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D-8000 München 2(DE)(54) **Thickener compositions for water-based hydraulic and metalworking fluid compositions.**

(57) The present invention provides for a thickener composition characterized by: (1) at least one water-soluble, thermoplastic, organic polymer having a weight average molecular weight of at least about 10,000 which comprises hydrophobic segments, each containing at least one monovalent hydrophobic group covalently bonded to the polymer, wherein the polymer has an amount of hydrophobe bunching comprising at least two monovalent hydrophobic groups per hydrophobic segment, sufficient to provide for enhanced thickening of aqueous solutions containing the polymer, and (2) at least one ethoxylated alcohol selected from the group consisting of C₉-C₁₅ saturated alcohols with between about 5 and 20 moles of ethylene oxide per mole of alcohol and having an HLB between 11 and 14, and C₉-C₁₈ unsaturated alcohols with between about 5 and 20 moles of ethylene oxide per mole of alcohol and having an HLB between 11 and 14. Said thickener compositions as well as hydraulic fluid and metalworking fluid concentrates, aqueous concentrates and water-based hydraulic fluid and metalworking fluid or lubricant compositions are thickened to an oil-like viscosity by said low solids combination of thickeners.

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This invention relates to thickener compositions for water-based hydraulic fluid compositions and metalworking fluid or lubricant compositions, which are thickened to an oil-like viscosity by the interaction of thickeners at a low solids concentration. More particularly, this invention relates to thickener compositions, hydraulic fluid and metalworking fluid concentrates, aqueous concentrates and water-based hydraulic fluid and metalworking lubricant compositions employing polyurethanes and ethoxylated alcohols.

In hydraulic machinery, mechanical force is imparted to a fluid, known as hydraulic fluid, in the form of pressure by means of a hydraulic pump. The energy imparted to the hydraulic fluid is utilized by transforming this pressure energy back to mechanical energy by a hydraulic motor mechanism. In this manner, the hydraulic fluid is utilized as a pressure and volume transmitting medium. Therefore, the main function of a hydraulic fluid is power transfer.

According to U.S. Patent No. 4,312,768 to Nassry, any non-compressible fluid can perform the function of a hydraulic fluid, including water. However, heavy emphasis has been placed on the development of petroleum oils for use as hydraulic fluids. Petroleum-based hydraulic fluids are said to offer several advantages over water-based hydraulic fluids. First, water-based fluids are said to suffer from the development of rust of the ferrous components of the mechanical equipment. Second, oil-based products have been reported to prevent the wear of machinery by lubricating the equipment. Third, oil-based products are believed to exhibit greater viscosity than water-based ones and thus account for the reduction of fluid leakage in the mechanical equipment utilized. Finally, the development of technology for fluid additives has advanced to such an extent that improvement in viscosity, foam stability, wear prevention and corrosion prevention properties is further enhanced by the use of such additives in oil-based hydraulic fluids.

However, even with the reported advantages of oil-based fluids, they continue to suffer from such deficiencies as flammability, higher costs, environmental pollution and/or disposal problems.

Additional important characteristics that a hydraulic fluid should possess include pump volume efficiency, which is closely related to its rheological properties, and good wear resistance. Low wear rates increase the pump life of a hydraulic fluid. Additionally, compositions which are stable throughout a temperature range not only maintain their viscosity, but also their chemical integrity.

Metalworking fluid compositions should also function to reduce friction and heat generation, hence to provide lubrication and cooling in the cutting area in order to extend tool life and improve workpiece finish. These two major effects, lubrication and cooling, are best accomplished by oil-based and water-based fluids, respectively. "Cutting and Grinding Fluids: Selection and Application", p. 5, R.K. Springborn (Ed.), Am. Soc. Tool & Mfg. Engs. (Dearborn, Michigan 1967).

Finally, the contamination of machine tool lubricants, i.e., hydraulic fluids by metalworking fluids and vice-versa, can be a serious problem. If the problem of contamination is ignored, costly repair of machines will result, together with increased machine down-time and loss of production. Multi-purpose fluids have been proposed to overcome this problem. However, there does not exist, to date, a water-based hydraulic and metalworking fluid which is free of the defects of petroleum-based fluids and which can provide enhanced viscosity, lubrication, stability and wear properties required for hydraulic machinery and the like.

Urethane polymers employed in aqueous thickening compositions are disclosed in U.S. Patent No. 4,426,485 to Hoy. It is said that these urethane polymers provide better thickening and leveling characteristics than do traditional cellulosic thickening agents in waterborne coatings. Such thickened compositions are stated to be useful in a wide variety of applications. However, only latex compositions are mentioned. Additionally, no reference or suggestion is made to the use of these urethane polymers in hydraulic or lubricant systems in association with the specific ethoxylated alcohols of this invention.

The application of shear to compositions containing the above-described urethane polymers decreases their viscosity to a significantly greater extent than when these urethane polymers are used in the presence of at least one of the ethoxylated alcohols of this invention.

British Patent No. 1,069,735 also discloses the use of urethane polymers as a thickening agent for aqueous preparations. These urethane polymers are the reaction products of polyethylene glycol ethers and isocyanates. These compositions are stated to be suitable for emulsions of cutting oils. However, this patent does not disclose or suggest the use of such urethane polymers in combination with the specific ethoxylated alcohols of this invention.

Applicants' allowed patent application, Serial No. 680,710, filed December 12, 1984, discloses the use of these same urethane polymers with the dimer esters disclosed in U.S. Patent No. 4,317,740, to obtain thickened compositions useful as hydraulic or metalworking fluids.

U.S. Patent No. 4,395,351 to Camp discloses polyether-based thickeners for aqueous systems. These thickeners are mixtures of a polyether and an ethoxylated phosphate ester, or the ester and a water-soluble amine. This patent, however, does not disclose or suggest the use of specific ethoxylated alcohols of this invention in combination with the urethane polymers of this invention to achieve the superior viscosity and

shear stability characteristics of the subject invention. Furthermore, this patent teaches that the selection of suitable thickening agents is an empirical and complex task. "The diversity of available thickening agents is an indication that not all are equally useful. It is not unusual to find some thickening agents which perform well in a certain environment and not at all in another environment. In [fact], in some uses, no one thickening agent is completely satisfactory and there is a continual need and a continuing search for new thickening agents to satisfy many unmet needs." (col. 1, lines 17-24).

