 grams of acrylamide (AM), 80 grams of sodium dodecyl sulfate (SDS), 2.0 grams (1.0 mole percent) of N-n-octyl acrylamide and 2425 grams of distilled water were mixed to form a homogeneous transparent solution. The reaction fluid was deoxygenated by sparging with nitrogen (N_2) for 2 hours while heating to bring the temperature up to 50°C. At temperature the initiator, 0.05 grams of potassium persulfate ($K_2S_2O_8$) in 10 ml of deoxygenated water was added. The reaction was maintained at 50°C with gentle agitation for 18 hours. While maintaining the reaction temperature at 50°C, 200 ml of 50% sodium hydroxide (NaOH) or 0.40 moles of NaOH were added and allowed to react for 1 hour to partially hydrolyze acrylamide monomer. The resulting terpolymer was isolated by precipitating in 5 liters of methanol. The swollen polymer mass was ground in a Waring blender, washed with methanol and vacuum oven dried at 40°C for 16 hours. This HRAM polymer is designated HRAM-1. Nitrogen and sodium analysis, along with potentiometric titration, showed that the polymer contained 18 mole percent sodium acrylate groups. The weight average molecular weight of the polymer as determined by light scattering was found to be 3,000,000. The corresponding mole ratio of x:y:z of Formula 1 is 1:0.22:0.012 and the associated mole % for each of monomer species II, III and IV was 81, 18 and 1 mole % respectively.

Comparative Example 1 (HPAM-1)

Preparation of HPAM Polymer

A partially hydrolyzed polyacrylamide (HPAM) copolymer was synthesized using a similar procedure as described in Example 1. Using the same reactor set-up, 75 grams of acrylamide, 80 grams of SDS and 2,425 grams of distilled water were mixed and sparged with nitrogen for 12 hours while heating to 50°C. The initiator, 0.05 grams of $K_2S_2O_8$, in 10 ml. of deoxygenated water was then added. The reaction was maintained at 50°C with gentle agitation for 18 hours and then 200 ml. of 50% NaOH (0.40 moles) was added and allowed to react for 1 hour. The resulting HPAM polymer was then isolated by precipitation in 5 liters of methanol, ground and washed with methanol in a Waring blender and vacuum oven dried at 40°C for 16 hours. This partially hydrolyzed polyacrylamide, designated HPAM-1, was a white, friable material having 18 mole % sodium acrylate groups, 82 mole % acrylamide, and a weight average molecular weight of 3,000,000.

Thus, HPAM-1 differs from HRAM-1 in that it lacks a C_8 hydrophobe attached to the backbone, i.e., no N-octyl acrylamide monomer was used and only monomer species II and III are present in the HPAM-1 polymer..

Example 2 (HRAM-2)

The procedure for Example 1 was repeated except that the reaction temperature was maintained at 45 °C for 16 hours, hydrolysis reaction time was increased to 2 hours and the total monomer concentration in the reaction mixture was increased to 4.5 wt. % from 3 wt. % for HRAM-1.

The resulting HRAM polymer contains 18 mole % sodium acrylate monomer, a weight average molecular weight of about 4,500,000 and is designated HRAM-2. The corresponding x:y:z mole ratio of Formula 1 for HRAM-2 was 1:0.22:0.012 and the associated mole % of monomer species II, III and IV was 81, 18, and 1, respectively.

Comparative Example 2 (PAM-1)

The procedure of Comparative Example 1 is repeated with the exception that the hydrolysis step with NaOH is eliminated. The resulting polymer has a molecular weight of 3,000,000 and is designated PAM-1.

Example 3 (RAM-1)

The procedure of Example 1 is repeated except that 1.5 g (0.75 mole%) of N-octylacrylamide is employed and the hydrolysis step with NaOH is eliminated. The resulting polymer has a weight average molecular weight of 3,000,000 and is designated RAM-1. The mole ratio of acrylamide to N-octylacrylamide in the final polymer (i.e. x:z: in Formula 1) is 1:.0075 with a corresponding mole % of monomer Species II and IV of 99.25 and 0.75 respectively.

Example 4 (RAM-2)

The procedure of Example 1 is repeated except that the hydrolysis step with NaOH is eliminated. The resulting polymer has a weight average molecular weight of 3,000,000, a mole ratio (x:z) of acrylamide:N-octylacrylamide of 1:0.01, and is designated RAM-2. The corresponding mole % monomer species II and IV is 99, and 1, respectively.

Comparative Examples 3-6 (HPAM-2 to -5)

Part A

A series of polymers was prepared using an inverse emulsion polymerization technique. The oil phase was prepared as follows: 8% (24 gms) Span 80 surfactant was admixed with 300 g Isopar M (isoparaffinic base oil) 0.0412 gms of AIBN initiator and 50 ml toluene.

The aqueous phase was prepared using: 19.4 gms of 50 wt. % NaOH, 17.5 gms of acrylic acid (30.0 mole %), 41.0

gms acrylamide monomer and 55.7 gms water, and 0.0134 g IPA. The NaOH, H_2O and acrylic acid were blended and the pH adjusted to 9, followed by addition of acrylamide and isopropyl alcohol (IPA). The emulsion was formed by adding 125 g of oil phase to 125 g aqueous phase giving a phase ratio of 1:1. The initiator azo-bis isobutyronitrile (AIBN) was added to oil phase. The reaction was performed at 45°C under Argon for 5 hours. The polymer was precipitated in a 50/50 mixture of acetone/methanol, washed with acetone, filtered and dried in vacuum over 35°C. This polymer, designated as HPAM-2, contained 30 mole % sodium acrylate groups, and possessed a weight average molecular weight of about 5,000,000.

Part B

The above procedure was repeated two more times except that the acrylic acid content was adjusted relative to acrylamide monomer to give respectively 10 and 20 mole % sodium acrylate groups.

The polymer containing 10 mole % sodium acrylate groups was designated HPAM-3 and possessed a weight average molecular weight of 6,000,000.

The polymer containing 20 mole % sodium acrylate was designated HPAM-4 and possessed a weight average molecular weight of 6,500,000. For the preparation of HPAM-3 and -4 no IPA was used as a chain transfer agent.

Part C

The solution polymerization procedure of Example 2 was repeated except that no hydrophobic monomer (i.e. N-n-octy(acrylamide)) was employed. The initiator was employed at a concentration of 0.000167 mole/L and the solids content of the reaction mixture was 4.5%. The resulting polymer was designated HPAM-5 and contained 16 mole % sodium acrylate monomer and 84 mole % acrylamide, i.e. an x:y:z mole ratio of 1:0.190:0. The weight average molecular weight of HPAM-5 was 4,300,000.

