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(54) **Formulation of a metalworking fluid**

(57) This invention relates to a composition that is a novel improvement of non-oil containing metalworking fluids, also known as synthetic metalworking fluids. The invention is a non-oil containing metalworking lubricant composition, having an engineered particle size of greater than 200 nanometers upon dilution. The expansive particle size results in a substantial increase in lubricity, suitable for the heavy-duty operations previously attainable only with oil-containing products. Additionally, this non-oil containing metalworking lubricant incorporates the best of the positive attributes of oil-containing products into its composition, including excellent corrosion inhibition and heavy-duty operation capable lubricity.

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Description

TECHNICAL FIELD

[0001] This invention relates to a composition that is a novel improvement of non-oil containing metalworking fluids, also known as synthetic metalworking fluids. Metalworking fluids are classified into two main segments, oil containing and non-oil containing. The oil-containing segment comprises straight oils/soluble oils/semi-synthetics, all of which utilize mineral oil as the primary lubricant. The non-oil segment is known as synthetics, which use surfactants/polymers/fatty acids as the main lubricant. The invention consists of an adaptation of synthetic metalworking fluid that demonstrates an engineered increase in lubricity while still providing corrosion protection and microbial control.

BACKGROUND

[0002] The water reducible metalworking fluids market is primarily segmented into two product classes, oil-containing and non-oil containing. Two types of products make-up the oil containing line, soluble oils and semi-synthetics, and both contain mineral oil as their primary lubricity ingredient. The non-oil containing products are called synthetics and have EO/PO polymers, surfactant or fatty acids or combinations thereof as their primary lubricity ingredient.

[0003] The soluble oil and semi-synthetic products enjoy an eighty percent share of the market while the synthetics comprise 10% of the market. The remaining 10% is held by the non-water reducible straight oils segment. The two existing classifications have advantages and drawbacks. The oil-containing sectors have the advantages of excellent lubricity, a wide range of applications and that the mineral oil provides barrier protection of sumps from corrosion. The drawbacks of oil-containing metalworking fluids are that water hardness often impacts the fluid stability, that foaming is a frequent problem due to their inclusion of higher detergency emulsifiers, in their increased dirt load entrainment, in their increased disposal and tank clean-out impacts and in their increased microbial problems.

[0004] The current synthetic segment of the metalworking fluids market has the advantage of not having the cleaning issues of oils, having good hard water stability and microbial control, and a long sump life. The drawbacks of the existing synthetics are reduced physical lubricity when compared to oil-containing products on an equal cost basis, increased sump and machine maintenance corrosion issues, and the potential for skin irritation to those working with the fluid.

[0005] The use of synthetics is encouraged for a variety of factors from environmental issues to the microbial advantages. However, most customers continue to use oil containing products because of their good lubricity at a low comparative cost, and because of the increased maintenance corrosion issues associated with synthetics. Synthetic sumps, lacking the protective barrier film provided by oil, can corrode and "freeze" machining system bolts, making maintenance difficult. Additionally, high lubricity performance synthetic products are expensive when compared with similar lubricity performance oil containing products. Their reduced physical lubricity on a cost basis with semi-synthetics restrains their use in heavy-duty operations.

[0006] The current invention has developed an entirely new class of metalworking fluid products. This new chemistry incorporates a synergistic blend of carboxylic acid salts/boundary lube fatty acids and EO/PO polymers, which at an optimized pH range react to form a moiety with enhanced particle size and exceptional lubricity. In addition, use dilutions are opaque and mimic the appearance of oil-based solutions.

SUMMARY

[0007] The current invention describes the following key aspects:

1. It is an advantage of the invention to achieve the lubricity of oil containing products, using surfactants/polymers.
2. It is an advantage of the invention to achieve a lubricity/cost performance point approaching that of oil containing products.
3. It is an advantage of the invention to reduce worker irritation associated with higher pH.
4. It is an advantage of the invention to achieve rust protection of oil containing products
5. Ability to have an alkanolamine free chemistry.

