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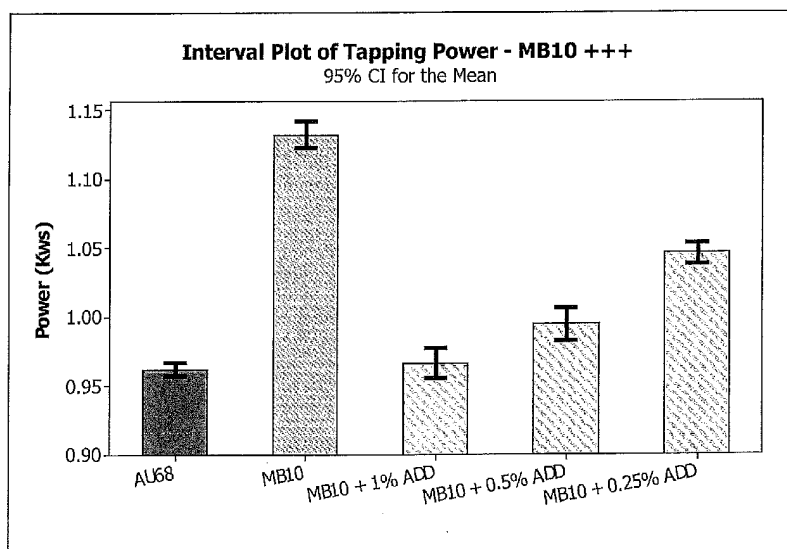
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(54) **MICELLAR EMULSIONS USEFUL FOR METALWORKING APPLICATIONS**

(57) This disclosure relates generally to emulsions, particularly micelle-containing emulsions useful as metalworking fluids and concentrates and treatments therefor. More particularly, the disclosure relates to emulsions

comprising water, one or more surfactants, one or more sulfurized additives, and, optionally, one or more oleaginous materials; methods for preparing such emulsions; and methods of using such emulsions.

FIG. 1



Description**BACKGROUND OF THE DISCLOSURE****Field of the Disclosure**

[0001] This disclosure relates generally to micellar emulsions. This disclosure relates more particularly to micellar emulsions useful as metalworking fluids and as concentrates therefor, methods for preparing such emulsions, and methods of using such emulsions.

Technical Background

[0002] Metalworking fluids find many applications within the metalworking industry. They are typically used in destructive metalworking (i.e., applications in which material is substantially removed from the workpiece, such as in the form of chips or other particles, such as milling or grinding) and in deformation metalworking (i.e., applications in which material is not substantially removed from the workpiece, such as rolling). In order to provide lubrication and heat control, a metalworking fluid is often used in a metalworking process, for example, at a surface between a tool and a workpiece. Known metalworking fluids are generally emulsions comprising common constituents: an aqueous component, and an oleaginous component and a surfactant dispersed in the aqueous component. Such oleaginous components are typically derived from hydrocarbon sources, for example, the hydrocarbons resulting from refining of crude oil or shale oil, or the hydrocarbons resulting from esterification.

[0003] Conventional aqueous components and oleaginous components used in metalworking fluids are naturally immiscible. Therefore, stable incorporation of aqueous components into an oleaginous base or oleaginous components into an aqueous base generally involves the use of emulsifiers such as surfactants to create an emulsion. Use of surfactants, however, can cause issues with foaming, and so defoamers or anti-foam compounds are often used in such fluids. A popular class of defoamers / anti-foam compounds for use with metalworking fluids are those having a silicon component. These compounds-typically water insoluble-are also insoluble in the metalworking fluid precursors or in the final, diluted metalworking fluid. Therefore, although they are useful in reducing the foaming of the metalworking fluid in use, these components create solubility and stability issues in the final emulsion.

[0004] It would be advantageous, however, to produce emulsions suitable for use as metalworking fluids as complete, stable emulsions without the use of defoamers, anti-foaming compounds, and/or excess or additional surfactants. In addition, it would be advantageous to produce such emulsions with no residual immiscible components. Such emulsions should be stable with no separation of the individual components during storage or use.

[0005] Prior to using the conventional metalworking fluids in metalworking applications, the user generally dilutes them prior to use. Thus, it would also be advantageous to provide the metalworking fluid emulsions that can be used in lower concentrations, without losing lubrication performance. Such emulsions would be more cost effective and sustainable than the conventional metalworking fluids.

SUMMARY OF THE DISCLOSURE

[0006] The present inventors have noted that, while surfactants have to be provided in an amount that is sufficient ensure the complete emulsification of the components, using too much surfactant can result in foaming of the emulsified mixture, either immediately on mixing or during use. The present inventors have found simple, cost-efficient, and sustainable emulsions that do not require the use of excess surfactants and/or defoamers and anti-foaming compounds. The emulsions of the disclosure can, for example, also provide improved lubrication performance, for example on aluminum alloys, even at lower concentrations as compared to commercially available metalworking fluids.

[0007] Thus, one aspect of the disclosure provides an emulsion including:

water;
 one or more surfactants;
 one or more sulfurized additives selected from sulfurized fatty acid esters, sulfurized fatty oil, sulfurized and polymerized fatty esters, and sulfurized polyolefins; and
 optionally, one or more oleaginous materials;
 wherein the emulsion is in the form of a micellar emulsion (for example, with the one or more surfactants forming a plurality of micelles, each comprising surfactant molecules disposed around a hydrophobic core comprising the one or more sulfurized additives and, optionally, one or more oleaginous materials).

[0008] In certain embodiments according to this aspect of the invention, the one or more oleaginous materials are

present in the emulsion (e.g., in the micelles). In certain such embodiments, the emulsions can be provided in relatively concentrated form, suitable, for example, for use as a top-treat additive, or a concentrate suitable for dilution to provide a metalworking fluid. In other such embodiments, the emulsions can be provided in relatively dilute form, suitable, for example, for use as a metalworking fluid.

[0009] In other embodiments according to this aspect of the invention, the one or more oleaginous materials are not substantially present in the emulsion. In certain such embodiments, the emulsions can be provided in relatively concentrated form, suitable, for example, as use as a top-treat additive.

[0010] In other such embodiments, the one or more oleaginous materials may be present in the emulsion, but are not substantially present in micelles together with the sulfurized additive. Such emulsions can be provided in a relatively dilute form, for example, having the sulfurized additive-containing micelles present together with micelles containing one or more oleaginous materials. Such materials can be formed by top-treating an existing metalworking fluid (i.e., which contains micelles containing one or more oleaginous materials).

[0011] In certain embodiments of the emulsions of the disclosure, the one or more surfactants is substantially bound into the micelles.

[0012] In certain embodiments of the emulsions of the disclosure, the emulsion is substantially free of defoamers and anti-foam compounds.

[0013] In another aspect of the disclosure a method for providing a top-treated metalworking fluid includes providing an existing metalworking fluid (e.g., containing a plurality of micelles including one or more oleaginous materials) and combining it with an emulsion of the disclosure.

[0014] Another aspect of the disclosure provides a method for preparing a metalworking fluid, including combining an emulsion of the disclosure with an aqueous fluid. The aqueous fluid can be, for example, water or some aqueous solution, or alternatively can be an existing metalworking fluid (e.g., a metalworking fluid that is partially spent, thus top-treating the other metalworking fluid).

[0015] Another aspect of the disclosure provided a method of working a metal, the method including contacting a surface of a metal article with a metalworking fluid of the disclosure; and forming the surface of the metal article to a desired shape while in contact with the metalworking fluid.

[0016] Another aspect of the disclosure provides a method of preparing an emulsion (e.g., an emulsion as described herein), the method comprising:

mixing water, one or more surfactants, one or more sulfurized additives selected from sulfurized fatty acid esters, sulfurized fatty oil, sulfurized and polymerized fatty esters, and sulfurized polyolefins, and, optionally, one or more oleaginous materials under a shear force to produce the top- treat emulsion.

[0017] Another aspect of the disclosure provides a method of preparing an emulsion (e.g., an emulsion as described herein), the method comprising:

obtaining a first fluid comprising one or more surfactants dissolved in water;
obtaining a second fluid comprising one or more sulfurized additives selected from sulfurized fatty acid esters, sulfurized fatty oil, sulfurized and polymerized fatty esters, and sulfurized polyolefins and, optionally, one or more oleaginous materials; and contacting the first fluid with the second fluids under a shear force to produce an emulsion.

[0018] Another aspect of the disclosure provides a method of preparing an emulsion (e.g., an emulsion as described herein), the method comprising:

obtaining a first fluid comprising one or more surfactants in aqueous solution;
obtaining a second fluid comprising one or more sulfurized additives selected from sulfurized fatty acid esters, sulfurized fatty oil, sulfurized and polymerized fatty esters, and sulfurized polyolefins, and, optionally, one or more oleaginous materials;
contacting the first fluid with the second fluid under a shear force to produce an intermediate fluid; and
contacting the intermediate fluid with an aqueous medium under laminar flow to obtain the emulsion.

BRIEF DESCRIPTION OF THE DRAWINGS

[0019] The accompanying drawings are included to provide a further understanding of the compositions and methods of the disclosure, and are incorporated in and constitute a part of this specification. The drawings illustrate one or more embodiment(s) of the disclosure, and together with the description serve to explain the principles and operation of the disclosure.

FIG. 1 is graph illustrating the tapping torque test on wrought automotive grade aluminum alloy 6061-T6 using the emulsions of the disclosure.

FIG. 2 is graph illustrating the tapping torque test on cast automotive grade aluminum alloy 356 using the emulsions of the disclosure.

FIG. 3 illustrates foam performance of an emulsion according to one embodiment of the disclosure.

FIG. 4 is a graph illustrating the power required to machine 24 holes of M8 diameter in a block of steel (42CrMo⁴)

FIG. 5 is a graph illustrating the power required to machine 24 holes of M8 diameter in a block of aluminum.

DETAILED DESCRIPTION

[0020] The particulars shown herein are by way of example and for purposes of illustrative discussion of the preferred embodiments of the present invention only and are presented in the cause of providing what is believed to be the most useful and readily understood description of the principles and conceptual aspects of various embodiments of the invention. In this regard, no attempt is made to show structural details of the invention in more detail than is necessary for the fundamental understanding of the invention, the description taken with the drawings and/or examples making apparent to those skilled in the art how the several forms of the invention may be embodied in practice. Thus, before the disclosed processes and devices are described, it is to be understood that the aspects described herein are not limited to specific embodiments, apparatus, or configurations, and as such can, of course, vary. It is also to be understood that the terminology used herein is for the purpose of describing particular aspects only and, unless specifically defined herein, is not intended to be limiting.

[0021] The terms "a," "an," "the" and similar referents used in the context of describing the invention (especially in the context of the following embodiments and claims) are to be construed to cover both the singular and the plural, unless otherwise indicated herein or clearly contradicted by context. Recitation of ranges of values herein is merely intended to serve as a shorthand method of referring individually to each separate value falling within the range. Unless otherwise indicated herein, each individual value is incorporated into the specification as if it were individually recited herein. Ranges can be expressed herein as from "about" one particular value, and/or to "about" another particular value. When such a range is expressed, another aspect includes from the one particular value and/or to the other particular value. Similarly, when values are expressed as approximations, by use of the antecedent "about," it will be understood that the particular value forms another aspect. It will be further understood that the endpoints of each of the ranges are significant both in relation to the other endpoint, and independently of the other endpoint.

[0022] All methods described herein can be performed in any suitable order of steps unless otherwise indicated herein or otherwise clearly contradicted by context. The use of any and all examples, or exemplary language (e.g., "such as") provided herein is intended merely to better illuminate the invention and does not pose a limitation on the scope of the invention otherwise claimed. No language in the specification should be construed as indicating any non-claimed element essential to the practice of the invention.

[0023] Unless the context clearly requires otherwise, throughout the description and the claims, the words 'comprise', 'comprising', and the like are to be construed in an inclusive sense as opposed to an exclusive or exhaustive sense; that is to say, in the sense of "including, but not limited to". Words using the singular or plural number also include the plural and singular number, respectively. Additionally, the words "herein," "above," and "below" and words of similar import, when used in this application, shall refer to this application as a whole and not to any particular portions of the application.

[0024] As will be understood by one of ordinary skill in the art, each embodiment disclosed herein can comprise, consist essentially of or consist of its particular stated element, step, ingredient or component. As used herein, the transition term "comprise" or "comprises" means includes, but is not limited to, and allows for the inclusion of unspecified elements, steps, ingredients, or components, even in major amounts. The transitional phrase "consisting of" excludes any element, step, ingredient or component not specified. The transitional phrase "consisting essentially of" limits the scope of the embodiment to the specified elements, steps, ingredients or components and to those that do not materially affect the embodiment.

[0025] Unless otherwise indicated, all numbers expressing quantities of ingredients, properties such as molecular weight, reaction conditions, and so forth used in the specification and claims are to be understood as being modified in all instances by the term "about." Accordingly, unless indicated to the contrary, the numerical parameters set forth in the specification and attached claims are approximations that may vary depending upon the desired properties sought to be obtained by the present invention. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, each numerical parameter should at least be construed in light of the number

of reported significant digits and by applying ordinary rounding techniques. When further clarity is required, the term "about" has the meaning reasonably ascribed to it by a person skilled in the art when used in conjunction with a stated numerical value or range, i.e., denoting somewhat more or somewhat less than the stated value or range, to within a range of $\pm 20\%$ of the stated value; $\pm 19\%$ of the stated value; $\pm 18\%$ of the stated value; $\pm 17\%$ of the stated value; $\pm 16\%$ of the stated value; $\pm 15\%$ of the stated value; $\pm 14\%$ of the stated value; $\pm 13\%$ of the stated value; $\pm 12\%$ of the stated value; $\pm 11\%$ of the stated value; $\pm 10\%$ of the stated value; $\pm 9\%$ of the stated value; $\pm 8\%$ of the stated value; $\pm 7\%$ of the stated value; $\pm 6\%$ of the stated value; $\pm 5\%$ of the stated value; $\pm 4\%$ of the stated value; $\pm 3\%$ of the stated value; $\pm 2\%$ of the stated value; or $\pm 1\%$ of the stated value.