Comparative Example 7

A polymer was obtained under the trade name Dow Pusher 700 which is a partially carboxylated polyacrylamide described in U.S. Patent No. 3,039,529. This polymer possessed a weight average molecular weight of about 7,000,000 and was designated HPAM-6.

Example 5

Part A

Preparation of Base Concentrate

A base o/w microemulsified concentrate suitable for use as a water-based cutting fluid was prepared by blending the following components in the following amounts:

Component No.	Component	wt. %
1	Deionized water	35.0
2	Diethanolamine (DEA)	30.0
3	Boric acid	3.8
4	Tartaric acid	6.2
5	1-diethanolamino-methylbenzotriazole	0.2
6	Sodium C_{24} alkylbenzene sulfonate (HLB=6)	7.0
7	Tall oil fatty acid (HLB as the DEA soap = 16)	1.8
8	Diethylene glycol monobutyl ether	4.0
9	Solvent 90 N (oil)	12.0

The o/w phase weight ratio of the concentrate is 0.34:1. The resulting concentrate forms a clear microemulsion and is designated Base Concentrate-1 (i.e., BC-1). The calculated (as described herein) average HLB of the surfactants in the concentrate is 8. However, the effective HLB is somewhat higher than 8 due to the high concentration of DEA.

Part B

To BC-1 is added 2 wt. % (based on the final concentrate weight) of HRAM-1 prepared in accordance with Example 1. The resulting polymer modified concentrate is designated BC-1/HRAM-1 (2%).

Part C

To BC-1 is added 2 wt. % of HPAM-1 prepared in accordance with Comparative Example 1. The resulting polymer modified concentrate is designated BC-1/HPAM-1 (2%)

Observations

The addition of 2% of the HPAM-1 polymer to BC-1 resulted in a very opaque fluid which phase separated on standing into two phases. Approximately 40 vol. % of the sample settled as a very viscous essentially colorless (pale yellow) aqueous phase. Almost all of the volume of the bottom phase could be accounted for by the water and polymer present in the sample. Above this aqueous polymer phase was a fluid clear amber surfactant phase containing oil, emulsifiers and most of the alkanolamine.

The separation of an aqueous phase is believed to have been caused by the high water solubility of the polymer which allows it to extract water from the microemulsion. Since the polymer is too hydrophilic to interact with the surfactant and oil, its phase separates with its associated water. The surfactant stays with the upper oil phase and this phase separation shows up as a lipophilic shift.

In contrast to the incompatible BC-1/HPAM-1 (2%) system, the addition of 2 % of the HRAM-1 polymer to the same BC-1 concentrate, resulted in a homogeneous clear stable fluid with significantly enhanced viscosity. It is believed that the hydrophobic C_8 groups on the HRAM-1 polymer counteracted the lipophilic shift caused by the highly water soluble hydrolyzed polyacrylamide. No phase separation occurred because the C_8 groups reduced the polymer hydrophilicity so there was less tendency to extract water from the microemulsion. In addition, these lipophilic groups provided for greater interaction with surfactants and oil which also contributed to emulsion stability. The combination of these two factors allowed the system to remain a clear viscous single phase.

Part F

The low shear viscosity of a BC-1/HRAM-1 microemulsion concentrate prepared in accordance with Part B was measured on a Brookfield Viscometer using a #4 Spindle at 23°C. The results are summarized at Table 1 below.

Table 1

Brookfield Viscosity of 2% HRAM-1 in BC-1

RPM	Shear Rate Sec^{-1}	Viscosity cP
0.6	0.125	23,000
1.5	.314	20,800
3.0	.627	18,600
6.0	1.254	15,800
12.0	2.51	12,700

Table 1 (Cont'd.)
Brookfield Viscosity of 2% HRAM-1 in BC-1

RPM	Shear Rate Sec^{-1}	Viscosity cP
30.0	6.27	9,200
60.0	12.54	7,320

For comparison, BC-1 without polymer has a Newtonian viscosity of 102 cP at comparable shear rates using a Contraves Low Shear 30 Rheometer.

Example 6

Part A

To a sample of BC-1 was added HRAM-1 polymer in an amount sufficient to make a microemulsion concentrate having 1 weight percent HRAM-1 present therein, based on the final concentrate weight. The resulting microemulsion concentrate is designated BC-1/HRAM-1 (1%).

Part B

Samples of BC-1 and BC-1/HRAM-1 (1%) were each diluted with sufficient synthetic hard water to yield a water-based microemulsified functional fluid containing 5 weight % of the original BC-1 and BC-1/HRAM-1 (1%) respectively. The synthetic hard water is a solution of 66 ppm $MgSO_4 \cdot 7H_2O$ and 227.5 ppm $CaCl_2 \cdot 2H_2O$ in deionized water (DIN).

The water-based functional fluid derived from diluting BC-1 is designated WBFF-1 and the fluid derived from diluting BC-1/HRAM-1 (1%) is designated WBFF-1/HRAM-1 (.05%).

Part C

Viscosity as a function of shear rate was measured at 25°C on WBFF-1 and WBFF-1/HRAM-1 (.05%). Results are given at Table 2. Viscosity at 25°C was measured on the Contraves LS-30 viscometer while viscosity at high shear (>10 sec^{-1}) was measured using a Haake Rotovisco CV-100 viscometer.

Table 2

WBFF-1/HRAM-1		WBFF-1	
Viscosity (cP)	Shear Rate (sec^{-1})	Viscosity (cP)	Shear Rate (sec^{-1})
209	0.0811	0.92	0.512
207	0.1498	0.93	1.285
203	0.277	0.94	1.747
203	0.512	0.93	2.37
225	1.285	0.93	3.23
250	1.747	0.95	4.39
283	2.37	0.95	5.96
325	3.23	0.94	8.11
373	4.39	0.95	11.02
411	5.96	0.95	14.98
589	10	0.95	20.4
431	20	0.94	27.7
357	30		
294	40		
246	50		
210	60		
192	70		
164	80		
147	90		
122	100		
60	200		
38	300		
27	400		
21.5	500		
18	600		
16	700		
14	800		
13	900		
12	1000		

HRAM in the presence of microemulsions shows the unusual property of shear-thickening (dilatancy) at low shear rates reaching a viscosity almost 3 orders of magnitude greater than the non-polymer system. Above 10 sec^{-1} it shows the more usual property of shear-thinning (pseudoplasticity).