DETAILED DESCRIPTION

Metalworking

[0008] Metalworking is the shaping of metallic work-pieces to conform to a desired set of geometric specifications. Metalworking comprises two basic categories, cutting and forming. Cutting operations include grinding, turning, milling, tapping, broaching and hobbing. Forming operations include hot and cold rolling, drawing, forging, stamping and blanking.

Metalworking fluids are essential in both cutting and forming operations. They must provide for lubrication between the work-piece and tool and also provide cooling by removing the heat generated during the metalworking operations.

Lubricants - Polymeric Lubricity Agents

[0009] Lubrication is defined as the reduction of friction between two moving surfaces. The two main types of lubrication in metalworking operations are hydrodynamic and boundary/extreme pressure (EP). Hydrodynamic lubrication involves separating the moving surfaces by a film of fluid lubricant. Boundary/EP lubrication minimizes the wear experienced when surfaces rub together. polymeric lubricity agents can provide both types of lubrication.

[0010] These can be comprised of one or more of the following: block copolymers consisting of a central polyoxypropylene block with a polyoxyethylene chain at either end, block copolymers consisting of a central polyoxyethylene block with a polyoxypropylene chain at either end, tetrablock copolymers derived from the sequential addition of ethylene oxide and propylene oxide to ethylenediamine, ethylene oxide/ propylene oxide copolymers having at least one terminal hydroxyl group, water-soluble lubricant base stocks of random copolymers of ethylene oxide and propylene oxide, a water-soluble polyoxyethylene or polyoxypropylene alcohol or a water-soluble carboxylic acid ester of such alcohol, alcohol-started base stocks of all polyoxypropylene groups with one terminal hydroxyl group, monobasic and dibasic acid esters, polyol esters, polyalkylene glycol esters, polyalkylene glycols grafted with organic acids, phosphate esters, polyisobutylenes, polyacrylonitriles, polyacrylamides, polyvinylpyrrolidones, polyvinyl alcohols and copolymers of acrylic acid or methacrylic acid and an acrylic ester.

Carboxylic Acid Salts

[0011] Partially neutralized carboxylic acids salts provide a lipophylic moiety for the polymeric lubricity agents to network with and provide for the engineering of a larger particle size. The pH of the partial neutralization is dependent upon the alkaline agent used. Many of these carboxylic acid salts additionally provide their own boundary lubrication as well. The carboxylic acids can be linear or branched, saturated or unsaturated, fatty or oil, animal or vegetable, cis or trans configured, dicarboxylic, tricarboxylic, esterified, amines, amides, or ethoxylated. The following are some of the examples of the carboxylic acids: caproic/hexanoic acid, enanthic/heptanoic acid, caprylic/octanoic acid, pelargonic/ nonanoic acid, isononanoic acid, capric/decanoic acid, neodecanoic acid, lauric/dodecanoic acid, stearic/octadecanoic acid, arachidic/eicosanoic acid, palmitic/hexadecanoic acid, erucic acid, oleic acid, arachidonic acid, linoleic acid, linolenic acid, myristic/tetradecanoic acid, behenic/docosanoic acid, alpha-linolenic acid, docosahexaenoic acid, ricinoleic acid, butyric acid, lard oil, tallow oil, butter, coconut oil, palm oil, cottonseed oil, wheat germ oil, soya oil, olive oil, corn oil, sunflower oil and rapeseed/canola oil.