Various efforts to produce thickened, water-based hydraulic and metalworking fluids have been proposed. For example, U.S. Patent No. 4,312,768 to Nassry discloses the preparation of thickened, water-based hydraulic and metalworking fluids. These fluids contain a water-soluble polyoxyethylated aliphatic ester, a sulfurized metallic compound, a phosphate ester salt, and a polyether polyol thickening agent, which is further modified by reaction with an alpha-olefin epoxide. However, there is no suggestion in this patent that fluids having excellent hydraulic and metalworking properties can be provided by the utilization of polyurethanes which interact with the specific ethoxylated alcohols of the subject invention.

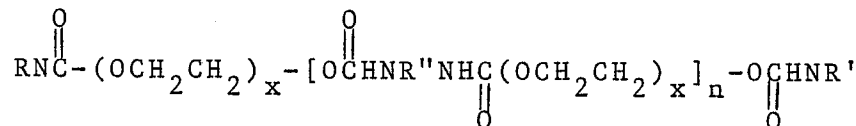
Accordingly, a need exists for thickened, water-based hydraulic and metalworking fluid compositions and concentrates which maintain a high viscosity after shear stress, in addition to providing sufficient lubrication, safety, environmental compatibility and reduced cost.

The present invention provides for thickener compositions for water-based hydraulic fluid and/or metalworking fluid or lubricant compositions characterized by

(1) at least one water-soluble, thermoplastic, organic polymer having a weight average molecular weight of at least about 10,000 which comprises hydrophobic segments, each containing at least one monovalent hydrophobic group covalently bonded to the polymer, wherein the polymer has an amount of hydrophobe bunching comprising at least two monovalent hydrophobic groups per hydrophobic segment, sufficient to provide for enhanced thickening of aqueous solutions containing the polymer, and

(2) at least one ethoxylated alcohol selected from the group consisting of C₉-C₁₅ saturated alcohols with between about 5 and 20 moles of ethylene oxide per mole of alcohol and having an HLB between 11 and 14, and C₉-C₁₈ unsaturated alcohols with between about 5 and 20 moles of ethylene oxide per mole of alcohol and having an HLB between 11 and 14.

In a more limited aspect, the polymer is a urethane polymer of the structure:



wherein R and R' are each C₁₂-C₁₈ alkyls; R'' is a C₇-C₃₆ alkyl; x is an integer from 90 to 455 and n is an integer from 1 to 4.

Mixtures of ethoxylated alcohols that are nominally outside the scope of the above description of ethoxylated alcohols can be combined to improve their stability, viscosity and shear stability properties when formulated with the polyurethanes of this invention. These ethoxylated alcohols can be described as mixtures of ethoxylated alcohols selected from the group consisting of: (1) a mixture of C₉-C₁₈ saturated alcohols with between about 2 and 25 moles of ethylene oxide per mole of alcohol and having an HLB greater than about 4 and less than 11 or greater than 14 and less than about 17, or (2) a mixture of C₉-C₁₈ unsaturated alcohols with between about 2 and 25 moles of ethylene oxide per mole of alcohol and having an HLB greater than about 4 and less than 11 or greater than 14 and less than about 17, or (3) a mixture at least one alcohol from (1) and at least one alcohol from (2). It is critical that the HLB of these mixtures be between 11 and 14 to show improvement in the above-stated properties and therefore act similarly to the ethoxylated alcohols described above.

In other embodiments, this invention relates to fluid concentrates for water-based hydraulic fluid compositions comprising at least one polyurethane of the invention, at least one ethoxylated alcohol of the invention, and one or more of the following: extreme pressure or antiwear additives, dispersants, nonionic or anionic surfactants, ferrous and/or non-ferrous corrosion inhibitors, and amines.

In still further embodiments, this invention relates to concentrates comprising at least one polyurethane of the invention and at least one ethoxylated alcohol of the invention and any of the adjuvants set forth above in an aqueous carrier. In addition, the invention relates to aqueous hydraulic and metalworking compositions and formulations ready for use, which can include the aqueous concentrates diluted to a desired degree for immediate use.

It has been found that the combination of polyurethane and ethoxylated alcohol produces an unexpect-

edly enhanced thickening effect to yield oil-like viscosities which exhibit shear stability. In addition to these enhanced Newtonian rheological characteristics, this thickener combination also contributes to lubrication and emulsification in aqueous hydraulic and metalworking fluids. This combination is unique in that neither of its individual components, the polyurethane or the ethoxylated alcohol, alone, will give the superior rheological properties. Further, the superior viscosity and lubrication properties are obtained at surprisingly low total actives concentrations.

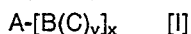
The shear stability observed with the fluid compositions of this invention is believed to be significantly greater than the stability values expected from the mere sum of its individual components, e.g., the polyurethane and the ethoxylated alcohol.

DESCRIPTION OF PREFERRED EMBODIMENTS

Polymers, such as disclosed in U.S. Patent No. 4,426,485 to Hoy, which herein is incorporated by reference, may be utilized as one component of the thickener composition in accordance with this invention.

These polymers are described as water-soluble, thermoplastic, organic polymers having segments of bunched, monovalent, hydrophobic groups and an average molecular weight of at least about 10,000. The polymers have an amount of hydrophobic segments, such that each contain at least one monovalent hydrophobic group covalently bonded to the polymer, wherein at least two monovalent hydrophobic groups are present per hydrophobic segment, sufficient to provide for enhanced thickening of aqueous solutions containing the polymer.