The viscosity response of the WBFF-1/HRAM-1 (.05%) is attributed to intermolecular associations of the polymer in the emulsion, thereby increasing viscosity without increasing the molecular weight of the individual molecules. In fact, the associations break down with increased shear rate, providing low viscosity at high shear rate, and reform at low shear rate to again achieve a high viscosity. Moreover, molecular weight is not degraded at high shear rate because the reversible associations are broken, not the molecule.

Example 7

Part A (HRAM-3)

HRAM polymer was prepared in accordance with Example 1, except that the degree of hydrolysis was 20 mole % (i.e., polymer contained 20 mole % Na acrylate) rather than 18 %, and 1.25 mole % of N-octylacrylamide was used instead of 1 mole %. The weight average molecular weight of the polymer was about 3,000,000.

The resulting polymer is designated HRAM-3 and has an x:y:z mole ratio of 1:0.25:0.016 and a corresponding mole % of monomer species II, III and IV of 78.75, 20, and 1.25 respectively.

Part B

A microemulsion base was prepared using tetradecane as the oil phase and water-containing 2% NaCl as the aqueous phase. The surfactant is a blend of (1) sodium

C_{12} alkyl benzene sulfonate and (2) sodium C_{12} alkylxylene sulfonate at a respective weight ratio of 33:67.

The surfactant blend is present in the microemulsion at a concentration of 2 weight percent. The phase weight ratio of oil:water is 3:97 and the microemulsion contains 95 vol. % water containing NaCl.

The resulting microemulsion base is designated MEB-1 and represents a water-based functional fluid without any additional additives.

Part C

To different samples of MEB-1 is added 1500 ppm of either HRAM-3 or HPAM-1. The microemulsion containing HRAM-3 is designated MEB-1/HRAM-3 and the microemulsion containing HPAM-1 is designated MEB-1/HPAM-1.

Part D

Aqueous solutions were prepared by dissolving 1500 ppm of either HRAM-3 or HPAM-1 in water-containing 2 wt. % NaCl. The aqueous solution containing HRAM-3 is designated AS/HRAM-3 and the aqueous solution containing HPAM-1 is designated AS/HPAM-1.

Part E

The viscosities of MEB-1, MEB-1/HRAM-3, and AS/HRAM-3 (collectively referred to herein as Data Set-1) and of MEB-1/HPAM-1, and AS/HPAM-1 (collectively referred to herein as Data Set-2) at low and high shear rates was evaluated as per Example 6, Part C. The results are summarized at Table 3 for Data Set-1, and Data Set-2.

Table 3

Shear: 1/sec	(MEB-1) Vis.,cP	AS/HRAM-3 Vis.,cP	MEB-1/HRAM-3 Vis.,cP	AS/HPAM-1 Vis.,cp	MEB-1/HPAM-1 Vis.,cP
0.0323		9.05	22.6		
0.0439					
0.0596	1.05	9.5	22.7	3.5	3.5
0.0811		9.8			
0.1102		10.5	22.7	3.8	3.3
0.1498		10.2			
0.204		10.4	22.8	3.7	3.2
0.277		10.6			
0.376		11.2		3.7	3.2
0.512		11.6	23.3		
0.695		11.8		3.8	3.2
0.945		11.3	23.7		
1.285	1.06	11.0	24.9	3.8	3.2
1.747		11.2	24.7	3.7	3.2
2.37		11.7	24.6	3.8	3.2
3.23		11.4	24.6	3.8	3.2
4.39		11.4	24.6		3.3
5.96		11.3	24.4	3.9	3.3
8.11		11.1	24.4		3.3
11.0	1.15	11.4	24.6	3.8	3.3
14.9		10.8	24.9		3.3
20.4			25.5	3.8	3.3
27.7		10.6	26.7		3.3
37.6	1.15	10.3		3.8	3.3
40			30		
50			54		
51.2		10.8			3.3
60			95		
69.5		11.3		3.8	3.3
70			132		
80					
85			112		
94.5		10.9			3.3
100			96		
125			77		
128.5	1.14			3.6	3.3
150		9.6			
200		8.1	60		3.1
250					
300		6.5	59		3.0
350					
400		5.6	50.3		3.0
450		5.2			
500		5.1			3.0
600		4.7	31.5		2.9
700		4.4			2.9
800		4.1	22.5		2.8
900		3.9			2.8
1000		3.7	18		2.8

As can be seen from Table 3, the viscosity of the MEB-1/HRAM-3 microemulsion is higher than either the corresponding aqueous solution AS/HRAM-3 or the microemulsion MEB-1 without polymer at all. Thus, the thickening effect of the HRAM polymer in a microemulsion is synergistic relative to aqueous solution or microemulsion alone.

Moreover, just as the AS/HRAM-3 aqueous solution begins to decrease in viscosity at higher shear rates of about 100 sec^{-1}, the MEB-1/HRAM-3 fluid increases in viscosity.

In contrast, the microemulsion containing HPAM, i.e., MEB-1/HPAM-1 has a lower viscosity than the aqueous solution AS/HPAM-1 due, it is believed, to repulsive interactions between polymer and emulsion.

Example 8

Part A

Using a large 2 gallon sample of BC-1/HRAM-1 (2%) prepared in accordance with Example 5, Part B, several dilutions of this microemulsion concentrate were prepared ranging from 10% down to 1% to form different water-based functional fluids. These dilutions were made with the synthetic hard water described at Example 6, Part B. The concentration in weight % of BC-1/HRAM-1 (2%) in each dilution and resulting concentration of HRAM-1 therein are provided at Table 4 below in both ppm and wt % based on the final fluid. The corresponding water-based functional fluid number designation is also provided.

Table 4

Water-Based Functional Fluid Number	Concentration of BC-1/HRAM-1 (2%) (wt.%)	Concentration of HRAM-1 in Fluid (ppm)	(wt.%)	O:W Phase Weight Ratio
WBFF-2	10	2000	0.2	0.0128:1
WBFF-3	5	1000	0.1	0.0062:1
WBFF-4	3	600	0.06	0.0037:1
WBFF-5	1	200	0.02	0.0012:1

Part B

The viscosity performances of WBFF-2 to 5 were tested at low and high shear rates, as per Example 6, Part C, and the results summarized at Table 4A. WBFF-2 formed a clear highly viscous fluid; WBFF-5 had a grainy appearance but was stable. The intermediate WBFF-3 and -4 dilutions were clear liquids.

