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(54) **Compositions and methods**

(57) The present invention provides an additive package composition for a metalworking fluid comprising the following water-soluble components: (a) at least one neutralised dicarboxylic acid, in which the dicarboxylic acid has a carbon number of 6 to 12 carbons and/or at least one neutralised tricarboxylic acid, in which the tricarboxylic acid has a carbon number of up to 30 carbons; (b) at least one neutralised mono-substituted phosphate ester; (c) at least one neutralised thio acid; and (d) water, and a metalworking fluid composition comprising each of components (a) to (d) and additional component (e), which is at least one ethylene oxide, propylene oxide copolymer. Also provided is a method of cold rolling a metal which employs the metalworking fluid composition described herein and/or a metalworking fluid comprising the additive package composition described herein.

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Description

[0001] This invention relates to a metalworking fluid composition and an additive package composition for such a metalworking fluid, as well as to a method for their use.

[0002] Metalworking fluids are lubricants which may be used in metalworking operations such as for example, turning, cutting, drilling, grinding, rolling, drawing and the like. Water based metalworking fluid compositions may comprise a solution, dispersion or emulsion of components in water. Such components may be combined with the water as one or more additive packages. The combination of additive packages with water may be undertaken as part of the process for manufacturing the metalworking fluid; the resulting metalworking fluid being stored ready for use. Alternatively, the combination of additive packages with water may be undertaken immediately prior to the use of the metalworking fluid.

[0003] It is desirable that metalworking fluid compositions for use in metalworking operations such as rolling, drawing and the like exhibit one or more of the following properties: extreme pressure lubricating ability, anti wear lubricating properties, anticorrosion properties, cooling properties.

[0004] In particular, it is desirable that metalworking fluid compositions for use in metalworking operations such as rolling or drawing do not have a tendency to form deposits on the surface of the metal, or to form sticky residue on the apparatus employed in metalworking (sometimes called 'caking'). Also, it is desirable that metalworking fluid compositions for use in metalworking operations such as rolling do not have a tendency to exhibit wide variations in the coefficient of friction during use.

[0005] US 5569406 relates to stamping lubricant compositions which have decreased volatile organics content values and exhibit improved lubricity. The stamping lubricant of US 5569406 may comprise (a) from about 70 to about 95% by weight of water; (b) optionally up to about 3% by weight of a (POP)n (POE)m C8 -C18 alkylalcohol wherein n and m are independently a number from about 3 to about 8; (c) from about 0.1 to about 4% by weight of an alkali metal salt of a phosphate ester of a (POE)n' C8 -C18 alkylalcohol wherein n' is a number from about 3 to about 8; (d) from about 2 to about 8% by weight of a polyester of a dimer acid; or from about 3 to about 12% by weight of a polyester derivative; and (e) from about 1 to about 6% by weight of a trialkanolamine.

[0006] JP 08302380 relates to a water-soluble lubricating fluid for cold rolling metal, which is prepared by dissolving, in water, a dicarboxylic acid as a water-soluble thickener and a C_4 or higher thio acid salt, an ethylene oxide adduct of a phosphoric ester, or a salt thereof as a water-soluble lubricity improver.

[0007] WO 2004/096959 relates to a lubricant composition for a high load carrying oil comprising a mixture of a neutral alkyl phosphorous compound and a sulphur carrier.

[0008] US 3933658 relates to a metalworking fluid composition and an additive for a metalworking fluid composition which imparts extreme pressure, antiwear and corrosion-inhibiting properties to the metalworking fluid composition. The additive comprises a phosphate ester and a sulphur compound. The composition comprises the additive used in an oil based vehicle.

[0009] US 5650097 relates to a steel anticorrosion and lubricity composition consisting essentially of a surfactant and at least one neutralised alkyl phosphate.

[0010] There remains a need for a metalworking fluid composition which avoids, or at least mitigates one or more of the problems identified above.

[0011] Thus, according to one aspect of the present invention, there is provided an additive package composition for a metalworking fluid comprising the following water-soluble components:

(a) at least one neutralised dicarboxylic acid, in which the dicarboxylic acid has a carbon number of 6 to 12 carbons and/or at least one neutralised tricarboxylic acid, in which the tricarboxylic acid has a carbon number of up to 30 carbons;
(b) at least one neutralised mono-substituted phosphate ester;
(c) at least one neutralised thio acid; and
(d) water.