[0026] All percentages, ratios and proportions herein are by weight, unless otherwise specified.

[0027] Notwithstanding that the numerical ranges and parameters setting forth the broad scope of the invention are approximations, the numerical values set forth in the specific examples are reported as precisely as possible. Any numerical value, however, inherently contains certain errors necessarily resulting from the standard deviation found in their respective testing measurements.

[0028] Groupings of alternative elements or embodiments of the invention disclosed herein are not to be construed as limitations. Each group member may be referred to and claimed individually or in any combination with other members of the group or other elements found herein. It is anticipated that one or more members of a group may be included in, or deleted from, a group for reasons of convenience and/or patentability. When any such inclusion or deletion occurs, the specification is deemed to contain the group as modified thus fulfilling the written description of all Markush groups used in the appended claims.

[0029] Some embodiments of this invention are described herein, including the best mode known to the inventors for carrying out the invention. Of course, variations on these described embodiments will become apparent to those of ordinary skill in the art upon reading the foregoing description. The inventor expects skilled artisans to employ such variations as appropriate, and the inventors intend for the invention to be practiced otherwise than specifically described herein. Accordingly, this invention includes all modifications and equivalents of the subject matter recited in the claims appended hereto as permitted by applicable law. Moreover, any combination of the above-described elements in all possible variations thereof is encompassed by the invention unless otherwise indicated herein or otherwise clearly contradicted by context.

[0030] Furthermore, numerous references have been made to patents and printed publications throughout this specification. Each of the cited references and printed publications are individually incorporated herein by reference in their entirety.

[0031] In closing, it is to be understood that the embodiments of the invention disclosed herein are illustrative of the principles of the present invention. Other modifications that may be employed are within the scope of the invention. Thus, by way of example, but not of limitation, alternative configurations of the present invention may be utilized in accordance with the teachings herein. Accordingly, the present invention is not limited to that precisely as shown and described.

[0032] In general, the disclosed materials and methods, and apparatus provide improvements in emulsions (for example, suitable for use as metalworking fluid) that can, in various embodiments, be cost-efficient and sustainable, and provide good lubrication properties. Specifically, the inventors have found that, in certain desirable embodiments, the emulsions of the disclosure do not include excess surfactant not bound up in micelles. As such, the inventors have determined that, in certain embodiments, the emulsions of the disclosure need not include defoamers and anti-foaming compounds. The emulsions of the disclosure can also, in certain embodiments, provide improved lubrication performance, for example on aluminum alloys, even at lower concentrations as compared to commercially available metalworking fluids.

[0033] Thus, one aspect of the disclosure provides an emulsion including:

water;
one or more oleaginous materials;
one or more surfactants; and
one or more sulfurized additives selected from sulfurized fatty acid esters, sulfurized fatty oil, sulfurized and polymerized fatty esters, and sulfurized polyolefins;

wherein the emulsion is in the form of a micellar emulsion (e.g., with the one or more surfactants forming a plurality of micelles, each comprising surfactant molecules disposed around a hydrophobic core comprising the one or more oleaginous materials and the one or more sulfurized additives). Such an emulsion can be, for example, in the form of a metalworking fluid (e.g., at relatively high water concentrations), or metalworking fluid concentrate (e.g., at a concentration suitable for dilution to form a metalworking fluid). Such an emulsion may also be in the form of a top-treat, suitable for addition to a metalworking fluid.

[0034] The disclosure also provides an emulsion including:

water;
 one or more surfactants; and
 one or more sulfurized additives selected from sulfurized fatty acid esters, sulfurized fatty oil, sulfurized and polymerized fatty esters, and sulfurized polyolefins;

wherein the emulsion is in the form of a micellar emulsion (e.g., with the one or more surfactants forms a plurality of micelles, each comprising surfactant molecules disposed around a hydrophobic core comprising the one or more sulfurized additives).

[0035] In certain such embodiments, the emulsion is substantially free of non-sulfurized oleaginous materials. This emulsion can be formed, e.g., at relatively low water concentration suitable for use as a top-treat additive to be added to an existing metalworking fluid. In such cases, the emulsion may be referred to as a "top-treat" emulsion.

[0036] In other such embodiments, the one or more oleaginous materials may be present in the emulsion, but are not substantially present in micelles together with the sulfurized additive. Such emulsions can be provided in a relatively dilute form, for example, having the sulfurized additive-containing micelles present together with micelles containing one or more oleaginous materials. Such materials can be formed by top-treating an existing metalworking fluid (i.e., which contains micelles containing one or more oleaginous materials).

[0037] In certain desirable embodiments as otherwise described herein, the emulsion is substantially free of defoamers and anti-foam compounds. The present inventors have determined that the emulsification techniques described herein can provide emulsions that are not highly susceptible to foaming, despite not including substantial amounts of defoamers/anti-foam compounds. For example, in certain embodiments, the emulsion of the disclosure comprises no more than 2 wt % of the one or more one or more defoamers and anti-foam compounds based on the total weight of the emulsion, e.g., no more than 1 wt %, or no more than 0.5 wt %, or no more than 0.1 wt %, or no more than 0.01 wt %, or no more than 0.005 wt %, or even no more than 0.001 wt %.

[0038] Typical anti-foam/defoamer compositions commonly used in metalworking fluids include organo-modified siloxane antifoams, PDMS (polydimethylsiloxane) antifoams, and wax defoamers. Both organo-modified siloxane antifoams and PDMS antifoams are based on a poly-siloxane backbone. In a PDMS antifoam, only methyl groups and oxygen are bonded at the silicon atom. In organo-modified siloxane antifoams, organic side chains (such as copolymers of ethylene-/propylene-oxide are chemically bonded to the polysiloxane backbone. Typical wax defoamers include, but are not limited to, ethylene bis stearamide (EBS), paraffin waxes, ester waxes, and fatty alcohol wax. With each type of anti-foam/defoamer the foam is destroyed by the hydrophobic solid material in the anti-foam/defoamer breaking down the film that forms between the anti-foam/defoamer material and the droplets of foam. In certain embodiments as otherwise described herein, the emulsion of the disclosure comprises no more than 1 wt % total of organo-modified siloxane antifoams, PDMS (polydimethylsiloxane) antifoams, and wax defoamers, or no more than 2 wt % of the one or more one or more defoamers and anti-foam compounds based on the total weight of the emulsion, e.g., no more than 1 wt %, or no more than 0.5 wt %, or no more than 0.1 wt %, or no more than 0.01 wt %, or no more than 0.005 wt %, or even no more than 0.001 wt %.

[0039] Of course, in other embodiments, e.g., in a metalworking fluid of the disclosure, there can be defoamers and anti-foam compounds present, for example, arising from a metalworking fluid to which a top-treat emulsion as described herein is added.

[0040] The present inventors have determined that in certain embodiments the emulsions described herein can have substantially low foaming properties, even in the absence of defoamers and anti-foam additives. As used herein, the foaming performance of a material can be quantified using a comparative laboratory test. In the test to quantify foam performance, a graduated cylinder is filled halfway with an emulsion as described herein. Once the emulsion has settled in the cylinder it is inspected to determine whether there is any separation between the components of the emulsion and whether any foam is generated.

[0041] The results of using such a test method are illustrated in FIG. 3. A graduated cylinder was partially filled with (A) a dilution of an emulsion according to one embodiment of the disclosure prepared by the methods disclosed herein, or (B) a dilution of a composition prepared by single vessel batch blending. Both (A) and (B) are 5 wt% aqueous dilutions of materials containing an identical combination of oleaginous materials, surfactants, and sulfurized additives, differing only in the way they were made. Here, the emulsion of the disclosure (A) prepared by the methods disclosed herein shows no foaming. In contrast, the non-emulsified composition (B) obtained by single vessel batch blending shows significant foaming and emulsion instability. Using an emulsion in accordance with certain embodiments of the disclosure can result in there being virtually no foam (i.e., such emulsion is substantially free of foam), even in cases where there is substantially no defoamer or anti-foam compound present, as the generation of micelles in such an emulsion is highly efficient.

[0042] Notably, in use as metalworking fluids, the emulsions according to certain embodiments of the disclosure can provide for substantially no foam formation. Accordingly, in certain embodiments of the metalworking methods as described herein, no foam is visible on the surface of the workpiece.

[0043] As described above, the emulsions of the disclosure include water. The water is desirably present in a substantial amount, for example, at least about 8 wt%, or at least about 10 wt%, or at least about 15 wt%, at least about 20 wt%, at least about 30 wt%, or even at least about 40 wt%, of the emulsion. In certain embodiments, water is present in an amount of at least about 50 wt%, at least about 60 wt%, or even at least about 70 wt% of the emulsion. In certain
 5 embodiments, water is present in an amount of at least about 80 wt%, at least about 90 wt%, or even at least about 95 wt% of the emulsion. The amount of water used will depend on whether the emulsion is itself a metalworking fluid, in which case relatively high amounts of water may be used, or rather whether the emulsion is to be used as a concentrate or top-treat additive for a metalworking fluid, in which case, relatively low amounts of water may be used; based on the disclosure herein, the person of ordinary skill in the art will provide an appropriate water concentration for a desired use.
 10 Moreover, the person of ordinary skill in the art will appreciate that a variety of additives can be present; certain such additives can be dissolved in the water phase.

[0044] For example, when the emulsion is to be used as a concentrate or top-treat additive for a metalworking fluid, the amount of water can be, e.g., in the range of 8 wt% to 60 wt%. In certain such embodiments, the amount of water is in the range of about 8 wt% to about 50 wt%, or about 8 wt% to about 40 wt%, or about 8 wt% to about 30 wt%, or
 15 about 8 wt% to about 20 wt%, or about 8 wt% to about 15 wt%, or about 10 wt% to about 50 wt%, or about 10 wt% to about 40 wt%, or about 10 wt% to about 30 wt%, or about 10 wt% to about 20 wt%, or about 10 wt% to about 15 wt%, or about 15 wt% to about 50 wt%, or about 15 wt% to about 40 wt%, or about 15 wt% to about 30 wt%, or about 20 wt% to about 60 wt%, or about 20 wt% to about 50 wt%, or about 20 wt% to about 40 wt%.

[0045] In other embodiments, e.g., when the emulsion is to be used as a metalworking fluid itself, the amount of water can be, e.g., at least about 60 wt%, at least about 70 wt%, at least about 80 wt%, at least about 90 wt%, at least about
 20 95 wt%, or even at least about 97 wt%. In certain such embodiments, the amount of water is in the range of about 60 wt% to about 99%, or about 70 wt% to about 99 wt%, or about 80 wt% to about 99 wt%, or about 90 wt% to about 99 wt%, or about 95 wt% to about 99 wt%, or about 97 wt% to about 99 wt%, or about 60 wt% to about 98%, or about 70 wt% to about 98 wt%, or about 80 wt% to about 98 wt%, or about 90 wt% to about 98 wt%, or about 95 wt% to about 98 wt%.

[0046] As described above, certain emulsions of the disclosure comprise one or more oleaginous materials. The oleaginous material is oily, oil-based, or oil-containing material. In certain embodiments, the oleaginous material may be a lubricating composition.

[0047] The choice of suitable lubricating composition will depend upon the end application of the emulsion of the disclosure. Lubricating composition may be a fully formulated lubricant or may be a blend of components, wherein at
 30 least one component has lubricating properties. A fully formulated lubricant is typically based on a lubricating base oil stock. Many different lubricating base oils are known, including, but not limited to, synthetic oils, natural oils, or mixtures thereof. Base oils may also be used in refined or in unrefined state (i.e., with or without at least one purification step). Natural oil includes, but is not limited to, vegetable oil, paraffinic oil, naphthenic oils, paraffinic-naphthenic oil, petroleum oil, treated (e.g., solvent, acid, or distillates derived) paraffinic, naphthenic, or asphaltic oil, and oils derived from coal
 35 or shale. Synthetic oil includes, but is not limited to, hydrocarbon oil and halo-substituted hydrocarbon oil (such as polybutylenes, polypropylenes, propylene-isobutylene copolymers, chlorinated polybutylenes, poly(1-hexenes), poly(1-octenes), poly(1-decenes), dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di(2-ethylhexyl) benzenes, biphenyls, terphenyls, alkylated polyphenyls, alkylated diphenyl ethers, alkylated diphenyl sulfides, etc.), polyalphaolefins (PAOs), the linear or branched C₁₀-C₁₈ alkanes, the linear or branched haloalkanes, polyhaloalkanes, perhaloalkanes,
 40 cycloalkanes, alkyl-and/or halo-substituted cycloalkanes, aryl hydrocarbons, lower alkylaryl hydrocarbons, and haloaryl hydrocarbons.

[0048] Base oil stock categories have been defined by the American Petroleum Institute (API Publication 1509) providing a set of guidelines for all lubricant base oils. These are shown in Table 1. In certain embodiments, the lubricating composition is a Group I, II, III, IV, or V base oil as defined by the American Petroleum Institute (API Publication 1509).
 45

Table 1 - Base Oil Stocks API Guidelines

	Saturates	Sulphur content	Viscosity Index (VI)
Group I	<90 and/or	>0.03% and	≥80 and <120
Group II	≥90 and	≤0.03% and	≥80 and <120
Group III	≥90 and	≤0.03% and	≥120
Group IV	Includes polyalphaolefins (PAO) and GTL (gas-to-liquid) products		
Group V	All other base oils not included in Groups I, II, III or IV		

[0049] Group II and/or Group III base oils (such as hydrocracked and hydroprocessed base oils as well as synthetic

oils such as hydrocarbon oils, polyalphaolefins, alkyl aromatics, and synthetic esters) are well known base oils. Group III oil base stock tends to be highly paraffinic with saturates higher than 90%, a viscosity index over 125, low aromatic content (less than 3%), and an aniline point of at least 118. PAOs are typically derived from C₆, C₈, C₁₀, C₁₂, C₁₄, and C₁₆ olefins or mixtures thereof and have a viscosity index greater than 135. PAOs can be manufactured by catalytic oligomerisation (polymerisation to low molecular weight products) of linear α -olefin (otherwise known as LAO) monomers. This leads to the presence of two classes of materials, PAOs and HVI-PAOs (high viscosity index PAOs), with PAOs being formed in the presence of a catalyst such as AlCl₃ or BF₃, and HVI-PAOs being formed using a Friedel-Crafts catalyst or a reduced chromium catalyst.