Table 4A

Shear Rate		Viscosity, cP		
sec^{-1}	WBFF-5	WBFF-4	WBFF-3	WBFF-2
0.1498	3.5	20.4	93.2	
0.277	3.5	20.7	92.8	
0.512	3.4	21.0	92.1	
0.945	3.3	21.3	91.4	
1.285	3.2	20.5	91.0	
1.747	3.2	20.0	89.9	
2.37	3.2	19.9	93.2	
2.5				5400.0
3.23	3.2	19.8	100.4	
4.39	3.1	20.1	114.4	
5				2940.0
5.96	3.1	20.5	130.7	
8.11	3.0	21.7	151.6	
10				1680.0
11.02	2.9	25.2	170.8	
14.98	2.8	30.4	179.6	1170.0
20			178.0	930.0
20.4	2.7	33.3		
25				798.0
27.7	2.6	34.6		
37.6	2.6	33.6		
30			139.0	700.0
35				634.0
40			114.0	581.0
45				547.0
50			98.0	498.0
51.2	2.5	31.3		
60			86.0	430.0
69.5	2.4	28.5		
70			78.0	386.0
80			71.0	349.0
90			65.0	325.0
94.5	2.3	25.4		
100		19.0	60.0	294.0
120				
128.5	2.3			
140				207.0
160				180.0
180				154.0
200		12.0	41.0	136.0
300		9.0	29.0	
400		8.0	22.0	
500		7.0	18.0	
600		6.3	16.0	
700		5.8	14.0	
800		5.5	13.0	
900		5.2	12.0	
1000		4.9	11.0	

Referring to Table 4A, WBFF-5 exhibited a low viscosity (≈ 3 cP) only slightly dependent on shear. WBFF-4 showed a highly shear-dependent viscosity ranging from about 20 cP at low shear to about 5 cP at high shear. A viscosity maximum of about 35 cP occurred at 30 sec^{-1} which indicates a strong attractive polymer-microemulsion interaction.

A similar viscosity increase with increasing shear was noted for WBFF-3. Viscosity increased from about 90 cP at low shear to about 180 cP maximum at 15 sec^{-1}. At higher shear rates the viscosity decreased. WBFF-2 shows a viscosity in excess of 5,500 cP at very low shear gradually decreasing to about 136 cP at 200 sec^{-1}. A viscosity maximum at intermediate shear rates is not observed for WBFF-2.

Based on the above observations, it can be seen that one can control viscosity performance by controlling the amount of polymer thickener in the emulsion.

For metal working operations where a cooling effect is desired, it may be desirable to control the HRAM concentration to achieve a viscosity of below about 5 cP. At this concentration (e.g., .02 wt. % of HRAM), one observes near Newtonian Rheology but at a viscosity higher than water.

Example 9

A variety of polymers were investigated to determine their effect on the phase behavior and rheology of polymer-thickened microemulsified water-based functional fluids. Table 5 lists the structural variations which define the polymer's prepared in accordance with Examples 1 to 4 and Comparative Examples 1 to 7. These polymers were used to make Microemulsions (ME) as well as aqueous solutions of polymer + synthetic hard water. The composition of each microemulsion is the same except for the polymer type and amount.

Table 5 summarizes the phase behavior of each microemulsion or attempted microemulsion and designates each one with a WBFF number for ease of discussion.

Table 6 summarizes the low shear viscosity properties of the same microemulsions of Table 5 and in addition provides low shear viscosity data of corresponding aqueous solutions.

Table 7 does the same as Table 6 except it provides high shear viscosity data.

Only the HRAM and RAM polymer containing emulsions are within the scope of the present invention.

Table 5

Effect of Polymer Structure on Microemulsified Water-based Functional Fluid[1] Phase Behavior

		Polymer Structure			ME Type 2) and Appearance 3) at Polymer Concn. =		
WBFF No.	Polymer	Mole % anionic monomer	Mole % water insoluble monomer	Molecular weight x 10^{-6}	1000 ppm	1500 ppm	2000 ppm
6	PAM-1	0	0	3	s - sl. ppt.	s - sl. ppt	s - sl. ppt
7	RAM-1	0	0.75	3	u - 10 vol %	u - 16 vol %	u - 20 vol %
8	RAM-2	0	1.0	3	u - 10 vol %	u - 19 vol %	u - 21 vol %
9	HPAM-1	18	0	3	s - sl. cuff	s - sl. cuff	s - cuff
10	HRAM-1	18	1.0	3	s - clr. HVF	s - clr. HVF	s - clr. HVF
11	HRAM-2	18	1.0	4.5	s - clr. HVF	s - clr. HVF	s - clr. HVF
12	HPAM-2	10	0	5	s - clr. ME	s - sl. haze	s - sl. haze
13	HPAM-3	20	0	6	s - clr. ME	s - sl. haze	s - sl. haze
14	HPAM-4	30	0	6.5	s - sl. haze	s - sl. haze	s - sl. haze
15	HPAM-5	16	0	4.5	s - sl. cuff	s - cuff	s - cuff
16	HPAM-6	28	0	7	s - sl. ppt	s - cuff	s - cuff

---

1) Formulation: 5 wt. % BC-1, indicated polymer and polymer amounts and 95 wt % synthetic hard water containing 66 ppm $MgSO_4 \cdot 7H_2O$ + 227.5 ppm $CaCl_2 \cdot 2H_2O$.

2) s - single phase, u - upper phase ME (Microemulsion).

3) HVF - highly viscous fluid;
ppt - precipate (settles) - assumed aqueous droplets (borderline upper phase ME);
cuff - cream (floats) - assumed oil droplets (borderline lower phase ME).

Table 6

Comparative Low Shear Viscosity of Aqueous Polymer Solutions vs. Emulsified Water-Based Functional Fluids

Polymer	Vis (cP) at 1.3 sec^{-1} of 1000 ppm Polymer in Water$^{1)}$	Vis (cP) at 1.3 sec^{-1} of 1000 ppm Polymer in ME$^{2)}$	Vis (cP) at 1.3 sec^{-1} of 1500 ppm Polymer in Water$^{1)}$	Vis (cP) at 1.3 sec^{-1} of 1500 ppm Polymer in ME^{2}	Vis (cP) at 1.3 sec^{-1} of 2000 ppm Polymer in Water$^{1)}$	Vis (cP) at 1.3 sec^{-1} of 2000 ppm Polymer in ME$^{2)}$
PAM-1	1.7	1.5	2.0	1.9	2.6	2.2
RAM-1	2.1	—	3.2	—	5.3	—
RAM-2	3.9	—	5.6	—	15.8	—
HPAM-1	9.7	5.2	22.8	8.6	47.9	13.7
HRAM-1	7.7	113.3	16.9	—	32.8	—
HRAM-2	17.2	2,707.0	43.1	—	95.5	—
HPAM-2	20.3	7.3	45.8	14.0	91.4	22.3
HPAM-3	35.4	23.8	170.7	58.6	298.7	70.5
HPAM-4	103.6	72.5	441.9	100.1	528.3	110.7
HPAM-5	24.9	10.7	66.8	20.4	155.4	36.2
HPAM-6	29.0	15.4	102.6	28.6	226.1	52.8

---

1) Synthetic hard water as per footnote 2

2) Formulation: 5 wt. % BC-1 indicated polymer and polymer amounts and 95 w % synthetic hard water containing 66 ppm MgSO4 . 7H2O + 227.5 ppm CaCl2 . 2H2O.