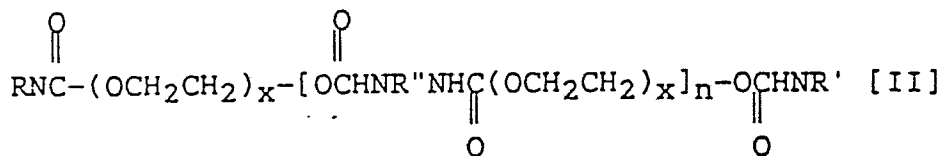
In a preferred embodiment, the polymers are structurally defined to include those compounds having the formula I:



wherein A is a water-soluble polymer segment; B is a connecting segment comprising a covalent bond or a polyvalent organic radical; C is a monovalent hydrophobic group; the number of hydrophobe segments, x, defined by B(C)_y, is greater than 0; the number of hydrophobes, C, for each hydrophobic segment, defined as y, is greater than or equal to 1 providing an average of all y values, of greater than 1, such that the polymer has an amount of bunching comprising at least two hydrophobes per hydrophobic segment sufficient to provide for enhanced thickening of aqueous solutions containing the polymer. The y value sets forth the number of hydrophobes per hydrophobic segment. The x value sets forth the average number of hydrophobic segments per molecule. The average number of hydrophobes per hydrophobic segment, y', is greater than 1. The average number of hydrophobes per hydrophobic segment, y, is defined as a total number of hydrophobes (i.e., the summation of all hydrophobes per hydrophobic segment, y_x), divided by the total number of hydrophobic segments, x.

The connecting segment, B, may be water-soluble or water-insoluble. The hydrophobic segments, B(C)_y, may be attached in a pendant fashion to x terminal and/or interior bonds of the water-soluble polymer backbone A; or the connecting segment, B, may be incorporated as part of the polymer backbone between a plurality of water-soluble, polymer segments.

A more preferred class of polymers of the invention include those polyurethane polymers having the following structural formula II.

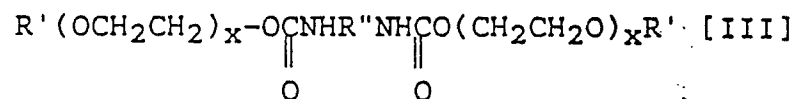


wherein R and R' are each C₁₂-C₁₈ alkyls; R'' is a C₇-C₃₆ alkyl; x is an integer from 90 to 455 and n is an integer from 1 to 4.

Such compounds are polyether polyurethanes preferably having a molecular weight from 600 to about 50,000, more preferably from 1,000 to about 14,000. An especially preferred polyurethane is sold under the trademark UCAR Thickener SCT-100 by Union Carbide Corp. That thickener is commercially available as a solution having 50% nonvolatiles in a solvent of 40% wt. butyl "Cellosolve" and 60% water and has a Brookfield viscosity, 50% of 3000 cp. Butyl "Cellosolve" is a specific type of butoxyethanol, i.e., the ether alcohol that conforms to the formula: C₄H₉OCH₂CH₂OH, and is sold by the Union Carbide Corp. SCT-200 also sold by the Union Carbide Corporation is believed to give similar results as SCT-100 when used in

accordance with the teachings of this invention.

Another class of especially preferred polyurethanes is represented by structural formula III as follows:

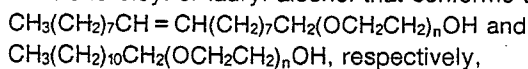


wherein R', R'' and x are as before. These include the polyurethanes sold by Borchigel of Germany, under the trademark Borchigel L-75, having an Mw of 27,792 and an Mn of 14,527.

The HLB value (the hydrophilic-lipophilic balance) of the urethane polymers is a significant parameter. HLB values ranging from about 10 to 20 are preferably used in accordance with this invention, although higher and lower values are possible.

In its broadest aspect, the ethoxylated alcohols of this invention consist of at least one ethoxylated alcohol selected from the group consisting of C₉-C₁₅ saturated alcohols with between about 5 and 20 moles of ethylene oxide per mole of alcohol and having an HLB between 11 and 14, and C₉-C₁₈ unsaturated alcohols with between about 5 and 20 moles of ethylene oxide per mole of alcohol and having an HLB between 11 and 14.

The ethoxylated alcohols of this invention are preferably selected from the group consisting of (1) at least one oleyl or lauryl alcohol that conforms to the formulas



wherein n is between about 5 and 20 and the oleyl or lauryl alcohol or mixture thereof has an HLB between 11 and 14; (2) pareth-25-9, which is a polyethylene glycol ether of a mixture of synthetic C₁₂-C₁₅ fatty alcohols with an average of 9 moles of ethylene oxide and an HLB of about 12.8; (3) pareth-91-6, which is a polyethylene glycol ether of a mixture of synthetic C₉-C₁₁ fatty alcohols with an average of 6 moles of ethylene oxide and an HLB of about 12.5; (4) pareth-15-9, which is a polyethylene glycol ether of a mixture of synthetic C₁₁-C₁₅ fatty alcohols with an average of 9 moles of ethylene oxide and an HLB of about 13.5; and (5) mixtures thereof. Oleyl alcohol having an average of 10 moles of ethylene oxide and an HLB of about 12.4 is preferred.

In another embodiment of this invention, mixtures of ethoxylated alcohols that are nominally outside the scope of the above description of ethoxylated alcohols can be combined to improve their stability, viscosity and shear stability properties when formulated with the polyurethanes of this invention. These ethoxylated alcohols can be described as mixtures of ethoxylated alcohols selected from the group consisting of: (1) a mixture of C₉-C₁₈ saturated alcohols with between about 2 and 25 moles of ethylene oxide per mole of alcohol and having an HLB greater than about 4 and less than 11 or greater than 14 and less than about 17, or (2) a mixture of C₉-C₁₈ unsaturated alcohols with between about 2 and 25 moles of ethylene oxide per mole of alcohol and having an HLB greater than about 4 and less than 11 or greater than 14 and less than about 17, or (3) a mixture of at least one alcohol from (1) and at least one alcohol from (2). It is critical that the HLB of these mixtures be between 11 and 14 to show improvement in the above-stated properties and therefore act similarly to ethoxylated alcohols described above. These mixtures include those shown in Table 3 as discussed herein.

In the thickener composition of the invention the weight ratio of polyurethane to ethoxylated alcohol can range from about 100:1 to 1:100, preferably from about 20:1 to 1:20, more preferably, from about 5:1 to 1:15, and, most preferably, from about 5:3 to 1:1.