Emulsifying/Dispersing Agents

[0012] Dilutions of the metalworking fluid composition result in an opaque emulsion. At concentrations above 10%, the emulsion requires stabilization. Emulsifying/dispersing agents provide stabilization of the engineered large particle emulsion. The emulsifiying/dispersing agents may be one or more of the following: alkanolamides, alkylaryl sulfonates, alkylaryl sulfonic acids, amine oxides, amide and amine soaps, block copolymers, carboxylated alcohols, carboxylic acids/fatty acids, ethoxylated alcohols, ethoxylated alkylphenols, ethoxylated amines/amides, ethoxylated fatty acids, ethoxylated fatty esters and oils, ethoxylated phenols, fatty amines and esters, glycerol esters, glycol esters, imidazolines and imidazoline derivatives, lignin and lignin derivatives, maleic or succinic anhydrides, methyl esters, monoglycerides and derivatives, naphthenic acids, olefin sulfonates, phosphate esters, polyalkylene glycols, polyethylene glycols, polyols, polymeric (polysaccharides, acrylic acid, acrylamide), propoxylated & ethoxylated fatty acids, alcohols or alkyl phenols, quaternary surfactants, sarcosine derivatives, soaps, sorbitan derivatives, sucrose and glucose esters and derivatives, sulfates and sulfonates of oils and fatty acids, sulfates and sulfonates ethoxylated alkylphenols, sulfates of alcohols, sulfates of ethoxylated alcohols, sulfates of fatty esters, sulfonates of dodecyl and tridecylbenzenes, sulfonates of naphthalene and alkyl naphthalene, sulfonates of petroleum, sulfosuccinamates, sulfosuccinates and derivatives, tridecyl and dodecyl benzene sulfonic acids.

Corrosion Inhibiting Component

[0013] Oil-containing products rely heavily on the oil itself to form a barrier coating of corrosion protection. Non-oil containing products need to attain this corrosion protection by chemical means. A corrosion inhibitor is a chemical compound that, when added in small concentration, stops or slows down the corrosion of metals and alloys.

[0014] Some of the mechanisms for the corrosion inhibitors effect are the formation of a passivation layer (a thin film on the surface of the material that stops access of the corrosive substance to the metal), inhibiting either the oxidation

or reduction part of the redox corrosion system (anodic and cathodic inhibitors), or scavenging the dissolved oxygen. There are many different compostions that fall into this group. Some examples are alkali and alkanolamine salts of carboxylic acids, undecandioic/dodecandioic acid and its salts, C4-22 carboxylic acids and their salts, boric acids, compounds and their salts, tolytriazole and its salts, benzotriazoles and its salts, imidazolines and its salts, alkanolamines and amides, sulfonates, alkali and alkanolamine salts of naphthenic acids, phosphate ester amine salts, alkali nitrites, alkali carbonates, carboxylic acid derivatives, alkylsulfonamide carboxylic acids, arylsulfonamide carboxylic acids, fatty sarkosides, phenoxy derivatives and sodium molybdate.

Alkalinity Agents

[0015] Alkalinity Agents provide for the desired pH of the product and, in some cases for reserve alkalinity and pH buffering. Examples of the alkalinity agents include but are not limited to alkanolamines - primary, secondary and tertiary, aminomethylpropanol (AMP-95), diglycolamine (DGA), monoethanolamine (MEA), monoisopropanolamine (MIPA), butylethanolamine (NBEA), dicylclohexylamine (DCHA), diethanolamine (DEA), butyldiethanolamine (NBDEA), triethanolamine (TEA), metal alkali hydroxides, potassium hydroxide, sodium hydroxide, magnesium hydroxide, lithium hydroxide, metal carbonates and bicarbonates, sodium carbonate, sodium bicarbonate, potassium carbonate and potassium bicarbonate.

[0016] The claimed invention has many attributes that make it varied from existing products. The fact that it is a synthetic product which incorporates the attributes of an oil-based product is novel. The positive attributes of currently available non-oil products are maintained in this composition as well and include environmental compliance, good cooling, good chip removal/settling characteristics, long sump life and good biological resistance.

[0017] The current invention is a non-oil containing metalworking fluid composition consisting of a volume average particle size of 125nm or greater when diluted between 0.1 and 50 percent, comprised of one or more polymeric lubricity agent(s), one or more carboxylic acid salt(s), one or more emulsifying/dispersing agent(s), a transport component which can be water and one or more corrosion inhibiting component(s). The invention has a pH of 3 or greater and may also include an alkalinity agent which can be one or more of the following a primary, secondary, tertiary and quaternary alkanolamine and can be a metal alkali hydroxide. The invention can also contain an anti-foaming agent and/or a biocide and a fungicide.

[0018] In the claimed invention, the working metal fluid composition, when diluted between 0.1 and 50 percent comprises a lubricity, measured by tapping torque instruments, of less than 8000 Newton-cm^{-1}.