Table 7
Comparative High Shear Viscosity of Polymer Solutions vs. Emulsified Water-Based Functional Fluids

	Vis (cP) at 28 sec^{-1} of 1000 ppm Polymer in		Vis (cP) at 28 sec^{-1} of 1500 ppm Polymer in		Vis (cP) at 28 sec^{-1} of 2000 ppm Polymer in		Vis (cP) at 1000 sec^{-1} of ME[2] with Polymer Concn. (ppm) =		
Polymer	Water[1]	ME[2]	Water[1]	ME[2]	Water[1]	ME[2]	1000	1500	2000
PAM-1	1.5	1.5	2.0	1.9	2.6	2.2	1.6	1.8	2.3
RAM-1	1.9	—	2.9	—	4.5	—	—	—	—
RAM-2	2.0	—	3.4	—	11.9	—	—	—	—
HPAM-1	8.7	5.1	18.3	8.4	32.9	12.8	3.1	4.4	5.8
HRAM-1	7.4	122.0	15.1	—	27.1	—	9.8	—	—
HRAM-2	12.8	122.3	26.9	—	48.8	—	9.9	—	—
HPAM-2	12.7	6.3	24.1	11.0	39.3	16.5	3.1	4.5	5.8
HPAM-3	16.7	15.3	49.7	29.5	70.7	33.8	5.0	6.7	7.5
HPAM-4	34.6	32.4	93.9	40.5	99.7	43.6	7.3	8.6	8.9
HPAM-5	15.4	8.5	30.8	15.1	52.4	23.9	3.7	5.1	6.6
HPAM-6	13.9	9.9	30.5	15.8	50.1	24.3	3.7	4.9	6.2

---

[1] Synthetic hard water as per footnote 2

[2] Formulation: 5 wt. % BC-1, indicated polymer and polymer amounts and 95 w % synthetic hard water containing 66 ppm $MgSO_4 \cdot 7H_2O$ + 227.5 ppm $CaCl_2 \cdot 2H_2O$.

Discussion of Results

The HRAM series of polymers encompass variations in the mole % of anionic monomer and mole % of C_8 amide water insoluble monomer hydrophobe in the polymer at the indicated molecular weights. HRAM-2 is similar to HRAM-1 except for a somewhat higher molecular weight. Phase behavior of WBFF-10 (HRAM-1) and WBFF-11 (HRAM-2) is similar with both polymers forming highly viscous single phase microemulsions.

As shown in Example 5, concentrates of polymer without hydrophobic groups (e.g., the HPAM and PAM series) cause phase separation resulting in either a cuff or precipitate, whereas the HRAM series containing polymers form clear viscous single phase emulsified systems.

The higher molecular weight of HRAM-2 provides higher viscosity at low shear (see Table 6) both in aqueous solution and microemulsions prepared with 5% BC-1. Polymer-microemulsion interaction is strongly influenced by HRAM molecular weight. At low shear rates, Table 6 shows that HRAM-2 gives a much larger viscosity enhancement to the microemulsion than does HRAM-1. At higher shear rates, however, this molecular weight effect is negligible (see Table 7).

The RAM-1 and RAM-2 polymers (i.e., 0 mole % water soluble anionic monomer) of Table 5 are more hydrophobic than the HRAM polymers and they drive some of the oil of the microemulsions into the upper phase. Table 5 shows that the volume of upper phase microemulsions increases with both increasing the RAM-1 and -2 polymer concentrations and % hydrophobe on the polymer. This observation is consistent with a strong interaction between the polymer hydrophobe and the surfactants and oil. The absence of hydrophilic anionic groups on the RAM-1 and -2 polymer backbone allows the polymer to phase separate with some of the surfactant and oil being driven into the upper phase. Higher polymer concentrations yield larger upper phase volumes. Because of phase separation, rheology was not measured. However, phase separation can be avoided and the microemulsion rebalanced by decreasing the % hydrophobe in RAM polymer (if the surfactant is not changed) or by altering the average HLB of the surfactant (either by changing the surfactant component ratios or the surfactant itself.) to adjust for the hydrophylic shift caused by the polymer.

Conversely, the absence of hydrophobic groups on the HPAM-1 polymer, weakens the polymer interaction with surfactants and oil so that part of the surfactant and oil creams to the surface (cuff). Because of the water affinity of the sodium carboxylate groups, the polymer remains dissolved in the aqueous phase. The incompatibility between HPAM-1 and microemulsified surfactants and oil is evidenced by the reduction in viscosity below that in aqueous solution (see Tables 6 and 7). Apparently, the microemulsion droplets affect polymer conformation resulting in a reduction in hydrodynamic radius and a viscosity decrease.

The data for HPAM's of higher molecular weight and varying water soluble anionic monomer content are consistent with the above observations. The HPAM-2 to 4 series of polymers as well as HPAM-6 (the commercial Dow Pusher 700) all show a viscosity loss in microemulsions compared with aqueous solutions (Tables 6 and 7). This relative loss in viscosity (microemulsion vs. aqueous solution) is believed to be due to repulsive polymer-microemulsion interaction which are greater the higher the polymer concentration.

The increase in viscosity with increasing water soluble anionic monomer content within the same system for both aqueous solution and microemulsions is apparently caused by the increased intramolecular repulsion between anionic groups on the polymer and consequent stretching of the polymer molecule.

However, the relative viscosity loss of microemulsions versus aqueous solutions for HPAM polymers caused by the repulsive polymer-microemulsion interaction is relatively independent of the anionic monomer content. This can be shown by dividing the viscosity of the aqueous polymer solution by that of the corresponding microemulsion. This was done for HPAM's 2 to 4 at two different shear rates and the results reported at Table 8.