[0012] According to a second aspect of the present invention there is provided a metalworking fluid composition comprising the following water-soluble components:

(a) at least one neutralised dicarboxylic acid, in which the dicarboxylic acid has a carbon number of 6 to 12 carbons and/or at least one neutralised tricarboxylic acid, in which the tricarboxylic acid has a carbon number of up to 30 carbons;
(b) at least one neutralised mono-substituted phosphate ester;
(c) at least one neutralised thio acid;
(d) water; and
(e) at least one ethylene oxide, propylene oxide co-polymer.

[0013] The present invention solves the technical problems identified above by the use of a combination of at least one neutralised dicarboxylic acid, in which the dicarboxylic acid has a carbon number of 6 to 12 carbons and/or at least one neutralised tricarboxylic acid, in which the tricarboxylic acid has a carbon number of up to 30 carbons; at least one neutralised mono-substituted phosphate ester; and at least one neutralised thio acid in solution with water in a composition for metalworking.

[0014] Throughout this specification the term "water-soluble" means completely soluble in water.

[0015] The compositions of the present invention preferably have a basic pH. More preferably, the compositions have a pH in the range 8.5 to 9.5.

[0016] The at least one neutralised dicarboxylic acid and/or the at least one neutralised tricarboxylic acid of component (a) of the compositions of the present invention may impart anticorrosion properties on the compositions of the present invention.

[0017] A neutralised dicarboxylic acid comprises a dicarboxylic acid which is neutralised with at least a stoichiometric amount of base to form a water-soluble salt. A neutralised tricarboxylic acid comprises a tricarboxylic acid which is neutralised with at least a stoichiometric amount of base to form a water-soluble salt. Preferably, an excess of base is employed to neutralise the acid. Neutralisation may take place in situ in the compositions of the present invention.

[0018] Component (a) may be at least one neutralised dicarboxylic acid, in which the dicarboxylic acid has a carbon number of 6 to 12 carbons. Preferably, the dicarboxylic acid has a carbon number of 10 to 12 carbon atoms. Suitable dicarboxylic acids include dodecandioic acid, undecandioic acid and decandioic acid (also known as sebacic acid).

[0019] Alternatively or additionally, component (a) may be at least one neutralised tricarboxylic acid, in which the tricarboxylic acid has a carbon number of up to 30 carbons. A suitable tricarboxylic acid is 2,4,6-tri(6-aminocaproicacid) 1,3,5-triazine.

[0020] In component (a), the base with which the dicarboxylic acid and/or the tricarboxylic acid is neutralised may be any base capable of neutralising the acid to form a water-soluble salt. The base may be a non-inorganic base, such as an amine. For example, the base may comprise one or more primary and/or tertiary alkanol amines. Suitable alkanol amines include monoethanolamine and triethanolamine.

[0021] In one embodiment of the present invention, component (a) may be a mixture of more than one neutralised dicarboxylic acid. For example, component (a) may be a mixture of dodecandioic, undecandioic and decandioic acids which are neutralised with a mixture of monoethanolamine and triethanolamine.

[0022] The at least one neutralised mono-substituted phosphate ester of component (b) of the compositions of the present invention may impart extreme pressure handling properties on the compositions of the present invention.

[0023] A neutralised mono-substituted phosphate ester comprises an acidic mono-substituted phosphate ester which is neutralised with at least a stoichiometric amount of a base to form a water-soluble salt. Preferably, an excess of base is employed to neutralise the mono-substituted phosphate ester. Neutralisation may take place in situ in the compositions of the present invention.

[0024] In component (b) of the compositions of the present invention the mono-substituted phosphate ester may be substituted with a polypropoxy chain. The polypropoxy chain may have a molecular weight in the range 2000-3000. For example, the polypropoxy chain may have a molecular weight of 2200. Alternatively, the mono-substituted phosphate ester may be substituted with a polyethoxy chain. The polyethoxy chain may comprise from 3 to 5 ethoxy units. Where the mono-substituted phosphate ester is substituted with a polyethoxy chain, the chain may terminate in an alkyl group. The terminating alkyl group may comprise a carbon chain of from 16 to 20 carbons. For example, the polyethoxy chain may comprise 4 ethoxy units and may terminate in a C 18 alkyl group.