[0019] It should be understood that nothing in the preceding description is meant to limit the scope of the invention as described in the claims. The description is only a sampling of the components of the invention and a sampling of the embodiment and additional embodiments are in no way limited or excluded because there is no mention of such embodiments. Any changes and modifications can be made without departing from the spirit and scope of the invention and without diminishing its intended advantages. It is therefore intended that such changes and modifications be covered by the appended claims

[0020] The foregoing may be better understood by reference to the following examples, which are intended to illustrate methods for carrying out the invention and are not intended to limit the scope of the invention.

Example 1

Material	A	B	C	D	E
Pluronic "R" block copolymer	0%	10%	20%	20%	20%
Carboxylic acid - alkali salts	10%	10%	10%	5%	0%
Emulsifiers	5%	5%	5%	5%	5%
Corrosion inhibitors	4%	4%	4%	4%	4%
RO water	Remainder	Remainder	Remainder	Remainder	Remainder

[0021] The materials of Example 1 were employed in a tapping torque operation involving the tapping of 6061 aluminum. The concentrates were first diluted to a 7.5% by volume solution before testing. The tapping torque test is a quantitative measure of the lubricity performance of metalworking fluids. It has an ASTM standard method designation of D5619. Tapping torque reflects the industrial machining process in a better way than other tests, which commonly consist of rubbing two metals together. It is an excellent method of discriminating MWF product machining performance in the laboratory. Tapping Torque results have been proven to correlate well with field machining performance.

[0022] The tapping torque instrument is designed to measure the lubricity of MWFs while actual cutting is performed.

During the tapping operation, the Tapping Torque instrument measures the instantaneous torque 250 times as the tap advances throughout the depth of the cut. Specialized software then facilitates data analysis. Tapping torque is expressed in units of N-m (Newton-meters) or N-cm (Newton-centimeters). Products with high lubricity will generate lower torque values. Conversely, low lubricity products will generate high torque values. In this way the instrument quantifies the differences in lubrication performance between products.

[0023] One drawback of the tapping torque instrument is in that the absolute torque values measured are dependent upon and will vary with the diameter of the tap used. Therefore, in order to cancel out these geometric effects it is efficacious to express the lubricity as the torque per area to describe the energy it takes for a tap to make one revolution. The equation for this is $E/A = (2\ \tau) / r^2$, where τ = torque value, r = the radius of the tap, E/A = energy per area and the units are $N\text{-}m^{-1}$ (Newtons per meter) or $N\text{-}cm^{-1}$ (Newtons per centimeter).

[0024] The data is presented in table form and the lubricity is depicted as E/A. The lower the E/A value, the better the lubricity and machining performance. All samples were diluted with water to 7.5% by volume before testing.

Material	A	B	C	D	E
Lubricity-E/A($N\text{-}cm^{-1}$)	6259	4285	3713	4233	5921

Example 2

[0025]

Material	A	B	C	D	E
Pluronic "R" block copolymer	0%	10%	20%	20%	20%
Carboxylic acid - alkali salts	10%	10%	10%	5%	0%
Emulsifiers	5%	5%	5%	5%	5%
Corrosion inhibitors	4%	4%	4%	4%	4%
RO water	Remainder	Remainder	Remainder	Remainder	Remainder

[0026] The materials of example 2 were employed in a particle size operation involving the measurement of the volume average particle size in nanometer units. The concentrates were first diluted with water to a 7.5% by volume solution before testing. The particle-sizing instrument uses high efficiency dynamic light scattering to quantify particle sizes of 20 to 100,000 nanometers.

[0027] All samples were diluted to 7.5% by volume before testing.

Material	A	B	C	D	E
Volume Average Particle Size (nanometers)	120	140	350	220	20

Example 3

[0028]

Material	Concentration (by volume)	Volume Average Particle Size (nanometers)	Appearance	Emulsion Stability
C from Example 1	7.5%	350	Milky white -opaque	Excellent
C from Example 1	15.0%	2000	Milky white -opaque	Excellent

Examples Summary

[0029] From examples 1-3 it is seen that optimal lubricity and particle size is obtained with sample C which combines 10% carboxylic acid - alkali salts and 20% Pluronic "R" block copolymer. This ratio gives the maximum volume average

particle size and maximum lubricity.