In another embodiment of the invention, an aqueous concentrate is formulated having from about 20 to 50% water based on the total weight of the composition. The aqueous concentrate contains from about 0.05 to 50 weight percent of said polyurethane thickener and from about 0.05 to 50 weight percent of said ethoxylated alcohol of the invention. Unless otherwise indicated all weights herein are in weight percent of the total composition.

In still another aspect, water-based functional fluids are formulated. For this purpose the aqueous concentrates of the invention may be diluted such that the water content of the final aqueous fluid composition is from about 60 to 99 percent by weight. In this embodiment the polyurethane and ethoxylated alcohol concentrations are each employed in amounts from about 0.05 to 25 weight percent, preferably from about 1 to 10 weight percent.

Non-aqueous hydraulic fluid concentrates, aqueous hydraulic fluid concentrates and aqueous functional fluid compositions, in accordance with this invention, may typically further comprise one or more of the following ingredients: extreme pressure or antiwear additives, dispersants, nonionic or anionic surfactants, ferrous and/or non-ferrous corrosion inhibitors, and amines.

The extreme pressure or antiwear components of the fluids of this invention are well known in the art and individual compounds are typically selected from the broad classes of materials useful for this purpose. Preferred antiwear additives are the metal salts of acid phosphates, chlorinated hydrocarbons, and acid thiophosphate hydroxycarbonyl esters, with zinc di(alkyl) or di(aryl) dithiophosphate being especially preferred.

5 Lubrizol 5604, a trademark of the Lubrizol Corporation, is an especially preferred antiwear additive. This primary alkyl zinc dithiophosphate has a specific gravity of 1.08 at 15.6°C. and a viscosity of 13.5 centistokes (cSt) at 100°C. Its chemical weight percentages of phosphorus, sulfur and zinc range from about 6.8-7.2, 14.3-15.3 and 7.4-8.2, respectively.

Another preferred antiwear additive is a proprietary composition available under the trademark Molyvan L-B from the R.T. Vanderbilt Company, Inc. Molyvan L-B contains molybdenum, sulfur and phosphorus in weight percentages of about 8.1, 12.3 and 6.4, respectively, has a viscosity of 9.07 centistokes at 100°C. and a flash point (COC) of 165.6°C.

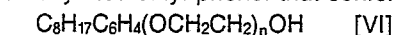
The concentration of such extreme pressure and antiwear components may range from about 0.05 to 20 percent by weight of the aqueous concentrate. The extreme pressure or antiwear additive concentration of a functional aqueous fluid composition typically varies from about 0.05 to 5 percent by weight. The concentration of extreme pressure or antiwear additive, in accordance with this invention, is not critical.

The dispersants used in accordance with this invention are well known in the art and individual compounds are typically selected from the broad classes of materials useful for this purpose. These compounds are useful for incorporating oil-soluble, water-insoluble functional additives into aqueous systems, i.e., antiwear, extreme pressure and load-carrying agents, such as dithiophosphates. For example, the dispersants (carboxylic solubilizer/surfactant combinations) disclosed in U.S. Patent No. 4,368,133 typically are used in water-based hydraulic fluids. These solubilizers are made by reacting an acylating agent with N-(hydroxyl-substituted hydroxycarbonyl) amines and surfactants.

A preferred dispersant utilized in accordance with this invention is available under the trademark 25 Lubrizol 5603 from The Lubrizol Corporation. That dispersant has a viscosity at 100°C. of 650 cSt, a specific gravity of 0.951 at 15.6°C., and a flash point (PMCC) of 83°C. The concentration of dispersant typically ranges from about 0.1 to 30 percent by weight in an aqueous concentrate. The dispersant concentration of an aqueous functional fluid composition typically varies from about 0.1 to 5 percent by weight. The concentration of dispersant, in accordance with this invention, is not critical.

30 The surfactants or wetting agents utilized in accordance with this invention can be either nonionic or anionic. The surfactant aids in the dispersal of the functional additives in the aqueous system. Typically, the surfactant is a hydrophilic surfactant and, generally has an HLB value in the range of about 10 to 20. See for example, McCutcheon's "Detergents and Emulsifiers", North American Edition, published by McCutcheon's Division, MC Publishing Corporation, Glen Rock, New Jersey, U.S.A., which is hereby incorporated by reference, for their disclosure in this regard.

Of these surfactants, nonionic surfactants are generally used. Among these are the alkylene oxide-treated products, such as ethylene oxide-treated phenols, esters, amines and amides. Ethylene oxide/propylene oxide block copolymers are also useful nonionic surfactants. Glycerol esters and sugar esters are also known to be nonionic surfactants. A typical nonionic surfactant class useful with the derivatives of the present invention are the alkylene oxide-treated alkyl phenols such as the ethylene oxide alkyl phenol condensates sold by the Rohm & Haas Company under the family mark, Triton. 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. Triton X-100 is a specific type of Octoxynol-9, the ethoxylated alkyl phenol that conforms generally to the formula VI:



where n is an integer having an average value of 9.

Another example is Triton X-45 which contains an average of 5 ethylene oxide units per molecule, has an HLB value of about 18.4 and a molecular weight of about 426. Triton X-45 is a specific type of Octoxynol-5, the ethoxylated alkyl phenol that conforms generally to the above-formula VI where n is an integer having an average value of 5.

The water-soluble esters of the ethoxylated $\text{C}_8\text{-C}_{36}$ aliphatic monohydric or polyhydric alcohols with aliphatic acids, and aliphatic dimer acids are typically utilized in accordance with this invention. Such ethoxylated esters have a hydrophilic-lipophilic balance (HLB) in the range of 10 to 20.

Representative water-soluble polyoxyethylated esters having about 5 to about 20 moles of oxide per mole are the polyoxyethylene derivatives of the following esters; sorbitan monooleate, sorbitan trioleate, sorbitan monostearate, sorbitan tristearate, sorbitan monopalmitate, sorbitan monoisostearate, and sorbitan monolaurate.

Another preferred surfactant is Sipon ESY, a registered trademark of Alcolac Inc. This compound is a

modified fatty alcohol, sulfate sodium laureth sulfate, containing approximately one ethylene oxide unit per molecule. Its empirical formula is $C_{12}H_{25}(OCH_2CH_2)_nOSO_3Na$, where $n = 1-4$.