[0050] Esters also form a useful base oil stock, including synthetic esters, as do GTL (gas-to-liquid) materials, particularly those derived from a hydrocarbon source. For example, the esters of dibasic acids with monoalcohols, or the polyol esters of monocarboxylic acid may be useful in the emulsions of the disclosure. Such esters should typically have a viscosity of less than 10,000 cP at -35°C, in accordance with ASTM D5293. In certain embodiments, the base oil will comprise one or more of esters and one or more of natural oils (such as paraffin oil).

[0051] In certain embodiments of the emulsions of the disclosure, the one or more oleaginous materials is a naphthenic oil.

[0052] In certain embodiments of the emulsions of the disclosure, the one or more oleaginous materials is an ester base oil stock.

[0053] In certain embodiments of the disclosure, the emulsion includes the one or more oleaginous materials in an amount up to about 70 wt% based on the total weight of the emulsion. For example, in certain embodiments of the emulsions as otherwise described herein, the one or more oleaginous materials is present in an amount up to about 50 wt%, or up to about 30 wt%, or up to about 15 wt%, or up to about 10 wt%, or up to about 5 wt%, or up to about 3 wt%, or up to about 2 wt%.

[0054] In certain embodiments, e.g., when the emulsion is to be used as a top-treat additive or a metalworking fluid concentrate, the one or more oleaginous materials is present in an amount of 15 wt% to 70 wt%, for example, 20 wt% to 70 wt%, or 25 wt% to 70 wt%, or 30 wt% to 70 wt%, or 40 wt% to 70 wt%, or 15 wt% to 50 wt%, or 20 wt% to 50 wt%, or 25 wt% to 50 wt%, or 30 wt% to 50 wt%. The oleaginous materials can be, for example, present in the micelles with the sulfurized additive, present in micelles different from those in which the sulfurized additive is disposed, or a combination thereof.

[0055] In certain embodiments, e.g., when the emulsion is to be used as a metalworking fluid, the one or more oleaginous materials is present in an amount in the range of 0.5 wt% to 15 wt%, e.g., 0.5 wt% to 10 wt%, or 0.5 wt% to 5 wt%, or 0.5 wt% to 3 wt%, or 0.5 wt% to 2 wt%, or 0.5 wt% to 1.5 wt%, or 1 wt% to 15 wt%, or 1 wt% to 10 wt%, or 1 wt% to 5 wt%, or 1 wt% to 3 wt%. Notably, the present inventors have determined that the compositions and methods of the present disclosure can allow for the use of relatively low amounts of oleaginous materials in a metalworking fluid. The oleaginous materials can be, for example, present in the micelles with the sulfurized additive, present in micelles different from those in which the sulfurized additive is disposed, or a combination thereof.

[0056] In certain embodiments, e.g., when the emulsion is to be used as a top-treat additive, there is substantially no non-sulfurized oleaginous material in the emulsion.

[0057] In certain other embodiments, e.g., when the emulsion is to be used as a top-treat additive, the one or more oleaginous materials are present in the micellar emulsion (e.g., in the micelles with the sulfurized additive). In certain such embodiments, the one or more oleaginous materials may be a heavy mineral oil basestock.

[0058] The oleaginous materials of the disclosure may have various viscosities depending on the end application of the emulsion of the disclosure. In certain embodiments of the emulsions as otherwise described herein, one or more oleaginous materials has a kinematic viscosity at 40 °C of up to 12000 cSt, e.g., 8000 to about 12000 cSt, or about 8000 to about 10000 cSt, or about 8000 to about 9000 cSt, or about 1 to about 8000 cSt, or about 1 to about 7000 cSt, or about 1 to about 6000 cSt, or about 1 to 5000 cSt or about 1 to about 4000 cSt, or about 1 to about 3000 cSt, or about 1 to about 2000 cSt, or about 1 to about 1000 cSt, as measured in accordance with ASTM D455.

[0059] The oleaginous materials of the disclosure may have high or very high viscosity index (VI), depending on the end application of the emulsion of the disclosure. VI is a measure for the change of viscosity if the oil with variations in temperature. The lower the VI, the greater the change of viscosity of the oil with temperature. In certain embodiments of the emulsions as otherwise described herein, one or more oleaginous materials has viscosity index of up to 120. In certain embodiments of the emulsions as otherwise described herein, one or more oleaginous materials has viscosity index of between 80 and 120.

[0060] As described above, the emulsions of the disclosure include one or more surfactants. The inventors have found that, in certain embodiments, the one or more surfactants is substantially bound into the micelle. For example, in certain embodiments, no more than 1 wt % of the one or more surfactants is present in the emulsion in an unbound state (i.e., not part of a micelle), based on the total weight of the emulsion. In certain embodiments, no more than 0.5 wt %, or no more than 0.1 wt %, or no more than 0.05 wt %, or even no more than 0.01 wt % is present in the emulsion in an unbound state, based on the total weight of the emulsion. The point at which an emulsion becomes substantially free of excess

surfactant can be determined by measuring the surface tension of the emulsion. Once the critical micelle concentration has been reached, and no more surfactant molecules are included in the surface layer(s), the surface tension of the emulsion exhibits a discontinuity. This may be detected by surface tension measurement techniques known to those skilled in the art. Other techniques for determining this point include nuclear magnetic resonance (NMR) techniques and optical scattering techniques. These include those taught in James-Smith et al, Journal of Colloid and Interface Science, 310: 590-598 (2007).

[0061] Surfactants suitable for use in the embodiments of the disclosure include ionic surfactants, non-ionic surfactants, or combinations thereof. In certain embodiments, for example, the main surfactant component may be a non-ionic surfactant and the minor surfactant component may be an ionic surfactant. Examples of ionic surfactants include, but are not limited to, potassium oleate, sodium laurate, potassium stearate, potassium caprolate, sodium palmitate, tetra-cosenyl benzene sulfonate, sodium nonylbenzene sulfonate and potassium dodecylbenzene sulfonate, sodium dodecyl sulfate, sodium dihexyl sulfosuccinate and sodium dioctyl sulfosuccinate, dodecyl ammonium hydrochloride, dodecyl trimethyl quaternary ammonium chloride, ethoxylated fatty amines, etc. Examples of non-ionic surfactant include, but are not limited to, saturated and unsaturated C₁₆ - C₁₈ fatty esters, C₁₆ - C₁₈ fatty alcohol ethoxylates - with an ethoxylation range of 0-9 moles (fatty alcohol polyglycol ethers), C₁₆-C₁₈ fatty alcohol ethoxylate and propoxylate, C₁₆-C₁₈ fatty acid ethoxylates and propoxylates, C₆/C₈/C₁₆₋₁₈ alkyl polyoxyethylene ether carboxylic acids with a 2 to 9 mole ethoxylation range, alkyl ether ethoxylate mono phosphate esters - alkyl chain C₁₆-C₁₈, with a 2 to 5 mole ethoxylation range, ethoxylated oleine with a 6/9 mole ethoxylation range, ethoxylated castor oils, and polyethylene glycol esters of C₁₆-C₁₈ fatty acids). The person of ordinary skill in the art will select desirable surfactants based on the disclosure herein.

[0062] In certain embodiments, the emulsions of the disclosure include one surfactant. In certain embodiments, the emulsions of the disclosure include at least two different surfactants.

[0063] The choice of suitable surfactant will depend on the desired hydrophilic-lipophilic balance (HLB) value. In certain embodiments of the emulsions as otherwise described herein, the one or more surfactants has an average HLB value of about 8 to about 16, e.g., from about 8 to about 14, or from about 9 to about 12, or from about 10 to about 16, or from about 12 to about 16.

[0064] In certain embodiments, the emulsions of the disclosure include one or more surfactants selected from saturated and unsaturated C₁₆ - C₁₈ fatty esters, C₁₆ - C₁₈ fatty alcohol ethoxylates, alkyl ether ethoxylate mono phosphate esters, C₁₆-C₁₈ fatty acid ethoxylates and propoxylates, and ethoxylated castor oils.

[0065] In certain embodiments of the disclosure, the emulsions of the disclosure include one or more surfactants in an amount within the range of about 0.1 wt% to about 10 wt% based on the total weight of the emulsion. For example, in certain embodiments of the emulsions as otherwise described herein, the one or more surfactants is present in an amount of about 0.01 wt% to about 8 wt%, or about 0.01 wt% to about 5 wt%, or about 0.01 wt% to about 2 wt%, or about 0.01 wt% to about 1 wt%, or about 0.1 wt% to about 10 wt%, or about 0.1 wt% to about 8 wt%, or about 0.1 wt% to about 5 wt%, or about 0.1 wt% to about 2 wt%, or about 0.1 wt% to about 1 wt%, or about 0.2 wt% to about 10 wt%, or about 0.2 wt% to about 8 wt%, or about 0.2 wt% to about 5 wt%, or about 0.2 wt% to about 2 wt%, or about 0.2 wt% to about 1 wt%, or about 0.5 wt% to about 10 wt%, or about 0.5 wt% to about 8 wt%, or about 0.5 wt% to about 5 wt%, or about 0.5 wt% to about 2 wt%, or about 1 wt% to about 10 wt%, or about 1 wt% to about 8 wt%, or about 1 wt% to about 5 wt%, or about 2 wt% to about 10 wt%, or about 2 wt% to about 8 wt%, or about 2 wt% to about 5 wt%, or about 0.25 wt% to about 5 wt%, or about 0.25 wt% to about 1 wt%, based on the total weight of the emulsion. The person of ordinary skill in the art will appreciate that relatively less surfactant can be present in dilute metalworking fluids than in concentrated materials.

[0066] As described above, the emulsions of the disclosure include one or more additives selected from sulfurized fatty acid esters, sulfurized fatty oil, sulfurized and polymerized fatty esters, and sulfurized polyolefins

[0067] In certain embodiments of the disclosure, the emulsion comprises one or more sulfurized additives in a total amount within the range of about 0.1 wt% to about 80 wt% based on the total weight of the emulsion. In certain embodiments, e.g., when used as a top-treat additive or a concentrate, the one or more sulfurized additives are present in an amount in the range of about 10 wt% to about 80 wt%, e.g., about 10 wt% to 70 wt%, or about 10 wt% to 60 wt%, or about 10 wt% to 50 wt%, or about 10 wt% to about 40 wt%, or about 10 wt% to about 30 wt%, or about 20 wt% to about 80 wt%, or about 20 wt% to about 70 wt%, or about 20 wt% to about 60 wt%, or about 20 wt% to about 50 wt%, or about 20 wt% to about 40 wt%, or about 30 wt% to about 80 wt%, or about 30 wt% to about 70 wt%, or about 30 wt% to about 60 wt%, or about 30 wt% to about 50 wt%, or about 50 wt% to about 80 wt%, or about 60 wt% to about 80 wt%, or about 50 wt% to about 70 wt%, or about 60 wt% to about 70 wt%, or about 65 wt% to about 75 wt%. In other embodiments, e.g., when used as a metalworking fluid, the one or more sulfurized additives are present in an amount in the range of about 0.1 wt% to about 10 wt%, e.g., about 0.2 wt% to about 10 wt%, or about 0.5 wt% to about 10 wt%, or about 1 wt% to about 10 wt%, or about 2 wt% to about 10 wt%, or about 0.1 wt% to about 5 wt%, or about 0.2 wt% to about 5 wt%, or about 0.5 wt% to about 5 wt%, or about 1 wt% to about 5 wt%, or about 2 wt% to about 5 wt%, or about 0.1 wt% to about 2 wt%, or about 0.2 wt% to about 2 wt%, or about 0.5 wt% to about 2 wt%, based on the total weight of the emulsion.

[0068] In certain embodiments, the one or more sulfurized additives is selected from sulfurized fatty acid esters. The

person of ordinary skill in the art will identify a suitable sulfurized fatty acid ester for use in a particular composition. In certain embodiments, the sulfurized fatty acid esters may be sulfurized saturated or unsaturated C₈ - C₂₂ fatty esters. Examples of sulfurized fatty acid esters include those sold under the names Roscan 278 and 389 (available from PCAS, Longjumeau, France), those sold under names RC2811 and RC 5250 (available from RheinChemie, Mannheim, Germany), and those sold under names DeoAdd LR11H, VP 332-1, VP 332-2, and VP-288 (available from DOG-Chemie, Hamburg, Germany). The sulfurized fatty acid ester of the disclosure may have, for example, a total sulfur content of between about 1 wt% and about 40 wt%, e.g., about 1 wt% to about 30 wt%, or about 1 wt% to about 25 wt%, or about 1 wt% to about 20 wt%, or about 1 wt% to about 15 wt%, or about 1 wt% to about 10 wt%, or about 10 wt% to about 40 wt%, or about 10 wt% to about 30 wt%, or about 10 wt% to about 25 wt%, or about 10 wt% to about 20 wt%, or about 10 wt% to about 15 wt%. The total sulfur content is measured using the ASTM D 1552 (LECO) test method. One particular sulfurized ester has the following characteristics: Sulfur content approx. 14.5 wt% (ASTM D 1552 (LECO)), density @ 15 °C 1.00 - 1.05 g/mL (DIN EN ISO 12185), viscosity (kinematic) @ 40 °C approx.. 5000 (DIN 51562 Part 1).