Table 8

Ratio of HPAM Viscosity in Aqueous Soln. vs. Microemulsion

Sec^{-1}	Mole % anionic monomer	Viscosity Ratio at Indicated Polymer Conc. 1000 PPM	1500 PPM	2000 PPM
1.3	10	2.78	3.27	4.09
	20	1.49	2.91	4.23
	30	1.49	4.41	4.77
	Average	1.92	3.53	4.36
28	10	2.02	2.19	2.38
	20	1.09	1.68	2.09
	30	1.07	2.32	2.29
	Average	1.39	2.06	2.52

These data were generated from the data in Tables 6 and 7. They reinforce the conclusion that increasing HPAM polymer concentration leads to greater repulsive polymer-microemulsion interaction (greater viscosity ratio). However, an anionic monomer content above about 10 mole % has little relative effect on the interaction. A small anionic monomer content is probably necessary for the repulsive interaction to take hold (see data for PAM-1, Tables 6 and 7), but once this level is exceeded, the microemulsion droplet has little added effect on polymer conformation.

Similarly, if the anionic monomer content of the HRAM polymer is too high, e.g., above about 30 mole %, the undesirable repulsive polymer - microemulsion interaction observed in connection with HPAM may occur along with an associated decrease in viscosity.

Thus, while RAM, HRAM and HPAM polymers were well-known thickeners for aqueous solution, their performance in emulsified systems is quite different with the RAM and HRAM polymers of the present invention increasing viscosity of the emulsion, while the latter HPAM polymers decrease viscosity of the emulsion.

Moreover, hydrophobically associating HRAM polymers of the present invention exhibit improved compatibility and enhanced viscosity relative to a conventional non-associating PAM polymers.

In addition, the associations of HRAM provide improved mechanical stability to the fluid system through two mechanisms. First, the increased stiffness imparted by the physical crosslinks result in improved shear stability. Second, the associations can be used to enhance viscosity with lower molecular weight polymers which are inherently more mechanically stable. In addition, some applications will require high temperature (130-160°F) stability, which can be built into the polymer backbone, e.g., by incorporation of more stable monomers into the polymer backbone, such as sulfonate monomers.

Example 10

Part A

To BC-1 concentrate was added sufficient HRAM-1 polymer to achieve a concentration therein of 1 weight percent. This concentrate is designated BC-1/HRAM-1 (1%). BC-1/HRAM-1 (1%) was then diluted with varying amounts of either distilled water, or tap water containing 70 ppm hardness.

The dilutions ranged from a concentrate:added water weight ratio of 1:1 (i.e., 5,000 ppm HRAM-1) to 16:1 (i.e., 600 ppm HRAM-1).

The resulting water-based functional fluids containing distilled water are designated DW/WBFF-1 to -6 whereas the tap-water containing water-based functional fluids are designated TW/WBFF-1 to -6. The appearance of each fluid was noted initially when made and one month after storage for the DW/type samples and the results are summarized at Table 9. The polymer content of the final fluid and dilution ratios of water:concentrate are also provided at Table 9.

In addition, the initial viscosity of each sample was determined at room temperature using a capillary tube (ubbelohoe) ASTM-D445 method, and the results provided at Table 9.

<u>Part B</u>

To demonstrate the anti-misting properties of the fluids of Part A, the Extensional Viscosity Equivalent of each sample after formulation was determined using the ductless siphon apparatus. To conduct this test, 100 gms. of each WBFF sample is placed in a 250 ml beaker. The sample beaker was then placed on a lab jack (Ace Model #19-1585-01), and the jack was adjusted so that a 1.5 inch long x 20 gauge syringe (flat tip) needle (0.023 in I.D.) (which is connected by 3 mm. o.d. siphon tubing to a siphon pump, and which is supported by a ring stand) touches the surface of the fluid sample (quiescent, room temperature liquid). A measurement is taken with the ruler in cm. of the height of the jack relative to a fixed point (e.g., lab bench surface). The vacuum is started to begin the siphon (-40 kPa constant vacuum), and the jack is slowly lowered (about 5 mm/sec) until the siphon breaks. A measure is taken of the jack height in cm. from the same fixed point, and the siphon break height is calculated by difference. The break height is repeated a total of five times, and the average is taken and reported as the Extensional Viscosity Equivalent

(EVE) value of the emulsion. The results are summarized at Table 9.

Table 9

Run No.	Fluid Designation	Oil:Water Phase Weight Ratio	HRAM ppm Net Polymer in Fluid	Dilution Ratio BC-1:Water	Initial Appear.	Initial Vis. cSt @ R.T.	Initial EVE (cm)	Month Stor.	Month Vis. cSt @ R.T.
1	DW/WBFF-1	.0075	600	1:16	CL/YEL	3.5	0.3	HZ/YEL	12.4
2	DW/WBFF-2	.010	800	1:11.5	CL/YEL	5.6	0.52	HZ/YEL	7.4
3	DW/WBFF-3	.0128	1000	1:9	CL/YEL	11.0	0.9	HZ/YEL	18.0
4	DW/WBFF-4	.0358	2500	1:3	CL/BR	256.2	2.82	HZ/BR*	403.0
5	DW/WBFF-5	.050	3300	1:2	CL/BR	554.6	2.74	HZ/BR*	770.8
6	DW/WBFF-6	.0889	5000	1:1	CL/BR	907.9	3.16	HZ/BR	1266.6
7	TW/WBFF-1	.0075	600	1:16	HZ/YEL	3.3	0.32		
8	TW/WBFF-2	.010	800	1:11.5	HZ/YEL	6.9	1.06	HZ/YEL	7.4
9	TW/WBFF-3	.0128	1000	1:9	HZ/YEL	27.1	1.36	HZ/YEL	18.0
10	TW/WBFF-4	.0358	2500	1:3	HZ/BR	268.5	2.70	HZ/BR*	403.0
11	TW/WBFF-5	.050	3300	1:2	HZ/BR	411.9	2.72	HZ/BR*	770.8
12	TW/WBFF-6	.0889	5000	1:1	HZ/BR	983.6	3.24	HZ/BR	1266.6

Notes: YEL = Yellow
BR = Brown
HZ = Hazy
* = Separation
CL = Clear

Discussion of Results

Referring to Table 9 it can be seen that all of Runs 7 to 12 appear hazy. This haze reflects a slight hard water instability. The haze is caused by precipitation of calcium salts (e.g., $CaCO_3$ and/or $CaSO_4$ wherein the calcium is derived from the hard water. However, because the emulsion is not affected, hard water instability is separate and distinct from emulsion instability.

Above about 400 ppm of $CaCO_3$ equivalent hardness this precipitate becomes extensive and it is desirable to remain below this level of hardness.

In contrast, distilled water samples are initially all clear.

After 1 month storage, however, polymer interactions are believed to destabilize the emulsion at higher polymer concentrations, e.g., Runs 4 and 5.

In addition, the viscosity increases after one month storage for Runs 1 to 6.