Among the useful anionic surfactants are the widely known metal carboxylate soaps, organosulfates, sulfonates, sulfocarboxylic acids and their salts, and phosphates.

5 The concentration of surfactant typically ranges from about 0.25 to 20 percent by weight aqueous concentrate. The surfactant concentration of an aqueous functional fluid composition typically varies from about 0.25 to 5 percent by weight. The concentration of surfactant, in accordance with this invention, is not critical.

10 The ferrous corrosion inhibitors act primarily as chelating agents for iron and its alloys. Such materials are well known in the art and individual compounds can be selected from the broad class of materials useful for this purpose. Boric acid and caprylic acid are preferred ferrous corrosion inhibitors. The concentration of ferrous corrosion inhibitor in aqueous concentrates typically varies from about 0.05 to 10 percent by weight. The concentration in an aqueous functional fluid composition typically varies from about 0.05 to 2 percent by weight. The concentration of ferrous corrosion inhibitor is not critical.

15 The non-ferrous corrosion inhibitors are used primarily as metal deactivators to chelate copper, aluminum, zinc and their alloys. Such materials are well known in the art and individual compounds can be selected from the broad classes of materials useful for this purpose, such as the various triazoles and thiazoles, as well as the amine derivatives of salicylidene. Representative specific examples of these metal deactivators are as follows: benzotriazole, tolyltriazole, 2-mercaptobenzothiazole, sodium 2-mercaptoben-
20 zothiazole, and N,N'-disalicylidene-1,2-propanediamine.

Benzotriazole is a preferred non-ferrous corrosion inhibitor. The aqueous concentrate concentration of the non-ferrous corrosion inhibitor may range from about 0.01 to 5 percent by weight. The concentration in an aqueous functional fluid composition typically varies from about 0.1 to 2 percent by weight. The concentration of non-ferrous corrosion inhibitor is not critical.

25 Amines are used to neutralize the acidity formed during working of the aqueous solution and present due to other acidic materials within the composition. The type of amine corrosion inhibitor is not critical. The amine also acts as a corrosion inhibitor. Representative amine-type corrosion inhibitors are methylethanolamine, diethanolamine, triethanolamine, morpholine, N-methylmorpholine, N-ethylmorpholine, ethylenediamine, dimethylaminopropylamine, dimethylethanolamine, alpha-and gamma-picoline, piperazine
30 and isopropylaminoethyl. Preferred amine corrosion inhibitors are morpholine and isopropylaminoethanol. The amine concentration of an aqueous concentrate typically ranges from about 0.05 to 25 percent by weight. The amine concentration in an aqueous functional fluid composition typically ranges from about 0.5 to 2 percent by weight. The amine concentration, in accordance with this invention, is not critical.

35 Additionally, biocides may be used to prevent microbial growth in these compositions. Biocides are well known in the art and any effective biocides may be utilized. Examples include phenolic derivatives, such as 2-phenyl phenol, 2-chlorophenol and 2,2'-methylene-bis (4-chlorophenol); formaldehyde release agents, such as the triazines, hexahydro-1,3,5-triethyl-s-triazine and hexahydro-1,3,5-tris (2-hydroxy-ethyl)-s-triazine, the imidazoles, e.g., 1,3-di(hydroxymethyl)-5,5-dimethyl-2,4-dioxolimidazole; aliphatic derivatives, such as, 2-bromo-2-nitropropane-1,3-diol;

40 organosulfur-nitrogen compounds, such as, the thiazoles, and 1,2-benzisothiazolin-3-one. These and other suitable biocides are disclosed in Tribology International, December 1983, Vol. 16 (6): 328-330. Preferred biocides are the triazines and sodium omadine.

The biocide concentration typically ranges from about 0.05 to 5 percent by weight of the total weight of the aqueous concentrate.

45 Methods for preparing the water-based hydraulic and metalworking fluids of this invention are well-known in the art. The basic procedure involves mixing the polyurethane and ethoxylated alcohol to form a thickener composition, followed by heating and adding the remaining components. In one aspect, a non-aqueous concentrate of the thickener composition and additives is provided. In another aspect, an aqueous concentrate is provided by employing a minor amount of water based on the weight of the total concentrate.

50 Preparations of the compositions of the invention are carried out using conventional equipment and at temperatures from room temperature to elevated temperatures, usually below 212°F., and often below 170°F. The non-aqueous or aqueous concentrate at a high active concentration is then diluted with water, wherein the total amount of water, used is in the amount required to provide the desired concentration of functional additives. This is often a convenient procedure, since the concentrate can be shipped to the point
55 of use before the water is added. Thus, the cost of shipping all or a substantial amount of the water in the final water-based functional fluid composition is saved.

In one aspect, only the water necessary to formulate the aqueous concentrate (which is determined primarily by ease of handling and convenience factors), need be shipped. Alternatively, the functional fluid

composition can be made directly or via a non-aqueous concentrate without going through the separate step of forming an aqueous concentrate.

The functional fluid compositions are easily formulated using distilled or deionized water, although tap water can also be used without adverse effects on fluid properties.

5 Typical ingredients of the aqueous concentrates of the invention are listed below:

Typical Percentage Ranges For
Hydraulic Fluid or Metalworking
Fluid Concentrate Components

10

<u>Component</u>	<u>Percent by Weight</u>
Polyurethane	0.05 - 50
15 Ethoxylated Alcohol	0.05 - 50
Amine	0.05 - 25
Corrosion Inhibitor	0.01 - 15
Antiwear Additive	0.05 - 20
Surfactant	0.25 - 20
20 Dispersant	0.10 - 30
Biocide	0.05 - 5
Water	20 - 50

25 The concentrates can be diluted to form fluid compositions prior to use, or if desired, the fluid compositions can be formed directly from the components. Typical functional water-based hydraulic or metalworking fluid compositions, in accordance with the teachings of this invention, may contain the components in the percentage ranges shown below.