[0069] In certain embodiments, the emulsion includes one or more sulfurized fatty acid esters in a total amount within the range of about 0.1 wt% to about 80 wt% based on the total weight of the emulsion. In certain embodiments, e.g., when used as a top-treat additive or a concentrate, the one or more sulfurized additives are present in an amount in the range of about 10 wt% to about 80 wt%, e.g., about 10 wt% to 70 wt%, or about 10 wt% to 60 wt%, or about 10 wt% to 50 wt%, or about 10 wt% to about 40 wt%, or about 10 wt% to about 30 wt%, or about 20 wt% to about 80 wt%, or about 20 wt% to about 70 wt%, or about 20 wt% to about 60 wt%, or about 20 wt% to about 50 wt%, or about 20 wt% to about 40 wt%, or about 30 wt% to about 80 wt%, or about 30 wt% to about 70 wt%, or about 30 wt% to about 60 wt%, or about 30 wt% to about 50 wt%, or about 50 wt% to about 80 wt%, or about 60 wt% to about 80 wt%, or about 50 wt% to about 70 wt%, or about 60 wt% to about 70 wt%, or about 65 wt% to about 75 wt%. In other embodiments, e.g., when used as a metalworking fluid, the one or more sulfurized additives are present in an amount in the range of about 0.1 wt% to about 10 wt%, e.g., about 0.2 wt% to about 10 wt%, or about 0.5 wt% to about 10 wt%, or about 1 wt% to about 10 wt%, or about 2 wt% to about 10 wt%, or about 0.1 wt% to about 5 wt%, or about 0.2 wt% to about 5 wt%, or about 0.5 wt% to 5 wt%, or about 1 wt% to about 5 wt%, or about 2 wt% to about 5 wt%, or about 0.1 wt% to about 2 wt%, or about 0.2 wt% to about 2 wt%, or about 0.5 wt% to about 2 wt, based on the total weight of the emulsion.

[0070] Notably, the present inventors have determined that, while high-viscosity sulfurized additives such as high-viscosity sulfurized fatty acid esters are generally difficult to emulsify and are prone to hydrolysis, they can be successfully and stably emulsified using the methods described herein. Thus, in certain embodiments of the emulsions as otherwise described herein, one or more of (e.g., each of) the one or more sulfurized additives has a kinematic viscosity at 40 °C of at least 1000 cSt. In certain such embodiments, one or more of (e.g., each of) the one or more sulfurized additives has a kinematic viscosity at 40 °C of at least 2000 cSt, or at least 4000 cSt, or about 4000 to about 50000 cSt, or about 4000 to about 25000 cSt, or about 4000 to about 20000 cSt, or about 4000 to about 10000 cSt, or about 5000 to about 50000 cSt, or about 5000 to about 25000 cSt, or about 5000 to about 20000 cSt, or about 5000 to about 10000 cSt. As used herein, kinematic viscosities are measured in accordance with ASTM D455.

[0071] As the person of ordinary skill in the art will appreciate, the ratio of the amount of oleaginous material and the one or more sulfurized additives selected from sulfurized fatty acid esters, sulfurized fatty oil, sulfurized and polymerized fatty esters, and sulfurized polyolefins to the amount of surfactant will be a factor that determines the micelle size. In certain embodiments as otherwise described herein, the weight ratio of the sum of the amounts of oleaginous materials and sulfurized additives to the amount of surfactant is in the range of 1 to 100. Similarly, in certain embodiments of the emulsions that are substantially free of oleaginous materials other than the sulfurized additives, the ratio of the total amount of the one or more sulfurized additives to the amount of surfactant will be a factor that determines the micelle size of the top-treat emulsion. In certain embodiments as otherwise described herein, the weight ratio of the amount of the one or more sulfurized additives to the amount of surfactant is in the range of 1 to 100.

[0072] As the person of ordinary skill in the art will appreciate based on the disclosure, the emulsions can also include a variety of other components, such as those conventional in compositions for metalworking fluid applications. Examples include, but are not limited to, corrosion inhibitors, rust inhibitors, lubricity enhancers, friction modifiers, chelating agents, coupling agents, yellow metals, esters, and biocides.

[0073] Suitable corrosion inhibitors include, but are not limited to, amine/alkali salts of short chain carboxylic mono acids, di- and tri-acids, short chain acidic phosphate esters, including alkoxylated esters, semi-succinate half esters, amide-carboxylic acid salts, fatty amides, and amine and alkali sulphonates, or their derivatives. Suitable yellow metals include, but are not limited to, benzotriazole or its derivatives and tolutriazole or its derivatives. Suitable esters include, but are not limited to, trimethylol propane (TMP), mono-, di- and tri- esters of C₈ - C₁₈ fatty acids, glycol esters of predominantly oleyl fatty acids, methyl or isopropyl esters of predominantly oleyl fatty acids or triglycerides, natural triglycerides (such as rapeseed), and modified natural oils (such as blown rapeseed). Suitable biocides (typically amine compounds) include, but are not limited to, formaldehyde releasing agents including ortho-formal, hexahydratriazine and derivatives, methylene bis morpholine, oxazoladine and derivatives, isothiazolinones and derivatives and iodo propyl butyl carbamate-fungicide.

[0074] In certain embodiments, the emulsion may further comprise one or more of corrosion inhibitors, rust inhibitors, lubricity enhancers, friction modifiers, chelating agents, coupling agent, yellow metals, esters, biocides, and combinations thereof, for example, present in an amount up to 15 wt%, for example, up to 10 wt%, up to 8 wt% or up to 5 wt%, based on the total weight of the emulsion. In certain such embodiments, one or more of corrosion inhibitors, rust inhibitors, lubricity enhancers, friction modifiers, chelating agents, coupling agent, yellow metals, esters, biocides, and combinations thereof are present in an amount in the range of about 0.01 wt% to about 15 wt%, or about 0.01 wt% to about 10 wt%, or about 0.01 wt% to about 8 wt%, or about 0.01 wt% to about 5 wt%, or about 0.01 wt% to about 1 wt%, or about 1 wt% to about 15 wt%, or about 1 wt% to about 10 wt%, or about 1 wt% to about 8 wt%, or about 1 wt% to about 5 wt%, or about 2 wt% to about 15 wt%, or about 2 wt% to about 10 wt%, or about 2 wt% to about 8 wt%, or about 2 wt% to about 5 wt%, or about 5 wt% to about 15 wt%, or about 5 wt% to about 10 wt%, based on the total weight of the emulsion.

[0075] The person of ordinary skill in the art will appreciate that a variety of other components can be present in the emulsions of the disclosure.

[0076] In one exemplary embodiment, an emulsion of the disclosure includes: about 10 to about 50 wt% of the one or more oleaginous materials; about 3 to about 8 wt% of the one or more surfactants; about 1 wt% to about 30 wt% of the one or more sulfurized additives selected from sulfurized fatty acid esters, sulfurized fatty oil, sulfurized and polymerized fatty esters, and sulfurized polyolefins; and at least 25 wt% water. In certain such embodiments, the emulsion further includes about 5.0 to about 10 wt% of a corrosion inhibitor. Such an emulsion can be, for example, used as a concentrate for a metalworking fluid.

[0077] In another exemplary embodiment, an emulsion of the disclosure includes: about 0.5 to about 5 wt% (e.g., about 0.5 to about 3 wt%) of the one or more oleaginous materials; about 0.01 to about 1 wt% of the one or more surfactants; about 0.1 wt% to about 5 wt% of the one or more sulfurized additives selected from sulfurized fatty acid esters, sulfurized fatty oil, sulfurized and polymerized fatty esters, and sulfurized polyolefins; and at least 90 wt% water. In certain such embodiments, the emulsion further includes about 2 to about 5 wt% of a corrosion inhibitor. Such an emulsion can be, for example, used as a metalworking fluid.

[0078] In another exemplary embodiment, an emulsion of the disclosure includes: about 1 to about 20 wt% of the one or more oleaginous materials; about 0.01 to about 5 wt% of the one or more surfactants; about 0.25 wt% to about 20 wt% of the one or more sulfurized additives selected from sulfurized fatty acid esters, sulfurized fatty oil, sulfurized and polymerized fatty esters, and sulfurized polyolefins; and at least 50 wt% water. In certain such embodiments, the emulsion further includes about 0.5 to about 2 wt% of a corrosion inhibitor.

[0079] In another exemplary embodiment, an emulsion of the disclosure includes: about 3 to about 8 wt% of the one or more surfactants; about 1 wt% to about 50 wt% of the one or more sulfurized additives selected from sulfurized fatty acid esters, sulfurized fatty oil, sulfurized and polymerized fatty esters, and sulfurized polyolefins; and at least 25 wt% water. In certain such embodiments, the emulsion is substantially free of a non-sulfurized oleaginous material. Such an emulsion can be, for example, used as a top-treatment for a metalworking fluid.

[0080] In another exemplary embodiment, an emulsion of the disclosure includes: about 3 to about 15 wt% of the one or more surfactants; about 50 wt% to about 80 wt% of the one or more sulfurized additives selected from sulfurized fatty acid esters, sulfurized fatty oil, sulfurized and polymerized fatty esters, and sulfurized polyolefins; and at least 8 wt% water. In certain such embodiments, the emulsion is substantially free of a non-sulfurized oleaginous material. Such emulsions can be, for example, used as a top-treatment for a metalworking fluid.

[0081] While additional components can be present in the emulsions as described above, in certain desirable embodiments, the chief constituents are water, one or more surfactants, and one or more sulfurized additives selected from sulfurized fatty acid esters, sulfurized fatty oil, sulfurized and polymerized fatty esters, and sulfurized polyolefins, and, optionally, one or more oleaginous materials. Accordingly, in certain embodiments as otherwise described herein, the total amount of water, one or more oleaginous materials, one or more surfactants, and one or more sulfurized additives selected from sulfurized fatty acid esters, sulfurized fatty oil, sulfurized and polymerized fatty esters, and sulfurized polyolefins in the emulsion is at least 70%, at least 80%, or at least 85 wt%, or at least 90 wt%, or at least 95 wt%, or at least 98 wt%, or even at least 99 wt%.

[0082] While additional components can be present in the top-treat emulsions as described above, in certain desirable embodiments, the chief constituents are water, one or more surfactants, and one or more sulfurized additives selected from sulfurized fatty acid esters, sulfurized fatty oil, sulfurized and polymerized fatty esters, and sulfurized polyolefins. Accordingly, in certain embodiments as otherwise described herein, the total amount of water, one or more surfactants, and one or more sulfurized additives selected from sulfurized fatty acid esters, sulfurized fatty oil, sulfurized and polymerized fatty esters, and sulfurized polyolefins in the top-treat emulsion is at least 80%, or at least 85 wt%, or at least 90 wt%, or at least 95 wt%, or at least 98 wt%, or even at least 99 wt%.

[0083] As the person of ordinary skill in the art will appreciate, a micelle is an aggregate of surfactant molecules dispersed in a colloid, where particles of a first material are suspended in a second material, creating a two-phase system. Unlike in a solution, the first material is insoluble or immiscible in the second material (i.e., it becomes an emulsion). In an aqueous solution, a micelle forms an aggregate with the hydrophobic tails of the surfactant molecules

facing inwards and the hydrophilic heads of the surfactant molecules facing outwards. This forms a normal-phase micelle, leading to an oil-in-water phase mixture. An inverse-phase micelle has the inverse structure, where the hydrophilic heads of the surfactant molecules face inwards and the hydrophobic tails face outwards. This leads to a water-in-oil phase mixture. The packing behaviour of the surfactant molecules may lead to a single layer of surfactant molecules around the core of the micelle, which, following surface energy considerations, may typically form a sphere. Thus, in certain embodiments, the micelles of the disclosure are generally spherical in structure.

[0084] Further layers of surfactant may also be packed around the outside of the micelle. This will be the case when further surfactant is added to the mixture. For example, when shear forces are applied to an oleaginous material, the molecules of the oleaginous material stretch. This stretching causes the molecules to flatten out and form a laminar structure, thus increasing the surface area any surfactant has available to be attracted to. Coupled with a laminar flow around the molecule of a dispersion of surfactant in water, the packing fraction of the surfactant increases from $\leq 1/3$ to $> 1/2$. Once the shear force is removed from the molecule, it forms a spherical micelle due to surface energy considerations, unless, of course, the structure of the surfactant causes the minimum surface energy configuration of a micelle to be laminar or cylindrical. For example, Gemini surfactants, sometimes known as dimeric surfactants, have two hydrophobic tails that distort the core of the micelle into an elongated ovoid shape. The surfactant packing fraction then reduces back to $\leq 1/3$ for spherical micelles, so any surfactant that had been attracted to the temporary laminar configuration of the molecule forms additional layers of surfactant around the micelle. Only odd numbers of layers form, however, because for a normal-phase micelle the even layers of surfactant molecules are arranged with the hydrophilic heads in contact with the hydrophilic heads of the first layer of surfactant molecules, and the hydrophobic tails pointing outwards. The inverse is true for an inverse-phase micelle. Therefore, in both cases, a micelle will have $1, 3, 5, 7 \dots n=2k+1$ layers of surfactant. This also results in effectively no free surfactant in any form within the emulsion as surfactant will be bound within these micelles, in multiple layers. As noted above, there is substantially no unbound surfactant present in the aqueous solution. The more surfactant added into the emulsion-the greater the number of layers of surfactant in the micelle. Thus, in certain embodiment, the surfactant molecules are disposed around a hydrophobic core in a single molecular layer. In certain other embodiments, the surfactant molecules are disposed around a hydrophobic core in three or more molecular layers. In certain embodiments, different molecular layers may comprise two or more surfactants. For example, a non-ionic surfactant may be present within the surface layers, and ionic surfactants may be present within the layer.

[0085] One further advantage of the emulsions and methods of certain embodiments of the disclosure is a relatively uniform size of the micelles in the emulsion. The present inventors have determined that use of the methods described herein can provide a micellar emulsion with a relatively uniform micellar size. The distribution of the average diameters of the micelles typically follows a Gaussian profile. The distribution of the average diameters of the micelles has a mean μ and a standard deviation σ , determined using conventional statistical analysis. In certain embodiments, the standard deviation σ is no more than 0.5μ , no more than 0.2μ , or even no more than 0.1μ . For example, for a mean average micelle diameter of $0.3 \mu\text{m}$, the standard deviation of the average micelle diameter is $0.06 \mu\text{m}$ or less. The average micelle diameter is an average of various diameter measurements taken for a particular micelle, which in the case of spherical micelles is approximately equal to the micelle diameter (since there is little or no variation of the diameter regardless of where the measurement is taken).