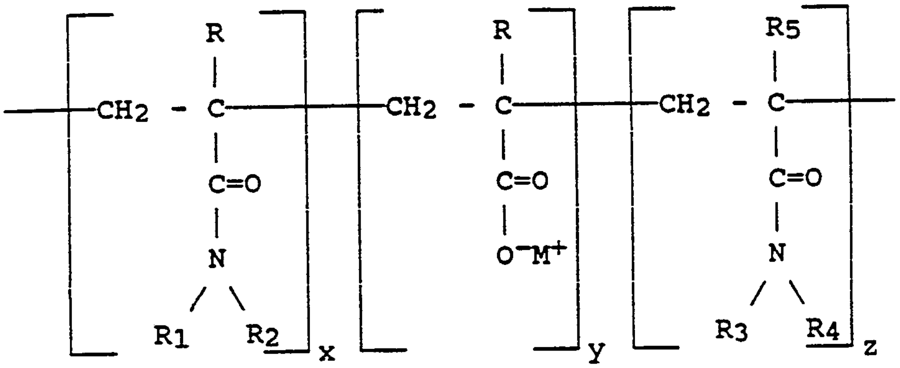
The EVE data suggests that adequate anti-misting can be achieved at polymer concentrations below 2500 ppm polymer while still preserving long term emulsion stability.

The principles, preferred embodiments, and modes of operation of the present invention have been described in the foregoing specification. The invention which is intended to be protected herein, however, is not to be construed as limited to the particular forms disclosed, since these are to be regarded as illustrative rather than restrictive. Variations and changes may be made by those skilled in the art without departing from the spirit of the invention.

CLAIMS:

1. An oil-in-water emulsion having an aqueous continuous phase and a base oil disperse phase comprising:

(A) polymer having water soluble nonionic monomer species, water soluble anionic monomer species and water insoluble monomer species present within the structure thereof at a respective mole ratio in the polymer of from about 1:0.030:0.0025 to about 1:0.40:0.080 and said polymer having at least about 60 mole % of the total monomer species present within the structure thereof represented by the formula:



$$-\left[CH_2-\underset{\substack{|\\C=O\\|\\N\\/\ \backslash\\R_1\quad R_2}}{\overset{\substack{R\\|}}{C}}\right]_x-\left[CH_2-\underset{\substack{|\\C=O\\|\\O^-M^+}}{\overset{\substack{R\\|}}{C}}\right]_y-\left[CH_2-\underset{\substack{|\\C=O\\|\\N\\/\ \backslash\\R_3\quad R_4}}{\overset{\substack{R_5\\|}}{C}}\right]_z- \qquad (I)$$

(II)	(III)	(IV)
nonionic water soluble monomer	anionic water soluble monomer	water-insoluble monomer

wherein in Formula I, monomer species II is water soluble nonionic, species III is water soluble anionic, and species IV is water insoluble and wherein R independently can represent hydrogen or unsubstituted or polar hydrocarbyl substituted methyl, R_1 and R_2 can independently represent unsubstituted or polar hydrocarbyl substituted C_1 to C_3 alkyl, provided that the number of carbons represented by $R_1 + R_2$ is not greater than about 4 when R_1 and R_2 are unsubstituted; R_3 and R_4 independently can represent hydrogen, alkyl, cycloalkyl, aryl, alkaryl and aralkyl, provided the number of carbons represented by $R_3 + R_4$ is at least 6; R_5 can represent hydrogen or alkyl; M is a cation selected from at least one member of the group consisting of Groups IA, IB, IIA, IIB of the periodic chart, ammonium and polar hydrocarbyl substituted ammonium; x, y and z are numbers which represent a mole ratio of monomer species II:III:IV within said polymer of from about 1:0.030:0.0025 to about 1:0.40:0.080;

(B) base oil;

(C) at least one surfactant; and

(D) water

said polymer being present in the aqueous phase in an amount sufficient to increase the kinematic viscosity at 24°C of the emulsion relative to the emulsion absent the polymer; and said base oil, surfactant, and water being present in amounts sufficient to produce an oil-in-water emulsion.

2. The emulsion of claim 1 wherein said polymer has a weight average molecular weight of from about 100,000 to about 10,000,000.

3. The emulsion of claim 1 wherein said polymer is a terpolymer consisting of monomer species II, III and IV.

4. The emulsion of claim 3 wherein in said polymer R, R_5, R_1 and R_2 are hydrogen, M is Na^+, K^+ or NH_4^+ and R_3 and R_4 independently represent hydrogen or C_1 to C_{22} alkyl.

5. The emulsion of claim 1 wherein sufficient polymer (A) is employed to achieve at least a 5% increase in shear viscosity of the fluid at 24°C relative to the viscosity of the same fluid absent the polymer.

6. The emulsion of claim 1 wherein the base oil is selected from the group consisting of mineral oil, and C_5 to C_{18} alkane.

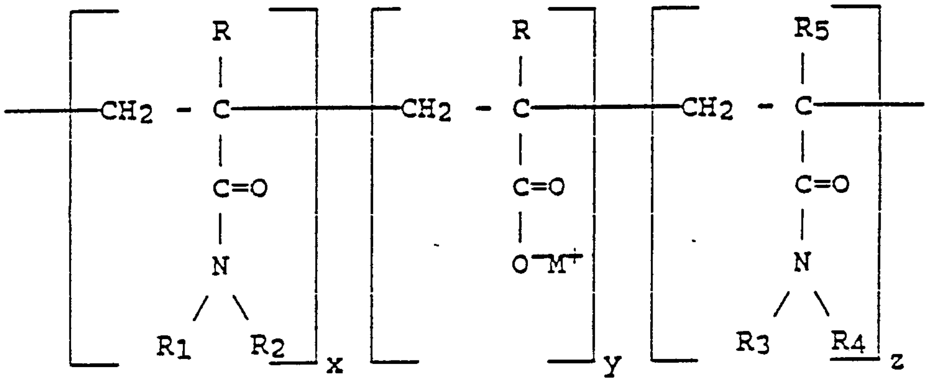
7. The emulsion of claim 1 wherein the surfactant has an average HLB of from about 7 to about 16.

8. The emulsion of claim 7 wherein said surfactant is selected from the group consisting of anionic and nonionic.

9. The emulsion of claim 8 wherein the surfactant comprises metal organo sulfonate.

10. The emulsion of claim 1 wherein the water is selected from the group consisting of deionized, distilled, and hard water having a $CaCO_3$ equivalent of not greater than about 400 ppm.