30 Typical Percentage Ranges For Hydraulic
Fluid or Metalworking Fluid Composition Components

<u>Component</u>	<u>Percent by Weight</u>
Polyurethane	1 - 5
Ethoxylated Alcohol	1 - 15
Antiwear Additive	0.25 - 2
Dispersant	0.25 - 5
35 Amine	0.1 - 5
Corrosion Inhibitor	0.01 - 2
Surfactant	0.1 - 10
Biocide	q.s.
40 Water	60 - 95

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The functional fluid compositions of this invention, when formulated as above, are transparent liquids having an oil-like viscosity, which are stable over long periods of storage at ambient temperature. Additionally, the hydraulic and metalworking fluids of this invention are oil-free and will not support combustion in contrast to petroleum oils. The fluids of this invention are ecologically clean and nonpolluting compositions when compared to existing petroleum-based hydraulic fluids.

50 The hydraulic fluids of the subject invention can be used in various applications requiring hydraulic pressures in the range of 20-2000 pounds per square inch, since they generally exhibit all the essential properties required such as lubricity, viscosity and corrosion protection. The hydraulic fluids of this invention are suitable for use in various types of hydraulic systems and are especially useful in systems in which vane-type pumps or the axial-piston pumps are used. Such pumps are used in hydraulic systems where pressure is required for molding, clamping, pressing metals, actuating devices such as doors, elevators, and other machinery or for closing dies in die-casting machines and in injection molding equipment and other applications.

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In the following Examples, certain preferred embodiments are illustrated.

EXAMPLE 1

To demonstrate the interaction of the polyurethane of the subject invention and the specific ethoxylated alcohol of the invention, two test formulations as shown in Table 1 were employed. Three percent of the ethoxylated alcohol and three percent polyurethane (SCT 100) were used in each formula.

Table 1

<u>Ingredient</u>	<u>Formula-1</u>	<u>Formula-2</u>
Ethoxylated Alcohol	3.0	3.0
Urethane (SCT-100)	3.0	3.0
Caprylic Acid	0.2	0.2
Morpholine	0.25	0.25
Monoethanolamine	0.10	0.10
2-Methyl Bentrizazole	0.05	0.05
Zinc Dithiophosphate L677	0.50	--
Zinc Dithiophosphate 5604	-	0.75
Deionized Water	Balance	Balance

The samples are labelled A through S and were formulated according to formula 1 or formula 2. To determine the effectiveness of various ethoxylated alcohol surfactants, hence to determine if they meet the objectives of this invention, sample formulas, as shown in Tables 2 and 3, were tested in glass containers for the following:

(1) Stability in Solution: Separation indicates poor association between the polyurethane and the ethoxylated alcohol.

(2) Viscosity at 100°F.: measured with a Kinematic Viscometer and given in centistokes (cst). An initial viscosity of about 40 cst meets the objectives of this invention.

(3) Stability after Heating to 125°F.: Since normal hydraulic pump temperature is between 100 120°F., this test measures the stability of the fluid on heating with time.

(4) Viscosity Change on Heating: This test measures the stability of the fluid on heating with time.

Table 2

Examples of Individual Ethoxylated Alcohol Surfactants Within the Scope of the Invention

<u>Sample/ Formula</u>	<u>Trade Name</u>	<u>Alcohol</u>	<u>Moles/ E.O.</u>	<u>Ill.B</u>	<u>Initial Stability in Solution</u>	<u>Viscosity at 100°F.(cst)</u>	<u>Stability at 125°F.</u>	<u>% Change in Viscosity/ Hours run</u>
A/1	Brij 97	oleyl alcohol	10	12.4	stable	85.86	stable	-15.2/810 hrs.
B/2	Peganol LA-9	lauryl alcohol	9	12.0	opaque	81.3 precipitate	slight	-10.7/496 hrs.
C/1	Tergitol 25-L-9	1° alcohol C ₁₂ -C ₁₅	9	12.8	slight haze	71.23	stable	-15.2/384 hrs.
D/1	Neodol 91-6	1° alcohol C ₉ -C ₁₁	6	12.5	slight haze	52.28	stable	-7.6/384 hrs.
E/1	Tergitol 15-S-9	2° alcohol C ₁₁ -C ₁₅	9	13.5	slight haze	58.73	stable	-15.3/384 hrs.

Examples of Individual Ethoxylated Alcohol Surfactants Not Within the Scope of the Invention

F/1	Brij 76	stearyl alcohol	10	12.4	gel	-	-	-
G/1	Brij 58	cetyl alcohol	20	15.7	separates	33.66	-	-
H/1	Brij 56	cetyl alcohol	10	12.9	gel	-	-	-
I/1	Brij 35	lauryl alcohol	23	16.9	separates	17.41	-	-
J/1	Brij 30	lauryl alcohol	4	9.7	separates	-	-	-
K/2	Brij 30	lauryl alcohol	4	9.7	separates	-	-	-
L/2	Brij 35	lauryl alcohol	23	16.9	opaque	23.99	precipitate	-33/233 hrs
M/1	Brij 98	oleyl alcohol	20	15.3	haze	20	-	-

1/ moles ethylene oxide per mole alcohol.

Table 3

Examples of Blending Individual Ethoxylated Alcohols to a Given M.B.

Sample	Trade Name ^{1/}	Alcohol	Moles Combined E.O.	M.B.	Indiv. M.B.	Initial Stability in Solution	Viscosity at 100°F. (cst)	Stability at 125°F.	% Change in Viscosity/ Hours run
N	1.23 Brij 92	oleyl alcohol	2	11.0	4.9	translucent	42.70	translucent	-0.7/184 hrs.
	1.77 Brij 99	oleyl alcohol	20		15.3				
O	0.96 Brij 92	oleyl alcohol	2		4.9	slight haze	62.79	slight haze	-8.1/184 hrs.
	2.04 Brij 99	oleyl alcohol	20	12.0	15.3				
P	0.66 Brij 92	oleyl alcohol	2		4.9	haze	60.46	haze	-7.7/184 hrs.
	2.34 Brij 99	oleyl alcohol	20	13.0	15.3				
Q	2.46 Peganol LA-4	lauryl alcohol	4		9.7	translucent	7.32	haze	-
	0.54 Brij 35	lauryl alcohol	23	11.0	16.9				
R	1.98 Peganol LA-4	lauryl alcohol	4	12.0	9.7	haze	50.76	haze	-13.4/184 hrs.
	1.02 Brij 35	lauryl alcohol	23		16.9				
S	1.36 Peganol LA-4	lauryl alcohol	4	13.0	9.7	haze	68.20	precipitate	-9.8/184 hrs.
	1.64 Brij 35	lauryl alcohol	23		16.9				

^{1/} The numbers preceding the trade name materials indicate the percentage of each ethoxylated alcohol used. All examples are formula type 2.