[0086] The advantage of having a narrow range of average micelle diameters lies in the ability of the emulsion, for example when used as a metalworking fluid, to fully cover a surface. In a fluid where there is a wide range of average micelle diameters, the coverage of the fluid across a surface is variable. This is due to regions of equal surface area having different volumes of fluid on them. If the average micelle diameter is in a small range, however, the surface coverage is far more efficient and extensive as the regions of equal surface area will have approximately equal volumes of fluid on them. This leads to more even wear and improved surface/interface protection.

[0087] In certain embodiments, the micelles have a mean average diameter of no more than about $1.5 \mu\text{m}$, for example, no more than about $1 \mu\text{m}$, no more than about $0.5 \mu\text{m}$, or even no more than about $0.4 \mu\text{m}$. In certain embodiments, the micelles have a mean average diameter in the range of about $0.1 \mu\text{m}$ to about $1.5 \mu\text{m}$, or about $0.1 \mu\text{m}$ to about $1 \mu\text{m}$, or about $0.1 \mu\text{m}$ to about $0.75 \mu\text{m}$, or about $0.1 \mu\text{m}$ to about $0.5 \mu\text{m}$, or about $0.1 \mu\text{m}$ to about $0.4 \mu\text{m}$, or about $0.05 \mu\text{m}$ to about $0.4 \mu\text{m}$, or about $0.2 \mu\text{m}$ to about $0.5 \mu\text{m}$, or about $0.3 \mu\text{m}$ to about $0.4 \mu\text{m}$. While there exist a variety of suitable measurement techniques to determine both the average micelle diameter and the distribution of average micelle diameters include, for use in quantification of values in the present disclosure, sizes are measured using laser particle size analysis using a Beckman Coulter Laser Diffraction PS Analyzer (LS 13 320), which uses Polarization Intensity Differential Scattering (PIDS) technology to determine particle size and size distribution.

[0088] As described above, the inventors have noted that use of a micellar emulsion with a relatively narrow micellar particle size distribution can result in a number of advantages. As the person of ordinary skill in the art will appreciate, the micellar size distribution can be characterized by d_{50} , d_{10} and d_{90} values, where d_{50} is the median particle size, d_{10} is the particle size at the 10th percentile of particles ranked by size, and d_{90} is the particle size at the 90th percentile of particles ranked by size. In certain embodiments, the micelles of a particular emulsion as otherwise described herein

have a d50 value in the range of 0.1 μm to 1.5 μm ; e.g., or about 0.1 μm to about 1 μm , or about 0.1 μm to about 0.75 μm , or about 0.1 μm to about 0.5 μm , or about 0.1 μm to about 0.4 μm , or about 0.05 μm to about 0.4 μm , or about 0.2 μm to about 0.5 μm , or about 0.3 μm to about 0.4 μm . In certain embodiments, d10 is no less than 50% of d50 and d90 is no more than 150% of d50. In certain embodiments, d10 is no less than 60% of d50 and d90 is no more than 140% of d50. In certain embodiments, d10 is no less than 70% of d50 and d90 is no more than 130% of d50. In certain embodiments, d10 is no less than 75% of d50 and d90 is no more than 125% of d50. In certain embodiments, d10 is no less than 80% of d50 and d90 is no more than 120% of d50. While there are a number of suitable measurement techniques to determine both the micellar particle size and the micellar particle size distribution, for quantification for purposes of this disclosure, laser particle size analysis using a Beckman Coulter Laser Diffraction PS Analyzer (LS 13 320) is used. This method employs Fraunhofer diffraction and Polarization Intensity Differential Scanning (PIDS) to determine the particle size.

[0089] In certain embodiments, the micelle size and size distribution described herein apply to the micelles containing a sulfurized additive (e.g., arising from a top-treat emulsion or a concentrate containing a sulfurized additive), and not to all micelles in a metalworking fluid.

[0090] As described above, the emulsions of the disclosure can be provided in a variety of concentrations. In certain embodiments, an emulsion of the disclosure is provided at a concentration that is itself suitable for use as a metalworking fluid, i.e. such an emulsion can be used undiluted in metalworking applications.

[0091] And in other embodiments, an emulsion of the disclosure is provided at a concentration suitable for use as a metalworking fluid concentrate, i.e., at a concentration that can be diluted with aqueous media to provide a metalworking fluid. And in other embodiments, a top-treat emulsion of the disclosure is used as a top-treat fluid to form a metalworking fluid from an existing metalworking fluid.

[0092] Accordingly, an emulsion of the disclosure may also be provided by diluting a more concentrated emulsion (e.g., a more concentrated emulsion of the disclosure).

[0093] Thus, one aspect of the disclosure provides a metalworking fluid prepared by combining an emulsion of the disclosure with an aqueous fluid. An emulsion of the disclosure may be diluted, for example, with a desired quantity of water or other aqueous fluid, to convert a metalworking concentrate to a metalworking fluid. In certain embodiments, the emulsion is used in an amount of about 0.25 wt% to about 20 wt% based on the total weight of the metalworking fluid; e.g., about 0.25 wt% to about 5 wt%, or about 1 wt% to about 10 wt%, or about 5 wt% to about 10 wt%, or about 5 wt% to about 6 wt%, or about 6 wt% to about 10%.

[0094] An emulsion of the disclosure may also be used as a top-treat fluid, e.g., to provide the sulfurized additive-containing micelles to a spent metalworking fluid or an existing metalworking fluid. In certain embodiments, the top-treat emulsion is used in an amount of about 0.5 wt% to about 20 wt% based on the total weight of the metalworking fluid; e.g., about 0.5 wt% to about 10 wt%, or about 0.5 wt% to about 5 wt%, or about 0.5 wt% to about 2%, or about 1 wt% to about 20 wt%, or about 1 wt% to about 10 wt%, or about 1 wt% to about 5 wt%. In certain embodiments, the dilution may be carried out more than once; for example, the process may effectively form a series of metalworking fluids with each subsequent fluid having a lower concentration of the emulsion of the disclosure. One of skill in the art may dilute the metalworking fluid until the desired viscosity and/or lubrication performance is achieved.

[0095] Another aspect of the disclosure provided a method of working a metal. Such method comprises contacting a surface of a metal article with the emulsion of the disclosure or the metalworking fluid of the disclosure, and forming the surface of the metal article to a desired shape. Working a metal may be destructive metalworking process, i.e., the process where chips are produced, such as drilling, grinding, milling, and turning, or a deforming metalworking process, i.e., the process where a material is deformed or shaped such that no chips are produced, for example such as steel rolling, tapping, and shearing. In certain embodiments, the metal is steel. In certain embodiments, the metal is aluminium. One of skill in the art will recognize that suitable emulsions of the disclosure and metalworking fluids of the disclosure may be selected based on the desired type of metal and of metalworking process.

[0096] A suitable method of preparing the emulsions of the disclosure is described in U.S. Patent Application Publication No. 2013/0201785, which is hereby incorporated herein by reference in its entirety. This publication discloses an apparatus for mixing oleaginous and aqueous materials under a shear force and laminar flow to create either an oil-in-water or a water-in-oil fluid. Thus, one aspect of the disclosure provides a method of preparing the emulsion of the disclosure, the method comprising obtaining a first fluid comprising one or more surfactants dissolved in water (e.g., in the form of an aqueous solution); obtaining a second fluid comprising one or more oleaginous materials and one or more sulfurized additives; contacting the first fluid with the second fluids under a shear force to produce an intermediate fluid. This intermediate fluid may be in the form of a colloidal emulsion, and may be free-flowing or gel-like. The intermediate fluid may also have a greater viscosity than either the first fluid or the second fluid, e.g., at least 5 % higher, or at least 10% higher, or at least 50% higher. This intermediate fluid may comprise micelles of the oleaginous material in the aqueous emulsion. Both the first fluid and the second fluid may be added to a chamber in which stirrers are used to mix the two fluids together under shear force by rotating at a rotational speed of about 1200 to about 1600 rpm. The shape of the chamber and size of the stirrers may be chosen to ensure that a region around the walls of the chamber is devoid of

turbulent flow. Thus, whilst an oleaginous material is under shear, an aqueous suspension of a surfactant can flow around the chamber in this region thereby producing a laminar flow. In certain embodiments, a third fluid may be added to the intermediate fluid under laminar flow (for example, increasing the water content of the aqueous fluid to decrease the viscosity of the resulting metalworking fluid).

[0097] Another aspect of the disclosure provides a method of preparing the top-treat emulsion of the disclosure, the method comprising obtaining a first fluid comprising one or more surfactants dissolved in water (e.g., in the form of an aqueous solution); obtaining a second fluid comprising one or more sulfurized additives; contacting the first fluid with the second fluids under a shear force to produce an intermediate fluid. This intermediate fluid may be in the form of a colloidal emulsion, and may be free-flowing or gel-like. The intermediate fluid may also have a greater viscosity than either the first fluid or the second fluid, e.g., at least 5 % higher, or at least 10% higher, or at least 50% higher. Both the first fluid and the second fluid may be mixed as noted above. In certain embodiments, a third fluid may be added to the intermediate fluid under laminar flow (for example, increasing the water content of the aqueous fluid to decrease the viscosity of the resulting emulsion).

[0098] The methods of the disclosure allow for materials with high viscosities to be emulsified into a stable emulsion. It is currently difficult to emulsify fluids having a viscosity of greater than approximately 100 to 150 cSt at 40 °C using the current techniques. The method of the disclosure can be used to emulsify fluids having a viscosity of 8,000 to 12,000 cSt at 40°C. The actual limit is dependent upon the temperature of the various components during emulsification. For example, it may be necessary to heat components up to around 90°C to achieve emulsification.

[0099] Not wishing to be bound by theory, it is believed that in certain embodiments substantially all of the surfactant becomes bound within the micelle structure as described above as a result of the shear mixing. That is, substantially all of the surfactant molecules form at least one layer over the surface of the core of the micelle. There is substantially no unbound surfactant present in such emulsions, where unbound surfactant is characterised as free surfactant molecules within the emulsion detectable alone without being part of a micelle. In practice, substantially all of the surfactant being bound within the micelle structure can result in the emulsion of the disclosure being substantially free of excess surfactant. In addition, the emulsion according to certain embodiments of the disclosure can be substantially foam-free, and does not foam when in use. As a result, the emulsions of the disclosure can, in certain embodiments, also be substantially free of defoamers and/or anti-foam compounds (i.e., in such embodiments, these are no longer required to compensate for any foaming of an oleaginous/aqueous emulsion).

[0100] Certain aspects of the disclosure are now explained further via the following nonlimiting examples.

EXAMPLES

General Formulation

[0101] Using the technology described in the U.S. Patent Publication 2013/0201785, the emulsions of the disclosure were prepared. Each emulsion comprised 10 wt% of oleaginous material, and 0.25 wt%, 0.5 wt%, or 1 wt% of a sulfurized additive, which was sulfurized fatty acid ester.

[0102] MB10 (available from Castrol, Lewiston, NY under label HYSOL MB 10) is a semi-synthetic metalworking fluid with a 10% mineral oil content; MB20 (available from Castrol, Lewiston, NY under label HYSOL MB 20) is a semi-synthetic metalworking fluid with a 20% mineral oil content; and MB50 (available from Castrol, Lewiston, NY under label HYSOL MB 20) is a semi-synthetic metalworking fluid with a 50% mineral oil content. AU68 (available from Castrol, Lewiston, NY under label ALUSOL AU 68) is a semi-synthetic metalworking fluid with a 20-40% mineral oil content.

[0103] The emulsions of the disclosure or commercially available metalworking fluids were diluted to a concentration of between 5 and 10 wt% and tested for power required to thread the pre-drilled hole using Mori Seiki NH4000 milling machine. The lower power indicates the improved lubrication performance.

Example 1

[0104] The emulsions of the disclosure and the commercially available metalworking fluids were diluted to 10 wt% concentration. FIG. 1 provides the tapping power test on wrought automotive grade aluminum alloy 6061-T6 (available, for example, from Alcoa, Chicago, IL). The results show that providing a sulfurized additive in the amount of 0.25 wt% (i.e., sample labeled as "MB10 + 0.25% ADD") outperformed the emulsion with no sulfurized additive (i.e., sample labeled as "MB10.") In addition, increasing the sulfurized additive content from 0.25 wt% (i.e., sample labeled as "MB10 + 0.25% ADD") to 1 wt% (i.e., sample labeled as "MB10 + 1% ADD") significantly improved lubrication. While AU68 is better performing than MB10, it is significantly more expensive. The emulsion of the disclosure containing 1 wt% of the sulfurized additive performs as well as AU68 but is significantly more cost effective.

Example 2

[0105] Softer cast aluminum, such as cast automotive grade aluminum alloy 356 (available, for example, from Alcoa, Chicago, IL), is more difficult to tap because the metal tends to be softer and stickier when cut than wrought alloys. On this type of alloy, MB10 does not lubricate sufficiently to prevent machinery damage. As a result, metalworking fluids with higher mineral oil content need to be used, such as MB20 and MB50.

[0106] The emulsions of the disclosure were diluted to a concentration of 5 wt%, where MB20, MB50, and AU68 were diluted to a concentration of 8 wt%. As shown in FIG. 2, the emulsions of the disclosure comprising between 0.25 and 1 wt% of the sulfurized additive all outperformed MB20 and MB50.

Example 3

[0107] An example of the top-treat emulsion of the disclosure was prepared using the general procedure noted above. The specific amounts and materials are noted in Table 2.