[0025] The base with which the mono-substituted phosphate ester is neutralised may be any base capable of neutralising the mono-substituted phosphate ester to form a water-soluble salt. The base may be a non-inorganic base, such as an amine. The amine may be one or more primary and/or tertiary alkanol amines. Suitable alkanol amines include monoethanolamine and triethanolamine.

[0026] In one embodiment of the present invention, component (b) may be a mixture of more than one neutralised mono-substituted phosphate ester. For example, component (b) may be a mixture of neutralised polypropoxy substituted mono-substituted phosphate esters and/or neutralised polyethoxy substituted mono-substituted phosphate esters.

[0027] The at least one neutralised thio acid of component (c) of the compositions of the present invention may also impart extreme pressure handling properties on the compositions of the present invention.

[0028] A neutralised thio acid comprises thio acid which is neutralised with at least a stoichiometric amount of a base to form a water-soluble salt. Neutralisation may take place in situ in the compositions of the present invention.

[0029] The base with which the thio acid is neutralised may be any base capable of neutralising the thio acid to form a water-soluble salt. The base may be an inorganic base, such as an alkali or alkaline earth metal. For example, the base may comprise sodium or potassium.

[0030] Component (c) of the compositions of the present invention may be a potassium salt of a thio acid.

[0031] The water of component (d) of the compositions of the present invention may be potable water.

[0032] The additive package composition may comprise component (a) in an amount of 10 to 30 % by weight, com-

ponent (b) in an amount of greater than 0 to 25 % by weight, component (c) in an amount of greater than 0 to 10 % by weight (based on the total weight of the additive package) with water making up the balance of the composition.

[0033] Where the mono-substituted phosphate ester of component (b) is substituted with a polypropoxy group having a molecular weight in the range 2000-3000, the additive package preferably comprises component (b) in an amount of greater than 0 to 5 % by weight.

[0034] The metalworking fluid composition further comprises component (e) - at least one ethylene oxide, propylene oxide co-polymer. The ethylene oxide, propylene oxide co-polymer preferably has a cloud point of from 30 to 55°C. The at least one ethylene oxide, propylene oxide co-polymer preferably comprises from 15 to 50 % by weight ethylene oxide, and from 50 to 85 % by weight propylene oxide (based on the total weight of the co-polymer). The at least one ethylene oxide, propylene oxide co-polymer may be an ethylene oxide, propylene oxide block co-polymer. For example, the co-polymer may be a block co-polymer consisting of about 40 % by weight ethylene oxide and about 60 % by weight propylene oxide. Alternatively, the co-polymer may be a block co-polymer consisting of about 20 % by weight ethylene oxide and about 80 % by weight propylene oxide.

[0035] In one embodiment, component (e) may be a mixture of ethylene oxide, propylene oxide co-polymers. For example, component (e) may be a mixture of a block co-polymer consisting of about 40 % by weight ethylene oxide and about 60 % by weight propylene oxide and a block co-polymer consisting of about 20 % by weight ethylene oxide and about 80 % by weight propylene oxide.

[0036] The metalworking fluid composition may comprise component (a) in an amount of 0.2 to 6 % by weight, component (b) in an amount of greater than 0 to 2.5 % by weight, component (c) in an amount of greater than 0 to 1 % by weight, component (e) in an amount of greater than 0 to 8 % by weight (based on the total weight of the metal working composition) with water making up the balance of the composition.

[0037] Where the mono-substituted phosphate ester of component (b) is substituted with a polypropoxy group having a molecular weight in the range 2000-3000, the metalworking fluid composition preferably comprises component (b) in an amount of greater than 0 to 0.5 % by weight.

[0038] The compositions of the present invention may further comprise one or more of the following components: a yellow metal inhibitor, a biocide, a dispersant/wetting agent, a chelating agent; an antifoam and a coolant conditioner.