As shown in Table 2, the ethoxylated alcohols within the scope of this invention, i.e., ethoxylated alcohols with particular HLB and ethoxylation ranges, in combination with polyurethane meet the objectives of this invention; whereas those outside the scope of this invention do not.

5 As shown in Table 3, under certain circumstances, it may be possible to employ mixtures of ethoxylated alcohols wherein each ethoxylated alcohol of the mixture is nominally outside the scope of the desired HLB and/or ethoxylation values of the preferred ethoxylated alcohols. For example, Table 3, Example O, shows that an oleyl alcohol with about 2 moles of ethoxylation and an HLB of about 4.9 when combined with an oleyl alcohol with about 20 moles of ethoxylation and an HLB of about 15.3 yields similar
10 properties to those alcohols within the scope of the invention as shown in Table 2, i.e., as if it were an ethoxylated alcohol selected from the group consisting of C₉-C₁₅ saturated alcohols with between about 5 and 20 moles of ethylene oxide per mole of alcohol and having an HLB between 11 and 14, and C₉-C₁₈ unsaturated alcohols with between about 5 and 20 moles of ethylene oxide per mole of alcohol and having an HLB between 11 and 14. Stability in solution, viscosity and shear stability are not, however, as
15 satisfactory or desirable with compositions containing these mixtures as with compositions containing the preferred ethoxylated alcohols.

EXAMPLE 2

20 In evaluating the hydraulic fluids of this invention, a test generally referred to as the Vickers Vane Pump Test is employed. The apparatus used in this test is a hydraulic system which functions as follows: hydraulic fluid is drawn from a closed sump to the intake side of a Vickers V-104C-10 vane-type pump. The pump is driven by, and directly coupled to, a 25 horsepower, 1740 rpm electric motor. The fluid is di-
25 discharged from the pump through a pressure regulating valve. From there it passes through a calibrated venturi (used to measure flow rate) and back to the sump. Cooling of the fluid is accomplished by a heat exchanger through which cold water is circulated. No external heat is required; the fluid temperature being raised by the frictional heat resulting from the pump's work on the fluid. Excess heat is removed by passing the fluid through the heat exchanger prior to return to the sump. The Vickers V-104C-10 vane-type pump
30 comprises a cylindrical enclosure (the pump body) in which there is housed a so-called "pump cartridge". The "pump cartridge" assembly consists of front and rear circular, bronze bushings, a rotor, a cam-ring and rectangular vanes. The bushings and cam-ring are supported by the body of the pump and the rotor is connected to a shaft which is turned by an electric motor. A plurality of removable vanes are inserted into slots in the periphery of the rotor. The cam-ring encircles the rotor and the rotor and vanes are enclosed by
35 the cam-ring and bushings. The inner surface of the cam-ring is cam-shaped. Turning the rotor results in a change in displacement of each cavity enclosed by the rotor, the cam-ring, two adjacent vanes and the bushings. The body is ported to allow fluid to enter and leave the cavity as rotation occurs.

The Vickers Vane Pump Test procedure used herein specifically requires charging the system with 5 gallons of the test fluid and running at temperatures ranging from 100° to 135°F. at 750 to 1000 psi pump
40 discharge pressure (load). Wear data were made by weighing the cam-ring and the vanes of the "pump cartridge" before and after the test. At the conclusion of the test run and upon disassembly for weighing, visual examination of the system was made for signs of deposits, varnish, corrosion, etc.

The following test sample was prepared and compared to a commercially prepared formulation.

The test sample consists of:

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Formula 1% Wt

Brij 97 (oleyl alcohol 10 mole of EO)	3.0
SCT-100	3.0
Caprylic Acid	0.2
Morpholine	1.25
Monoethanolamine	0.2
Sodium 2-Methyl Benzotriazole (50% Solution)	0.2
Lubrizol 5604 (anti-wear properties)	0.5
Formula 2	0.25
Biocide	----
Tap Water	91.4

Formula 2

Triton X-45 (octyl phenoxy polyethoxy ethanol)	12.5
Sipon ESY (sodium lauryl ether sulfate)	12.5
Dimethylethanolamine	5.0
Lubrizol 5603 (dispersant)	70.0

The test sample was prepared by first heating Lubrizol 5603 to 130-150°F. and mixing in Triton X-45, Sipon ESY, and dimethyl ethanolamine to form an intermediate. Next, Brij 97, SCT-100, Cobratex 99 (benzotriazole), Lubrizol 5604, morpholine, and caprylic acid and other ingredients were mixed and heated to 150-160°F. Distilled water at 150°F. was added. The heat was cut and the intermediate added to this mixture and then cooled.

Comparative Example 1 is a commercially-available, water-thickened hydraulic fluid, Plurasafe P-1200 from the BASF Wyandotte Corporation. This proprietary composition was reported to have the following composition:

Comparative Sample 1ComponentWt. %

alkyl polyether (polyglycol)	43.5
sodium benzoate	1.5
2-amino-2-methyl-1-propanol	5.9
water	remainder

No urethane, was detected upon analysis. The Plurasafe P-1200 hydraulic fluid concentrate was diluted with nine parts of water to one part of concentrate prior to use.

Shear stability of these samples were measured by running viscosity at 100°F. before and after time on the Vickers 104C Vane Pump, following the procedure given above, and calculating the percent viscosity loss. As shown in Table 5, the compositions of this invention exhibited excellent shear stability.