Table 2

Component	Supplier Name	Weight %
sulfurized fatty acid ester	DeoAdd VP 288, D.O.G Deutsche Oelfabrik, Germany	69.9
glycerin (86%) (emulsifier)	Brenntag, Germany	8.8
sodium hydroxide (50% solution)	Natronlauge, Brenntag, Germany	0.15
12-hydroxystearic acid	Oleo-Chemie, Germany	1.14
Aqueous solution of alkyl poluglucosides C ₁₀ -C ₁₆ (surfactant)	Glucopon® 600 C SUP, BASF, Germany	1.96
ethoxylated linear primary alcohols C ₁₀ -C ₁₆ (surfactant)	Novel® 1618-80, Sasol, South Africa	5.45
water	-	12.6

Example 4

[0108] A series of experiments were carried out using Reichert wear testing, employing a load of 2Kg, and measuring both the noise of the wear (dB) and the depth of the wear scarring (μm). Each sample was prepared as a 5% emulsion in de-ionized water, with the tests carried out on steel. The results are provided in Table 3.

[0109] Example 3A was an emulsion of caprylic / capric triglyceride, NanoGel CCT (available from Clariant AG, Muttens, Switzerland) with 4 wt% of an ethoxylated phosphoric ester. Example 3B is an emulsion of NanoGel CCT with 3 wt% of an ethoxylated phosphoric ester, and 3 wt% of sulfurized fatty acid ester, DeoAdd VP332-1 (available from D.O.G. Deutsche Oelfabrik, Hamburg, Germany). Example 3C is an emulsion of NanoGel CCT and 4 wt% of DeoAdd VP332-1. Top Treat 1 was the DeoAdd VP332-1. As provided in Table 3, the inclusion of an optimum amount of a sulfurized additive improves performance.

Table 3

Materials	Sulfur/Phosphorous (% additive)	Noise Meter (average) dB	Wear Scar (mm ²)
Example 3A	-/4	50	16.7
Example 3B	3/3	0	2.1
Example 3C	4/-	0	1.8
Comparative example 1 (Hysol X ¹)	5/6	100	24.3
Comparative example 2 (LS0094SC ²)	5/4	90	27.4

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(continued)

Materials	Sulfur/Phosphorous (% additive)	Noise Meter (average) dB	Wear Scar (mm ²)
Comparative example 3 (Hysol MB 50 ³)	-/3	100	26.5
Comparative example 3 + 2% Top Treat 1	2/3	100	25
Comparative example 3+4% Top Treat 1	4/3	80	22.4
Comparative example 4 (Hysol 35 XBB ⁴)	- / -	100	26.5
Comparative example 4 + 2% Top Treat 1	2/-	87	25.3
Comparative example 4 + 4% Top Treat 1	4/-	42	19.1
Comparative example 2+ 2% Top Treat 1	7/4	11	9.5
Comparative example 2 + 4% Top Treat 1	9/4	7	6.3
¹ semi-synthetic metalworking fluid, available from Castrol, Lewiston, New York ² water soluble metalworking fluid, available from Castrol, Lewiston, New York ³ semi-synthetic metalworking fluid, available from Castrol, Lewiston, New York ⁴ semi-synthetic metalworking fluid, available from Castrol, Lewiston, New York			

Example 5

[0110] A series of experiments were carried out to determine the optimum dosing of the top treat into an emulsion of metalworking fluid. A series of Reichert tests were carried out, using a weight of 2Kg (first and second test runs), as summarized below. The noise measure (dB) and the depth of the wear scarring (μm) are presented in Table 4.

[0111] LD0094 and CFX are both metalworking products available from Castrol (Lewiston, New York), and Avantin 3309 is a coolant product for metalworking available from Carl Bechem GmbH (Hagen, Germany). The CFX product contains a sulfurized fatty acid ester (sold as VPP 228 by D. O. G. Deutshce Oelfabrik) and had been emulsified to create micelles of the ester in water. As provided in Table 4, the use of a small amount of the sulfurized fatty acid ester with a relatively weak concentration of the base metalworking fluid gives a performance increase. Without being bound to a particular theory, it is believed that the performance improvement is most likely a result of reduced competition of the sulfurized fatty acid ester micelles with other molecules at the metal surface.

Table 4

Ex. No.	Materials	Noise (dB)	Wear Scar (mm ²)
4A	LD0094 (10% concentration)	57	19.98
		45	19.59
4B	LD0094 (10% concentration) 0.5% Avantin 3309	15	13.82
		15	13.74
4C	LD0094 (10% concentration) 1.0% Avantin 3309	9	11.74
		11	12.29
4D	LD0094 (5% concentration) 1.0% Avantin 3309	11	12.55
		13	12.34
4E	LD0094 (10% concentration) 0.5% CFX	10	11.07
		8	11.07

(continued)

Ex. No.	Materials	Noise (dB)	Wear Scar (mm ²)
4F	LD0094 (5% concentration) 0.5% CFX	7	9.39
		6	8.66
4G	LD0094 (10% concentration) 1.0% CFX	6	8.85
		5	8.9
4H	LD0094 (5% concentration) 1.0% CFX	3	4.23
			4.27
4I	LD0094 (10% concentration) 0.5% CFX	12	11.81
		10	11.23
4J	LD0094 (10% concentration) 1.0% CFX	6	10.11
		5	9.78

Example 6

[0112] A machining test to determine the effect of adding sulfurized esters to metalworking fluids for use on different materials was carried out. The test comprised machining 24 holes using an M8 bit in firstly, a block of steel (42CrMo₄) 250 x 110 x 50 mm in size using a Sandvik M8 E308 threadformer. The tool was driven at a rotational speed of 1800rpm and a lateral speed of 45m/min. FIG. 4 illustrates the results for the power required to turn the tool and drill the holes at this rate. The test was then replicated on a block of aluminum of the same size. FIG. 5 illustrates the results for the power required to turn the tool and drill the holes at this rate.

[0113] FIG. 4 illustrates a base fluid comprising an 8% concentration of Hysol CGX 100 metalworking fluid available from Castrol Limited, a conventional high-phosphorous and high sulfur metalworking fluid. The top treat used was that shown in Example 5 above. The base fluid plus top treat required a lower power to machine the holes, indicating an improvement in the efficiency of the machining process due to the addition of a sulfurized ester component in the top treat.

[0114] FIG. 5 illustrates a base fluid comprising an 8% concentration of a base fluid comprising a micellar emulsion of a mineral oil, and a top treat comprising a micellar emulsion of a sulfurized ester and undecylenic acid. Again, the power required to machine the holes was lower when the top treat was employed in the metalworking fluid.

[0115] It is understood that the examples and embodiments described herein are for illustrative purposes only and that various modifications or changes in light thereof will be suggested to persons skilled in the art and are to be incorporated within the spirit and purview of this application and scope of the appended claims. All publications, patents, and patent applications cited herein are hereby incorporated herein by reference for all purposes.

Various embodiments of the disclosure include, but are not limited to:

1. An emulsion comprising:

water;

one or more surfactants;

one or more sulfurized additives selected from sulfurized fatty acid esters, sulfurized fatty oil, sulfurized and polymerized fatty esters, and sulfurized polyolefins; and

optionally, one or more oleaginous materials;

wherein the emulsion is in the form of a micellar emulsion.

2. The emulsion of embodiment 1, wherein the one or more surfactants is substantially bound into micelles of the micellar emulsion, e.g., wherein no more than 1 wt % of the one or more surfactants is present in the emulsion in an unbound state, based on the total weight of the emulsion.

3. The emulsion of embodiment 1, wherein no more than 0.5 wt %, or no more than 0.1 wt %, or no more than 0.05 wt %, or even no more than 0.01 wt % is present in the emulsion in an unbound state, based on the total weight of the emulsion.

4. The emulsion of any of embodiments 1-3, substantially free of defoamers and anti-foam compounds, e.g., wherein no more than 2 wt % of defoamers and anti-foam compounds (e.g., no more than 1 wt %, or no more than 0.5 wt

%, or no more than 0.1 wt %, or no more than 0.01 wt %, or even no more than 0.001 wt %) is present in the emulsion, based on the total weight of the emulsion.

5 The emulsion of any of embodiments 1-3, substantially free of defoamers and anti-foam compounds, e.g., wherein no more than 2 wt % (e.g., no more than 1 wt %, or no more than 0.5 wt %, or no more than 0.1 wt %, or no more than 0.01 wt %, or even no more than 0.001 wt %) total of organo-modified siloxane antifoams, PDMS (polydimethylsiloxane) antifoams, and wax defoamers is present in the emulsion, based on the total weight of the emulsion.

10 6. The emulsion of any of embodiments 1-5, wherein the emulsion has a foaming performance of no more than 5 mL, e.g., no more than 2 mL, no more than 1 mL, no more than 0.5 mL or even no more than 0.1 mL.

15 7. The emulsion of any of embodiments 1-6, wherein water is present in the emulsion in an amount in the range of about 8 wt% to about 60 wt%, e.g., in the range of about 8 wt% to about 50 wt%, or about 8 wt% to about 40 wt%, or about 8 wt% to about 30 wt%, or about 8 wt% to about 20 wt%, or about 8 wt% to about 15 wt%, or about 10 wt% to about 50 wt%, or about 10 wt% to about 40 wt%, or about 10 wt% to about 30 wt%, or about 10 wt% to about 20 wt%, or about 10 wt% to about 15 wt%, or about 15 wt% to about 50 wt%, or about 15 wt% to about 40 wt%, or about 15 wt% to about 30 wt%, or about 20 wt% to about 60 wt%, or about 20 wt% to about 50 wt%, or about 20 wt% to about 40 wt%.

20 8. The emulsion of any of embodiments 1-6, wherein water is present in the emulsion in an amount in the range of 60 wt% to 99%, e.g., in the range of 70 wt% to 99 wt%, or 80 wt% to 99 wt%, or 90 wt% to 99 wt%, or 95 wt% to 99 wt%, or 97 wt% to 99 wt%, or 60 wt% to 98%, or 70 wt% to 98 wt%, or 80 wt% to 98 wt%, or 90 wt% to 98 wt%, or 95 wt% to 98 wt%.

25 9. The emulsion of any of embodiments 1-6, wherein water is present in the emulsion in an amount at least 8 wt%, e.g., at least 10 wt%, at least 15 wt%, at least 20 wt%, at least 30 wt%, or even at least 40 wt%, of the emulsion

30 10. The emulsion of any of embodiments 1-9, wherein the one or more oleaginous materials comprises a lubricating composition.

11. The emulsion of embodiment 10, wherein the lubricating composition is a Group I, II, IV, or V base oil as defined by the American Petroleum Institute (API Publication 1509).

35 12. The emulsion of embodiment 10, wherein the lubricating composition is a base oil selected from vegetable oil, paraffinic oil, naphthenic oils, paraffinic-naphthenic oil, petroleum oil, treated (e.g., solvent, acid, or distillates derived) paraffinic, naphthenic, or asphaltic oil, oils derived from coal or shale, hydrocarbon oil and halo-substituted hydrocarbon oil (such as polybutylenes, polypropylenes, propylene-isobutylene copolymers, chlorinated polybutylenes, poly(l-hexenes), poly(l-octenes), poly(l-decenes), dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di(2-ethylhexyl) benzenes, biphenyls, terphenyls, alkylated polyphenyls, alkylated diphenyl ethers, alkylated diphenyl sulfides, etc.), polyalphaolefins (PAOs), the linear or branched C₁₀-C₁₈ alkanes, the linear or branched haloalkanes, polyhaloalkanes, perhaloalkanes, cycloalkanes, alkyl-and/or halo-substituted cycloalkanes, aryl hydrocarbons, lower alkylaryl hydrocarbons, and haloaryl hydrocarbons.

45 13. The emulsion of embodiment 10, wherein the lubricating composition is one or more naphthenic oils or an ester oil.

14. The emulsion of embodiment 10, wherein the lubricating composition is a heavy mineral oil.

50 15. The emulsion of any of embodiments 1-14, wherein the one or more oleaginous materials is present in an amount of 15 wt% to 70 wt%, for example, 20 wt% to 70 wt%, or 25 wt% to 70 wt%, or 30 wt% to 70 wt%, or 40 wt% to 70 wt%, or 15 wt% to 50 wt%, or 20 wt% to 50 wt%, or 25 wt% to 50 wt%, or 30 wt% to 50 wt%, based on the total weight of the emulsion.

55 16. The emulsion of any of embodiments 1-14, wherein the one or more oleaginous materials is present in an amount of 0.5 wt% to 15 wt%, e.g., 0.5 wt% to 10 wt%, or 0.5 wt% to 5 wt%, or 0.5 wt% to 3 wt%, or 0.5 wt% to 2 wt%, or 0.5 wt% to 1.5 wt%, or 1 wt% to 15 wt%, or 1 wt% to 10 wt%, or 1 wt% to 5 wt%, or 1 wt% to 3wt%, based on the total weight of the emulsion.

17. The emulsion of any of embodiments 1-16, wherein the one or more oleaginous materials has a kinematic

viscosity at 40 °C of up to 100 cSt, e.g., about 1 to about 100 cSt, or about 1 to about 50 cSt, or about 1 to about 25 cSt, or about 1 to about 20 cSt, or about 1 to about 10 cSt, or about 5 to about 100 cSt, or about 5 to about 50 cSt, or about 5 to about 25 cSt, or about 5 to about 20 cSt, or about 5 to about 10 cSt.

18. The emulsion of any of embodiments 1-17, wherein the one or more surfactants include an ionic surfactant (e.g., potassium oleate, sodium laurate, potassium stearate, potassium caprolate, sodium palmitate, tetracosenyl benzene sulfonate, sodium nonylbenzene sulfonate and potassium dodecylbenzene sulfonate, sodium dodecyl sulfate, sodium dihexyl sulfosuccinate and sodium dioctyl sulfosuccinate, dodecyl ammonium hydrochloride, dodecyl trimethyl quaternary ammonium chloride, ethoxylated fatty amines, etc.).