[0039] The yellow metal inhibitor may be present in the metalworking fluid composition in an amount of up to 3 % by weight (based on the total weight of the metalworking fluid composition). A suitable yellow metal inhibitor may comprise one or more triazole compounds. For example, the yellow metal inhibitor may comprise benzotriazole and/or tolutriazole.

[0040] The biocide may be present in the metalworking fluid composition in an amount of up to 0.3 % by weight. A suitable biocide may comprise may comprise n,n-methylene bis morpholene.

[0041] The dispersant/wetting agent may be present in the metalworking fluid composition in an amount of up to 1 % by weight. A suitable dispersant/wetting agent may comprise an ethylene oxide, propylene oxide adduct on ethylene diamine.

[0042] The chelating agent may be present in the metalworking fluid composition in an amount of up to 0.5 % by weight. A suitable chelating agent may comprise polyacrylic acid.

[0043] The antifoam may be present in the metalworking fluid composition in an amount of up to 0.1 % by weight. A suitable antifoam may comprise a polysiloxane.

[0044] The coolant conditioner may be present in the metalworking fluid composition in an amount of up to 0.5 % by weight.

[0045] The metalworking fluid composition of the present invention is particularly suitable for use as a lubricant in the cold rolling of metals. In the cold rolling of metals, metal is deformed by passing it between a pair of work rolls. A lubricant may be applied to the interfaces between the metal to be rolled and each work roll. Further, in a cold rolling mill, work rolls may be supported by support rolls, which prevent deformation of the work rolls. A lubricant may also be applied to the arc of contact between contacting rolls.

[0046] The metals on which such cold rolling may be carried out include ferrous metals, aluminium, copper, zinc, tin and copper-based alloys, such as bronze or brass. Preferably, the metalworking fluid composition of the present invention is employed in the cold rolling of ferrous metals, such as steel.

[0047] Thus, according to a further aspect of the present invention there is provided a method of cold rolling a metal comprising applying the metalworking fluid composition described herein and/or a metalworking fluid comprising the additive package composition described herein to: (i) the interfaces between the metal to be rolled and each work roll; and/or (ii) the arc of contact between contacting rolls.

[0048] The invention will now be described with reference to the following examples and figures. Figure 1 shows, in graph form, the varying cylinder loads and oscillation frequencies employed in friction testing. Figure 2 shows, in graph form, the friction properties of the composition of Example 1. Figure 3 shows, in graph form, the friction properties of the composition of Experiment A.

Example 1

[0049] An additive package composition was formulated by blending components. The components of the additive package composition and their concentrations are given in Table 1.

Table 1

Component	Concentration (% by weight)
Water	58.85
Monoethanolamine	4.75
Triethanolamine	15.00
Dicarboxylic acid mixture comprising: dodecandioic acid (42% by weight), undecandioic acid (31 % by weight), decandioic acid (5 % by weight)	6.00
Benzotriazole	1.00
n,n-methylene bis morpholene (50% aqueous solution)	6.00
Polyacrylic acid	0.40
Potassium salt of a thio acid	5.00
A mono-substituted phosphate ester substituted with a polypropoxy chain having a molecular weight of 2200	5.00

[0050] A metalworking fluid composition was then formulated by blending the additive package at 5 % by weight (based on the total weight of the metalworking fluid composition) with a polymer component at 2 % by weight and water. The polymer component was a mixture of a block co-polymer consisting of about 40 % by weight ethylene oxide and about 60 % by weight propylene oxide at 1 % by weight and a block co-polymer consisting of about 20 % by weight ethylene oxide and about 80 % by weight propylene oxide at 1 % by weight (based on the total weight of the metalworking fluid composition).

[0051] The composition of Example 1 is a composition according to the present invention.

Comparative Experiment A

[0052] A metalworking fluid composition was formed by blending a commercially available additive package, which does not comprise a neutralised mono-substituted phosphate ester and a neutralised thio acid, at 6 % by weight (based on the total weight of the metalworking fluid composition) with water.