[0030] Typical synthetic MWFs, when diluted, form clear solutions with particle size of less than 100 nanometers. Dilutions of sample C are milky-white opaque and as seen in examples 2 and 3, have particle sizes 3.5 to 20 times larger than the maximum size seen with typical synthetic MWFs.

[0031] It is also apparent from the examples that to a large degree, the lubricity is a function of its volume average particle size. Increasing volume average particle size results in increased lubricity.

[0032] From example 3 it is seen that increased concentration of sample C results in significantly larger volume average particle size. This explains the necessity of emulsifiers to stabilize higher concentrations of sample C. Without emulsifiers, the particle size of higher concentrations would continue to agglomerate to an unstable state.

[0033] It should be understood that various changes and modifications to the presently preferred embodiments described herein will be apparent to those skilled in the art. Such changes and modifications can be made without departing from the spirit and scope of the invention and without diminishing its intended advantages. It is therefore intended that such changes and modifications be covered by the appended claims.

Claims

1. A metalworking fluid composition with a volume average particle size of 125 nm or greater when diluted between 0.1 and 50 percent, the composition comprised of:

(a) one or more polymeric lubricity agents;
(b) one or more carboxylic acid salts;
(c) one or more emulsifying/dispersing agents;
(d) a transport component, optionally being water;
(e) optionally one or more of the following: a corrosion-inhibiting component, an alkalinity agent, an anti foaming agent, a biocide, and/or a fungicide; and
(f) optionally one or more oils at less than 10 percent.

2. The composition of claim 1, wherein the corrosion inhibiting component is selected from the group consisting of: alkali and alkanolamine salts of carboxylic acids; undecandioic/dodecandioic acid and its salts; C4-22 carboxylic acids and their salts; boric acid compounds and their salts; tolytriazole and its salts; benzotriazoles and its salts; imidazolines and its salts; alkanolamines and amides; sulfonates; alkali and alkanolamine salts of naphthenic acids; phosphate ester amine salts; alkali nitrites, alkali carbonates; carboxylic acid derivatives; alkylsulfonamide carboxylic acids; arylsulfonamide carboxylic acids; fatty sarkosides; phenoxy derivatives and sodium molybdate; and combinations thereof.

3. The composition of claim 1, wherein the pH is 3 or greater.

4. The composition of claim 1, wherein the alkalinity agent is selected from the group consisting of alkali metal hydroxides; alkanolamines - primary, secondary and tertiary; aminomethylpropanol (AMP-95); diglycolamine (DGA); monoethanolamine (MEA); monoisopropanolamine (MIPA); butylethanolamine (NBEA); dicylclohexylamine (DCHA); diethanolamine (DEA); butyldiethanolamine (NBDEA); triethanolamine (TEA); metal alkali hydroxides; potassium hydroxide; sodium hydroxide, magnesium hydroxide, lithium hydroxide, metal carbonates and bicarbonates; sodium carbonate; sodium bicarbonate; potassium carbonate and potassium bicarbonate; and combinations thereof.

5. The composition of claim 1, wherein the polymeric lubricity agent is selected from the group consisting of: block copolymers; polyethylene glycol block copolymers; polypropylene glycol block copolymers; polyethylene glycol/ polypropylene glycol block copolymer; block copolymers consisting of a central polyoxypropylene block with a polyoxyethylene chain at either end; block copolymers consisting of a central polyoxyethylene block with a polyoxypropylene chain at either end; tetrablock copolymers derived from the sequential addition of ethylene oxide and propylene oxide to ethylenediamine; ethylene oxide/ propylene oxide copolymers having at least one terminal hydroxyl group; water-soluble lubricant base stocks of random copolymers of ethylene oxide and propylene oxide; a water-soluble polyoxyethylene or polyoxypropylene alcohol or a water-soluble carboxylic acid ester of such alcohol; alcohol-started base stocks of all polyoxypropylene groups with one terminal hydroxyl group; monobasic and dibasic acid esters; polyol esters; polyalkylene glycol esters; polyalkylene glycols grafted with organic acids; phosphate esters; polyisobutylenes; polyacrylonitriles; polyacrylamides; polyvinylpyrrolidones; polyvinyl alcohols and copolymers of acrylic acid or methacrylic acid; an acrylic ester; and combinations thereof.