19. The emulsion of any of embodiments 1-17, wherein one or more surfactants include a non-ionic surfactant (e.g., saturated and unsaturated C₁₆ - C₁₈ fatty esters, C₁₆ - C₁₈ fatty alcohol ethoxylates - with an ethoxylation range of 0-9 moles (fatty alcohol polyglycol ethers), C₁₆-C₁₈ fatty alcohol ethoxylate and propoxylate, C₁₆-C₁₈ fatty acid ethoxylates and propoxylates, C₆/C₈/C₁₆₋₁₈ alkyl polyoxyethylene ether carboxylic acids with a 2 to 9 mole ethoxylation range, alkyl ether ethoxylate mono phosphate esters - alkyl chain C₁₆-C₁₈, with a 2 to 5 mole ethoxylation range, ethoxylated oleine with a 6/9 mole ethoxylation range, ethoxylated castor oils, and polyethylene glycol esters of C₁₆-C₁₈ fatty acids).

20. The emulsion of any of embodiments 1-19, wherein the one or more surfactants include is a mixture of an ionic surfactant and a non-ionic surfactant.

21. The emulsion of any of embodiments 1-20, wherein the one or more surfactants has an average hydrophilic-lipophilic balance (HLB) value of about 8 to about 16, e.g., from about 8 to about 14, or from about 9 to about 12, or from about 10 to about 16, or from about 12 to about 16.

22. The emulsion of any of embodiments 1-21, wherein the one or more surfactants is present in an amount of about 0.01 wt% to about 10 wt% based on the total weight of the emulsion.

23. The emulsion of any of embodiments 1-21, wherein the one or more surfactants is present in an amount of about 0.01 wt% to about 8 wt%, or about 0.01 wt% to about 5 wt%, or about 0.01 wt% to about 2 wt%, or about 0.01 wt% to about 1 wt%, or about 0.1 wt% to about 10 wt%, or about 0.1 wt% to about 8 wt%, or about 0.1 wt% to about 5 wt%, or about 0.1 wt% to about 2 wt%, or about 0.1 wt% to about 1 wt%, or about 0.2 wt% to about 10 wt%, or about 0.2 wt% to about 8 wt%, or about 0.2 wt% to about 5 wt%, or about 0.2 wt% to about 2 wt%, or about 0.2 wt% to about 1 wt%, or about 0.5 wt% to about 10 wt%, or about 0.5 wt% to about 8 wt%, or about 0.5 wt% to about 5 wt%, or about 0.5 wt% to about 2 wt%, or about 1 wt% to about 10 wt%, or about 1 wt% to about 8 wt%, or about 1 wt% to about 5 wt%, or about 2 wt% to about 10 wt%, or about 2 wt% to about 8 wt%, or about 2 wt% to about 5 wt%, or about 0.25 wt% to about 5 wt%, or about 0.25 wt% to about 1 wt%, based on the total weight of the emulsion.

24. The emulsion of any of embodiments 1-23, wherein the one or more sulfurized additives is selected from sulfurized fatty acid esters.

25. The emulsion of embodiment 24, wherein the sulfurized fatty acid ester has a total sulfur content of between about 1 wt% and about 40 wt% (, e.g., about 1 wt% to about 30 wt%, or about 1 wt% to about 25 wt%, or about 1 wt% to about 20 wt%, or about 1 wt% to about 15 wt%, or about 1 wt% to about 10 wt%, or about 10 wt% to about 40 wt%, or about 10 wt% to about 30 wt%, or about 10 wt% to about 25 wt%, or about 10 wt% to about 20 wt%, or about 10 wt% to about 15 wt%).

26. The emulsion of any of embodiments 1-25, wherein the one or more sulfurized additives is present in an amount of 10 wt% to 80 wt%, e.g., about 10 wt% to 70 wt%, or about 10 wt% to 60 wt%, or about 10 wt% to 50 wt%, or about 10 wt% to about 40 wt%, or about 10 wt% to about 30 wt%, or about 20 wt% to about 80 wt%, or about 20 wt% to about 70 wt%, or about 20 wt% to about 60 wt%, or about 20 wt% to about 50 wt%, or about 20 wt% to about 40 wt%, or about 30 wt% to about 80 wt%, or about 30 wt% to about 70 wt%, or about 30 wt% to about 60 wt%, or about 30 wt% to about 50 wt%, or about 50 wt% to about 80 wt%, or about 60 wt% to about 80 wt%, or about 50 wt% to about 70 wt%, or about 60 wt% to about 70 wt%, or about 65 wt% to about 75 wt%, based on the total weight of the emulsion.

27. The emulsion of any of embodiments 1-25, wherein the one or more sulfurized additives is present in an amount in the range of 0.1 wt% to 10 wt%, e.g., 0.2 wt% to 10 wt%, or 0.5 wt% to 10 wt%, or 1 wt% to 10 wt%, or 2 wt% to

10 wt%, or 0.1 wt% to 5 wt%, or 0.2 wt% to 5 wt%, or 0.5 wt% to 5 wt%, or 1 wt% to 5 wt%, or 2 wt% to 5 wt%, or 0.1 wt% to 2 wt%, or 0.2 wt% to 2 wt%, or 0.5 wt% to 2 wt%, based on the total weight of the emulsion.

28. The emulsion of any of embodiments 1-27, wherein one or more of (e.g., each of) the one or more sulfurized additives has a kinematic viscosity at 40 °C of at least 1000 cSt.

29. The emulsion of any of embodiments 1-27, one or more of (e.g., each of) the one or more sulfurized additives has a kinematic viscosity at 40 °C of at least 2000 cSt, or of at least 4000 cSt, e.g., about 4000 to about 50000 cSt, or about 4000 to about 25000 cSt, or about 4000 to about 20000 cSt, or about 4000 to about 10000 cSt, or about 5000 to about 50000 cSt, or about 5000 to about 25000 cSt, or about 5000 to about 20000 cSt, or about 5000 to about 10000 cSt.

30. The emulsion of any of embodiments 1-29, wherein the weight ratio of the amount of oleaginous material and the one or more sulfurized additives selected from sulfurized fatty acid esters, sulfurized fatty oil, sulfurized and polymerized fatty esters, and sulfurized polyolefins to the amount of surfactant is in the range of 1 to 100.

31. The emulsion of any of embodiments 1-30, further comprising one or more of corrosion inhibitors, rust inhibitors, lubricity enhancers, friction modifiers, chelating agents, coupling agents, yellow metals, esters, biocides, and combinations thereof (e.g., present in a total amount up to 15 wt%, for example, up to 10 wt%, up to 8 wt% or up to 5 wt%).

32. The emulsion of any of embodiments 1-31, wherein one or more of corrosion inhibitors, yellow metals, esters, biocides, and combinations thereof are present in an amount in the range of about 0.01 wt% to about 15 wt%, or about 0.01 wt% to about 10 wt%, or about 0.01 wt% to about 8 wt%, or about 0.01 wt% to about 5 wt%, or about 0.01 wt% to about 1 wt%, or about 1 wt% to about 15 wt%, or about 1 wt% to about 10 wt%, or about 1 wt% to about 8 wt%, or about 1 wt% to about 5 wt%, or about 2 wt% to about 15 wt%, or about 2 wt% to about 10 wt%, or about 2 wt% to about 8 wt%, or about 2 wt% to about 5 wt%, or about 5 wt% to about 15 wt%, or about 5 wt% to about 10 wt%, based on the total weight of the emulsion, based on the total weight of the emulsion).

33. The emulsion of any of embodiments 1-32, comprising about 10 to about 50 wt% of the one or more oleaginous materials; about 3 to about 8 wt% of the one or more surfactants; about 1 wt% to about 30 wt% of the one or more sulfurized additives selected from sulfurized fatty acid esters, sulfurized fatty oil, sulfurized and polymerized fatty esters, and sulfurized polyolefins; and at least 25 wt% water.

34. The emulsion of embodiment 33, further comprising about 5 to about 10 wt% of a corrosion inhibitor.

35. The emulsion of any of embodiments 1-32, comprising about 5 to about 20 wt% of the one or more oleaginous materials; about 0.01 to about 5 wt% of the one or more surfactants; about 0.25 wt% to about 20 wt% of the one or more sulfurized additives selected from sulfurized fatty acid esters, sulfurized fatty oil, sulfurized and polymerized fatty esters, and sulfurized polyolefins; and at least 50 wt% water.

36. The emulsion of any of embodiments 1-32, comprising about 1 to about 5 wt% of the one or more oleaginous materials; about 0.01 to about 1 wt% of the one or more surfactants; about 0.1 wt% to about 5 wt% of the one or more sulfurized additives selected from sulfurized fatty acid esters, sulfurized fatty oil, sulfurized and polymerized fatty esters, and sulfurized polyolefins; and at least 90 wt% water.

37. The emulsion of any of embodiments 1-32, comprising about 3 to about 15 wt% of the one or more surfactants; about 50 wt% to about 80 wt% of the one or more sulfurized additives selected from sulfurized fatty acid esters, sulfurized fatty oil, sulfurized and polymerized fatty esters, and sulfurized polyolefins; and at least 8 wt% water.

38. The emulsion of embodiment 37, substantially free of a non-sulfurized oleaginous material.

39. The emulsion of any of embodiments 1-38, wherein in the micellar emulsion, the one or more surfactants forms a plurality of micelles, each comprising surfactant molecules disposed around a hydrophobic core comprising the one or more sulfurized additives and optionally one or more oleaginous materials.

40. The emulsion of any of embodiments 39, wherein the micelles are generally spherical in structure.

41. The emulsion of any of embodiments 1-40, wherein the micelles have a distribution of average diameters having

a mean μ and a standard deviation σ , wherein the standard deviation σ is less than or equal to 0.5μ , for example, no more than 0.2μ , or no more than 0.1μ .

42. The emulsion of any of embodiments 1-41, wherein the micelles have a mean average diameter of no more than about $0.5\ \mu\text{m}$; e.g., no more than about $0.4\ \mu\text{m}$.

43. The emulsion of any of embodiments 1-41, wherein the micelles have a mean average diameter in the range of 0.1 to $1\ \mu\text{m}$.

44. A metalworking fluid prepared by combining the emulsion of any of embodiments 1-43 with an aqueous fluid.

45. The metalworking fluid of embodiment 44, wherein the emulsion is used in an amount of about $0.25\ \text{wt}\%$ to about $20\ \text{wt}\%$ based on the total weight of the metalworking fluid; e.g., about $0.25\ \text{wt}\%$ to about $5\ \text{wt}\%$, or about $1\ \text{wt}\%$ to about $10\ \text{wt}\%$, or about $5\ \text{wt}\%$ to about $10\ \text{wt}\%$, or about $5\ \text{wt}\%$ to about $6\ \text{wt}\%$, or about $6\ \text{wt}\%$ to about 10 .

46. A metalworking fluid in the form of an emulsion of any of embodiments 1-43.

47. A method of working a metal, the method comprising contacting a surface of a metal article with the emulsion of any one of embodiments 1-43 or the metalworking fluid of embodiment 44-46 and forming the surface of the metal article to a desired shape.

48. The method of embodiment 47, wherein forming the surface is a destructive metalworking process.

49. The method of embodiment 47, wherein forming the surface is a deforming metalworking process.

50. A method of preparing an emulsion according to any of embodiments 1-43, the method comprising:

obtaining a first fluid comprising one or more surfactants dissolved in water;
obtaining a second fluid comprising one or more sulfurized additives and, optionally, one or more oleaginous materials;
contacting the first fluid with the second fluids under a shear force to produce an intermediate fluid; and
recovering the emulsion from the intermediate fluid.

51. The method of embodiment 50, wherein contacting the first fluid and the second fluid comprises stirring at a rotational speed in the range of about 1200 to about $1600\ \text{rpm}$.

52. The method of embodiment 50 or 51, further comprising contacting the intermediate fluid with a third fluid under a lamellar flow prior to recovering the emulsion.

Claims

1. An emulsion comprising:

water;
one or more surfactants;
one or more sulfurized additives selected from sulfurized fatty acid esters, sulfurized fatty oil, sulfurized and polymerized fatty esters, and sulfurized polyolefins; and
optionally, one or more oleaginous materials;

wherein the emulsion is in the form of a micellar emulsion.

2. The emulsion of claim 1, wherein water is present in the emulsion in an amount at least $8\ \text{wt}\%$ of the emulsion.

3. The emulsion of claim 1 or claim 2, wherein substantially no oleaginous material is present in the emulsion.

4. The emulsion of claim 1 or claim 2, wherein the one or more oleaginous materials is present in the emulsion and

comprises a lubricating composition.