Friction testing

[0053] The friction properties of each of the metalworking fluid compositions of Example 1 and Experiment A were tested using a modified SRV, cylinder on plate test, in which a cylinder oscillates axially against a fixed plate, modified such that the plate was fixed to the base of a reservoir, the reservoir holding 1 ml of the composition tested. The test was operated at ambient temperature for 40 minutes with varying cylinder load and oscillation frequency, and a stroke length of 1mm. Measurements were taken at 1000 data points across the 40 minute test period. Figure 1 shows the cylinder loads and oscillation frequencies employed over the course of the modified SRV test. The friction coefficients for the composition of Example 1 at varying cylinder load and oscillation frequency are shown in Figure 2. The friction coefficients for the composition of Experiment A at varying cylinder load and oscillation frequency are shown in Figure 3.

[0054] Comparison of Figures 2 and 3 demonstrates that the composition according to the present invention provides a reduction in friction coefficient and a smoother friction coefficient profile over the course of the SRV test. Thus, the present invention provides improved lubricity properties.

Cleanliness Testing

[0055] The compositions of Example 1 and Experiment A were individually employed as lubricants in a 20 High reversing mill, used to intermediate and finish roll Austenitic grades of stainless steel. The composition was applied to

the interfaces between the metal rolled and the work rolls, and the arc of contact between contacting rolls. Over a 10 week trial period various grades of stainless steel were run through the mill.

[0056] When the composition of Example 1 was employed as the lubricant, no caking on any of the work rolls or support rolls was observed throughout the course of the trial.

[0057] When the composition of Experiment A was employed as the lubricant, caking was observed on work rolls and on support rolls.

[0058] Further, the surface of the rolled metal was visibly cleaner when the composition of Example 1 was employed as the lubricant than when the composition of Experiment A was employed as the lubricant.

[0059] Thus, the present invention provides improved cleanliness properties.

Claims

1. An additive package composition for a metalworking fluid comprising the following water-soluble components:

   (a) at least one neutralised dicarboxylic acid, in which the dicarboxylic acid has a carbon number of 6 to 12 carbons and/or at least one neutralised tricarboxylic acid, in which the tricarboxylic acid has a carbon number of up to 30 carbons;
   (b) at least one neutralised mono-substituted phosphate ester;
   (c) at least one neutralised thio acid; and
   (d) water.

2. A metalworking fluid composition comprising the following water-soluble components:

   (a) at least one neutralised dicarboxylic acid, in which the dicarboxylic acid has a carbon number of 6 to 12 carbons and/or at least one neutralised tricarboxylic acid, in which the tricarboxylic acid has a carbon number of up to 30 carbons;
   (b) at least one neutralised mono-substituted phosphate ester;
   (c) at least one neutralised thio acid;
   (d) water; and
   (e) at least one ethylene oxide, propylene oxide co-polymer.

3. A composition as claimed in claim 1 or claim 2 wherein the composition has a pH in the range 8.5 to 9.5.

4. A composition as claimed in any preceding claim wherein component (a) comprises at least one neutralised dicarboxylic acid, in which the dicarboxylic acid has a carbon number of 10 to 12 carbons.

5. A composition as claimed in any preceding claim wherein the base with which the dicarboxylic acid of component (a) is neutralised comprises one or more primary and/or tertiary alkanol amines.

6. A composition as claimed in any preceding claim wherein the mono-substituted phosphate ester of component (b) is substituted with a polypropoxy chain.

7. A composition as claimed in claim 6 wherein the polypropoxy chain has a molecular weight in the range 2000-3000.

8. A composition as claimed in any preceding claim wherein the mono-substituted phosphate ester of component (b) is substituted with a polyethoxy chain.

9. A composition as claimed in claim 7 wherein the polyethoxy chain comprises from 3 to 5 ethoxy units and terminates in an alkyl group having a carbon chain of from 16 to 20 carbons.

10. A composition as claimed in any preceding claim wherein the base with which the mono-substituted phosphate ester of component (b) is neutralised comprises one or more primary and/or tertiary alkanol amines.

11. A composition as claimed in any preceding claim wherein the base with which the thio acid of component (c) is neutralised is an alkali or alkaline earth metal.