6. The composition of claim 1, wherein the carboxylic acid salt is selected from the group consisting of: an alkali and/or alkanolamine salt of C_4- C_{22} carboxylic/fatty acids and esters; caproic/hexanoic acid; enanthic/heptanoic acid; caprylic/octanoic acid; pelargonic/nonanoic acid; isononanoic acid; capric/decanoic acid; neodecanoic acid; lauric/dodecanoic acid; stearic/octadecanoic acid; arachidic/eicosanoic acid; palmitic/hexadecanoic acid; erucic acid; oleic acid; arachidonic acid; linoleic acid; linolenic acid; myristic/tetradecanoic acid; behenic/docosanoic acid; alpha-linolenic acid; docosahexaenoic acid; ricinoleic acid; butyric acid; lard oil; tallow oil; butter; coconut oil; palm oil; cottonseed oil; wheat germ oil; soya oil; olive oil; corn oil; sunflower oil; rapeseed/canola oil; and combinations thereof.

7. The composition of claim 1, wherein the emulsifying/dispersing agent is selected from the group consisting of: alkanolamides; alkylaryl sulfonates; alkylaryl sulfonic acids; amine oxides; amide and amine soaps; block copolymers; carboxylated alcohols; carboxylic acids/fatty acids; ethoxylated alcohols; ethoxylated alkylphenols; ethoxylated amines/amides; ethoxylated fatty acids; ethoxylated fatty esters and oils; ethoxylated phenols; fatty amines and esters; glycerol esters; glycol esters; imidazolines and imidazoline derivatives; lignin and lignin derivatives; maleic or succinic anhydrides; methyl esters; monoglycerides and derivatives; naphthenic acids; olefin sulfonates; phosphate esters; polyethylene glycols; polyols; polymeric (polysaccharides, acrylic acid, acrylamide); propoxylated and ethoxylated fatty acids; alcohols or alkyl phenols; quaternary surfactants; sarcosine derivatives; soaps; sorbitan derivatives; sucrose and glucose esters and derivatives; sulfates and sulfonates of oils and fatty acids; sulfates and sulfonates ethoxylated alkylphenols; sulfates of alcohols; sulfates of ethoxylated alcohols; sulfates of fatty esters; sulfonates of dodecyl and tridecylbenzenes; sulfonates of naphthalene and alkyl naphthalene; sulfonates of petroleum; sulfosuccinamates; sulfosuccinates and derivatives; tridecyl and dodecyl benzene sulfonic acids; and combinations thereof.

8. The composition of claim 1, wherein the composition, when diluted between 0.1 and 50 percent comprises a lubricity, as measured by tapping torque instruments, of less than 8000 Newton-cm^{-1}.

9. A metalworking fluid composition comprising: 1 to 80 percent one or more block copolymers; 1 to 40 percent one or more carboxylic acid salts; 1 to 20 percent of one or more emulsifying agents; and a transport component.

10. The metalworking fluid composition of claim 9, including 5 to 40 percent or 15 to 25 percent of the block copolymer; 3 to 30 percent or 5 to 15 percent of the carboxylic acid salt; and/or 2 to 12 percent or 3 to 8 percent of the emulsifying agent.

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EUROPEAN SEARCH REPORT

Application Number
EP 08 25 2578

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
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X	US 5 706 684 A (GONG DELI [US] ET AL) 13 January 1998 (1998-01-13) * column 9 - column 11; examples fluid,2 * * column 10, line 48 - column 11, line 27 *	1-10	

TECHNICAL FIELDS SEARCHED (IPC)

C10M

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	27 February 2009	Pöllmann, Klaus

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 08 25 2578

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82