11. The use as a thickener in oil-in-water emulsion having an aqueous continuous phase and a base oil disperse phase of a polymer having water soluble nonionic monomer species, water soluble anionic monomer species and water insoluble monomer species present within the structure thereof at a respective mole ratio in the polymer of from about 1:0.030:0.0025 to about 1:0.40:0.080 and said polymer having at least about 60 mole % of the total monomer species present within the structure thereof represented by the formula:



$$\left[-CH_2-\underset{\underset{\underset{R_1\ \ R_2}{N}}{C=O}}{\overset{R}{C}}-\right]_x\left[-CH_2-\underset{\underset{O^-M^+}{C=O}}{\overset{R}{C}}-\right]_y\left[-CH_2-\underset{\underset{\underset{R_3\ \ R_4}{N}}{C=O}}{\overset{R_5}{C}}-\right]_z \qquad (I)$$

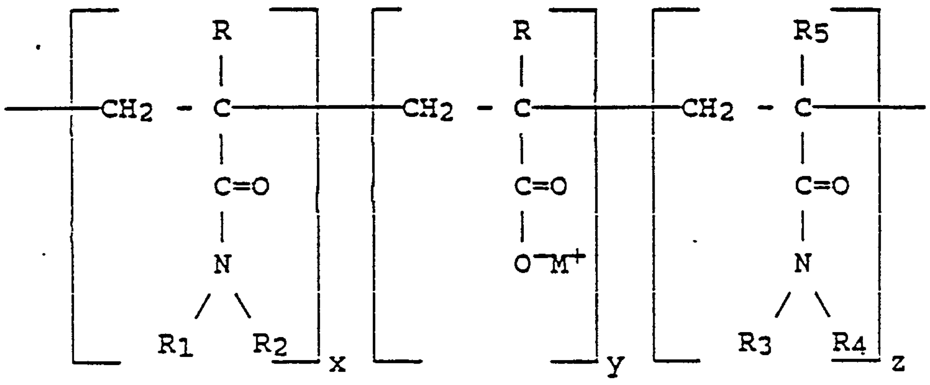
(II) nonionic water soluble monomer

(III) anionic water soluble monomer

(IV) water-insoluble monomer

wherein in Formula I, monomer species II is water soluble nonionic, species III is water soluble anionic, and species IV is water insoluble and wherein R independently can represent hydrogen or unsubstituted or polar hydrocarbyl substituted methyl, R_1 and R_2 can independently represent hydrogen or unsubstituted or polar hydrocarbyl substituted C_1 to C_3 alkyl, provided that the number of carbons represented by $R_1 + R_2$ is not greater than about 4 when R_1 and R_2 are unsubstituted; R_3 and R_4 independently can represent hydrogen, alkyl, cycloalkyl, aryl, alkaryl and aralkyl, provided the number of carbons represented by R_3 and R_4 is at least 6; R_5 can represent hydrogen or alkyl; M is a cation selected from at least one member of the group consisting of Groups IA, IB, IIA, IIB of the periodic chart, ammonium and polar hydrocarbyl substituted ammonium; x, y and z are numbers which represent a mole ratio of monomer species II:III:IV within said polymer of from about 1:0.030:0.0025 to about 1:0.40:0.080;

12. A concentrate for mixing with water to form an oil-in-water emulsion having an aqueous continuous phase and a base oil disperse phase comprising an oil solution of a polymer having water soluble nonionic monomer species, water soluble anionic monomer species and water insoluble monomer species present within the structure thereof at a respective mole ratio in the polymer of from about 1:0.030:0.0025 to about 1:0.40:0.080 and said polymer having at least about 60 mole % of the total monomer species present within the structure thereof represented by the formula:



$$-\left[CH_2-\overset{\displaystyle R}{\underset{\displaystyle C(=O)N R_1 R_2}{C}}\right]_x-\left[CH_2-\overset{\displaystyle R}{\underset{\displaystyle C(=O)O^-M^+}{C}}\right]_y-\left[CH_2-\overset{\displaystyle R_5}{\underset{\displaystyle C(=O)N R_3 R_4}{C}}\right]_z- \qquad (I)$$

(II) nonionic water soluble monomer

(III) anionic water soluble monomer

(IV) water-insoluble monomer

wherein in Formula I, monomer species II is water soluble nonionic, species III is water soluble anionic, and species IV is water insoluble and wherein R independently can represent hydrogen or unsubstituted or polar hydrocarbyl substituted methyl, R_1 and R_2 can independently represent hydrogen or unsubstituted or polar hydrocarbyl substituted C_1 to C_3 alkyl, provided that the number of carbons represented by $R_1 + R_2$ is not greater than about 4 when R_1 and R_2 are unsubstituted; R_3 and R_4 independently can represent hydrogen, alkyl, cycloalkyl, aryl, alkaryl and aralkyl, provided the number of carbons represented by R_3 and R_4 is at least 6; R_5 can represent hydrogen or alkyl; M is a cation selected from at least one member of the group consisting of Groups IA, IB, IIA, IIB of the periodic chart, ammonium and polar hydrocarbyl substituted ammonium; x, y and z are numbers which represent a mole ratio of monomer species II:III:IV within said polymer of from about 1:0.030:0.0025 to about 1:0.40:0.080;

-100-

Patents Act 1977
Examiner's report to the Comptroller under Section 17 (The Search Report)

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Relevant Technical fields

(i) UK Cl (Edition K) C3V (VAN,VAX,VAT); C3J (JAJ); C3P (PFE,PFF,PDT,PDH,PDR,PKH, PKF,PKG); C5F (FKE,FKK,FKG)

(ii) Int Cl (Edition 5) C08F, C08L, C10M

Search Examiner

B J BALDOCK

Databases (see over)

(i) UK Patent Office

(ii) ONLINE DATABASES: DERWENT WPI, WPIL

Date of Search

8.4.92

Documents considered relevant following a search in respect of claims 1 TO 12

Category (see over)	Identity of document and relevant passages	Relevant to claim(s)
X	EP 0228798 A1 (EXXON)	11
X	EP 0057875 A2 (DOW CHEMICAL)	1,11,12
X	US 4694058 (EXXON)	11
X	US 4673716 (EXXON)	11
X	US 4709759 (EXXON)	11
X	US 4694046 (EXXON)	11
A	US 4520182 (EXXON)	11
X	US 4432881 (DOW CHEMICAL)	1,11, 12
X	US 4521580 (EXXON)	1,11, 12
A	US 4443576 (NALCO)	1,11, 12

Category	Identity of document and relevant passages	Relevant to claim(s)

Categories of documents

X: Document indicating lack of novelty or of inventive step.

Y: Document indicating lack of inventive step if combined with one or more other documents of the same category.

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