Table 5
Shear Stability (Vickers 104C Vane Pump)

	<u>Test Time</u> <u>Hours</u>	<u>Viscosity at</u> <u>100°F. (cst)</u>	<u>Viscosity</u> <u>% Change</u>
5			
	<u>Comparative</u> <u>Example 1</u>		
	0	43.20	-
10	42.8	37.53	-13.1
	161.5	31.65	-26.7
	237.6	25.22	-41.6
	<u>Test</u> <u>Sample</u>		
15	0	110.47	-
	46.6	112.73	+2.0
	161.3	116.91	+5.8
	324.4	117.44	+6.3
	488.3	123.87	+12.1
20			

As shown in Table 6, the test sample of this invention exhibited less wear (weight loss of ring and vanes) than the comparative example.

Table 6
Wear Properties on a Hydraulic Pump
(weight loss of ring and vanes)
(Vickers 104C Vane Pump)

	<u>Test Time</u> <u>(hours)</u>	<u>Total Wear-Loss in Weight</u> <u>Ring and Vanes (grams)</u>
30		
	<u>Product</u>	
	<u>Comparative</u> <u>Example 1</u>	
	42.8	1.652
35	161.5	6.452
	237.6	11.606
	<u>Test</u> <u>Sample</u>	
	46.6	1.148
40	161.3	1.185
	324.4	1.198
	488.3	1.200

The present invention is not to be limited except as set forth in the following claims:

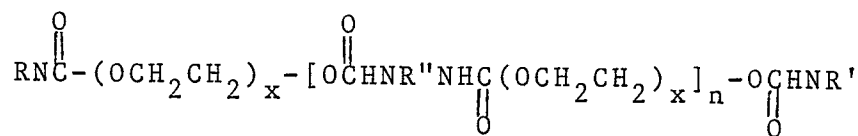
Claims

1. A thickener composition characterized by:

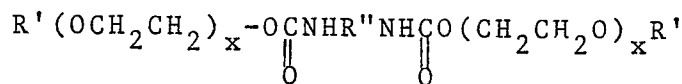
(1) at least one water-soluble, thermoplastic, organic polymer having a weight average molecular weight of at least about 10,000 which comprises hydrophobic segments, each containing at least one monovalent hydrophobic group covalently bonded to the polymer, wherein the polymer has an amount of hydrophobe bunching comprising at least two monovalent hydrophobic groups per hydrophobic segment, sufficient to provide for enhanced thickening of aqueous solutions containing the polymer, and

(2) at least one ethoxylated alcohol selected from the group consisting of C₉-C₁₅ saturated alcohols with between about 5 and 20 moles of ethylene oxide per mole of alcohol and having an HLB between 11 and 14, and C₉-C₁₈ unsaturated alcohols with between about 5 and 20 moles of ethylene oxide per mole of alcohol and having an HLB between 11 and 14.

2. The thickener composition according to claim 1, characterized in that the water-soluble, thermoplastic, organic polymer is a polyurethane having the following structure:

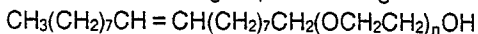


or

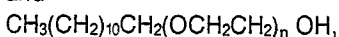


wherein R and R' are each C₁₂-C₁₈ alkyls; R'' is a C₇-C₃₆ alkyl; x is an integer from 90 to 455 and n is an integer from 1 to 4.

3. The thickener composition according to claim 1 or 2, characterized in that the ethoxylated alcohol is selected from the group consisting of at least one oleyl or lauryl alcohol that conforms to the formulas



and



respectively, wherein n is between about 5 and 20 and the alcohol or combined mixture of alcohols has an HLB of between 11 and 14; pareth-25-9, which is a polyethylene glycol ether of a mixture of synthetic C₁₂-C₁₅ fatty alcohols with an average of 9 moles of ethylene oxide and an HLB of about 12.8; pareth-91-6, which is a polyethylene glycol ether of a mixture of synthetic C₉-C₁₁ fatty alcohols with an average of 6 moles of ethylene oxide and an HLB of about 12.5; pareth-15-9, which is a polyethylene glycol ether of a mixture of synthetic C₁₁-C₁₅ fatty alcohols with an average of 9 moles of ethylene oxide and having an HLB of about 13.5; or mixtures thereof, and preferably is oleyl alcohol having about 10 moles of ethylene oxide per mole of alcohol and an HLB of about 12.4

4. The thickener composition according to claim 1, 2 or 3, characterized in that the ratio of polymer to ethoxylated alcohol ranges from about 100:1 to 1:100, preferably from about 5:3 to 1:1.

5. An aqueous concentrate characterized by comprising the thickener composition of any of claims 1-3.

6. The aqueous concentrate according to claim 5, characterized in that the polyurethane is present in a quantity of about 0.05 to 50 percent by weight of the total composition and/or the ethoxylated alcohol is present in a quantity of about 0.05 to 50 percent by weight of the total composition.

7. An aqueous functional fluid composition characterized by comprising the thickener of any of claims 1-3.

8. The aqueous functional fluid composition according to claim 7, characterized in that the polyurethane is present in a quantity from about 0.05 to 25 percent by weight of the total composition and/or the ethoxylated alcohol is present in a quantity from about 0.05 to 25 percent by weight of the total composition.

9. A thickener composition characterized by: (a) at least one water-soluble, thermoplastic, organic polymer having a weight average molecular weight of at least about 10,000 which comprises hydrophobic segments, each containing at least one monovalent hydrophobic group covalently bonded to the polymer, wherein the polymer has an amount of hydrophobe bunching comprising at least two monovalent hydrophobic groups per hydrophobic segment, sufficient to provide for enhanced thickening of aqueous solutions containing the polymer, and (b) (1) a mixture of C₉-C₁₈ saturated alcohols with between about 2 and 25 moles of ethylene oxide per mole of alcohol and having an HLB greater than about 4 and less than 11 or greater than 14 and less than about 17; or (2) a mixture of C₉-C₁₈ unsaturated alcohols with between about 2 and 25 moles of ethylene oxide per mole of alcohol and having an HLB greater than about 4 and less than 11 or greater than 14 and less than about 17; or (3) a mixture of at least one alcohol from (1) and at least one alcohol from (2); wherein the HLB of the mixture is between 11 and 14.