5. The emulsion of any of claim 4, wherein the one or more oleaginous materials is present in an amount of 15 wt% to 70 wt%, for example, 30 wt% to 70 wt%, or in an amount of 0.5 wt% to 15 wt%, e.g., 0.5 wt% to 3 wt%, based on the total weight of the emulsion.
6. The emulsion of any of claims 1-5, wherein the one or more surfactants is present in an amount of about 0.01 wt% to about 10 wt% based on the total weight of the emulsion.
7. The emulsion of any of claims 1-6, wherein the one or more sulfurized additives is present in an amount in the range of 10 wt% to 80 wt%, e.g., about 50 wt% to about 80 wt%, or in the range of 0.1 wt% to 10 wt%, e.g., 0.1 wt% to 2 wt%, based on the total weight of the emulsion.
8. The emulsion of any of claims 1-7, wherein one or more of (e.g., each of) the one or more sulfurized additives has a kinematic viscosity at 40 °C of at least 1000 cSt.
9. The emulsion of any of claims 1-8, wherein the weight ratio of the amount of oleaginous material and the one or more sulfurized additives selected from sulfurized fatty acid esters, sulfurized fatty oil, sulfurized and polymerized fatty esters, and sulfurized polyolefins to the amount of surfactant is in the range of 1 to 100.
10. The emulsion of any of claims 1-9, further comprising one or more of corrosion inhibitors, rust inhibitors, lubricity enhancers, friction modifiers, chelating agents, coupling agents, yellow metals, esters, biocides, and combinations thereof (e.g., present in a total amount up to 15 wt%, for example, up to 10 wt%, up to 8 wt% or up to 5 wt%).
11. The emulsion of any of embodiments 1-10, comprising about 1 to about 5 wt% of the one or more oleaginous materials; about 0.01 to about 1 wt% of the one or more surfactants; about 0.1 wt% to about 5 wt% of the one or more sulfurized additives selected from sulfurized fatty acid esters, sulfurized fatty oil, sulfurized and polymerized fatty esters, and sulfurized polyolefins; and at least 90 wt% water.
12. The emulsion of any of claims 1-10, comprising about 3 to about 15 wt% of the one or more surfactants; about 50 wt% to about 80 wt% of the one or more sulfurized additives selected from sulfurized fatty acid esters, sulfurized fatty oil, sulfurized and polymerized fatty esters, and sulfurized polyolefins; and at least 8 wt% water, optionally, substantially free of a non-sulfurized oleaginous material.
13. A metalworking fluid prepared by combining the emulsion of any of claims 1-12 with an aqueous fluid.
14. A method of working a metal, the method comprising contacting a surface of a metal article with the emulsion of any of embodiments 1-12 or the metalworking fluid of claim 13 and forming the surface of the metal article to a desired shape.
15. A method of preparing an emulsion according to any of claims 1-12, the method comprising:
 - obtaining a first fluid comprising one or more surfactants dissolved in water;
 - obtaining a second fluid comprising one or more sulfurized additives and, optionally, one or more oleaginous materials;
 - contacting the first fluid with the second fluids under a shear force to produce an intermediate fluid; and
 - recovering the emulsion from the intermediate fluid.

FIG. 1

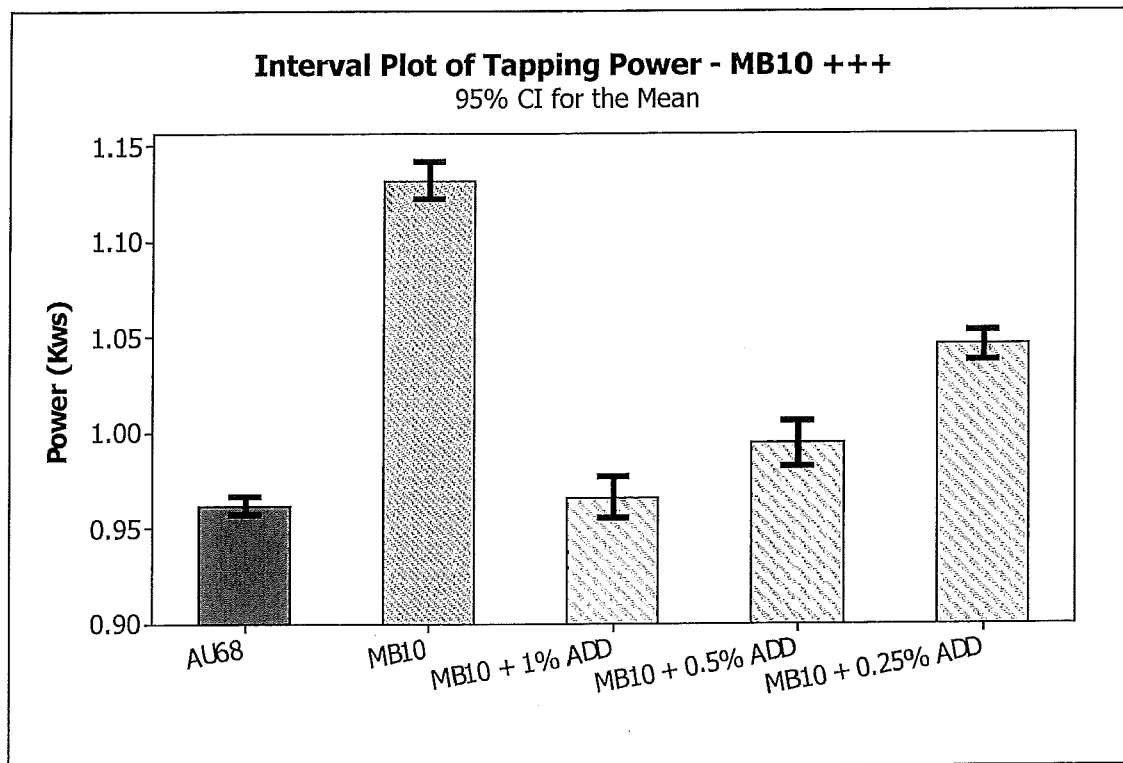


FIG. 2

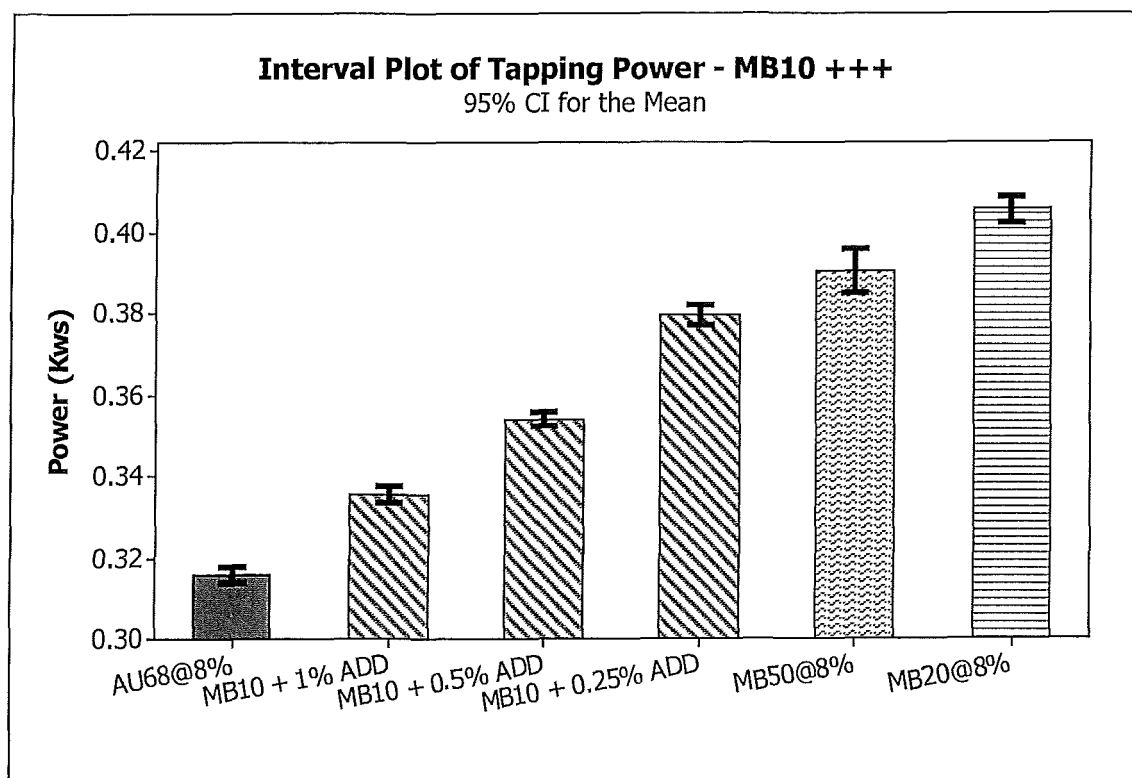
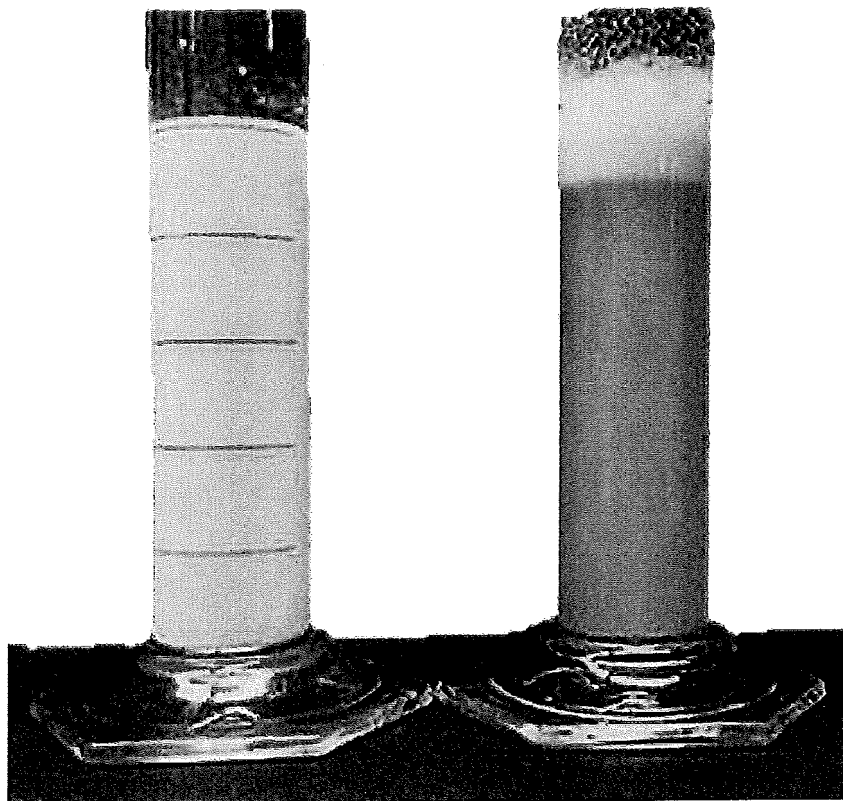


FIG. 3



A

B

FIG. 4

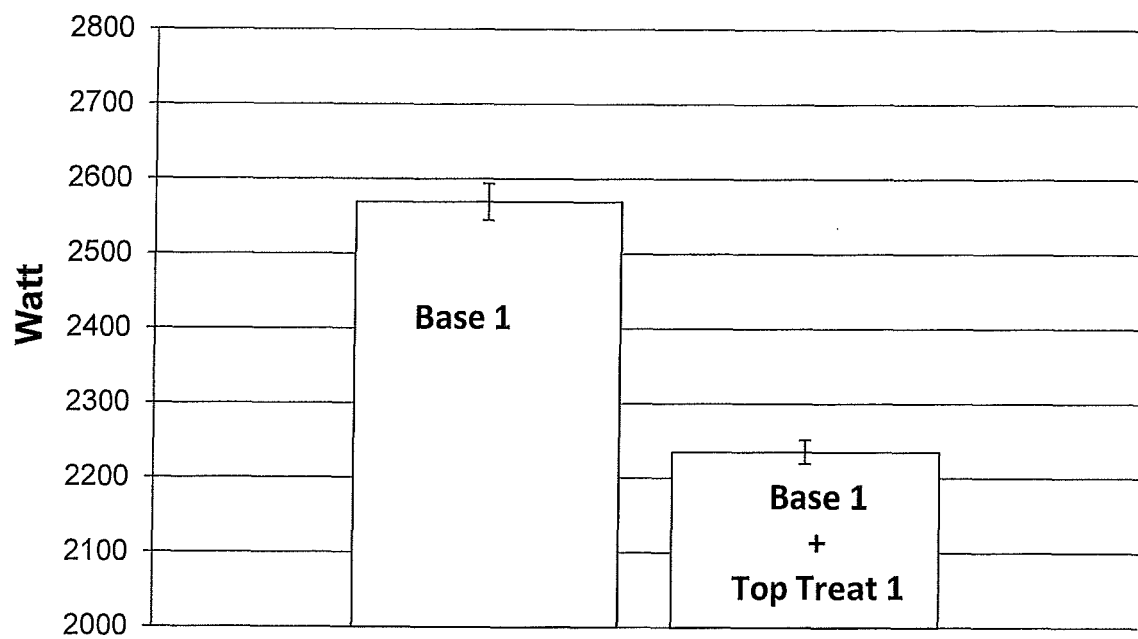
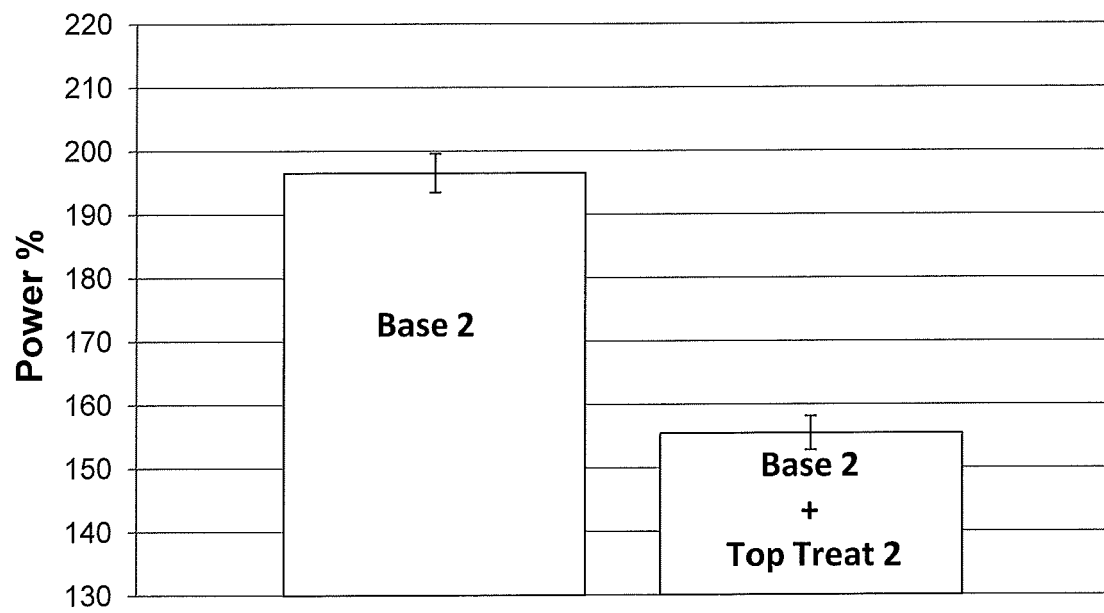


FIG. 5





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