12. A composition as claimed in claim 11 wherein component (c) is a potassium salt of a thio acid.

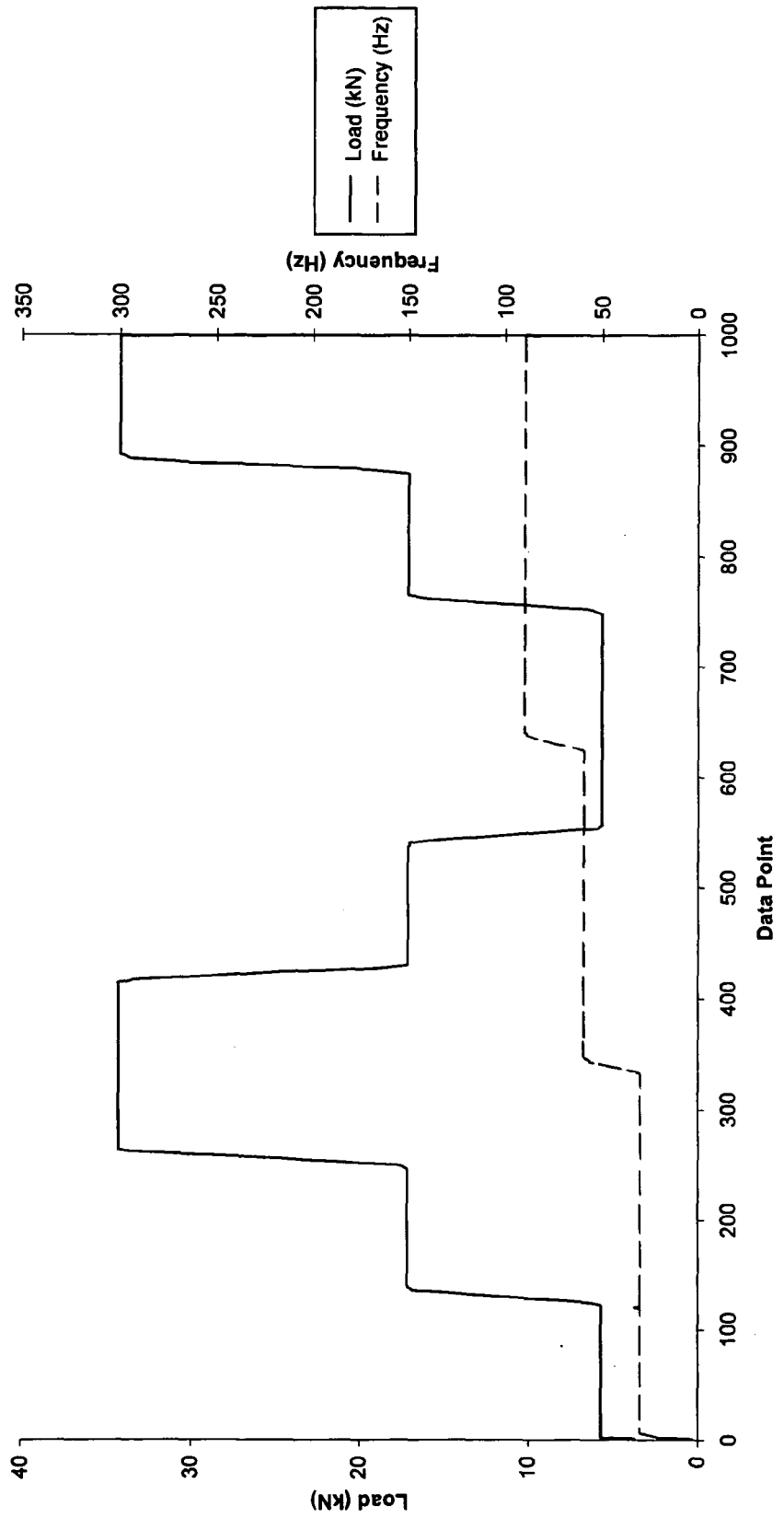
13. A composition as claimed in claim 2 wherein the at least one ethylene oxide, propylene oxide co-polymer of component (e) has a cloud point of from 30 to 55°C.

14. A composition as claimed in claim 2 or claim 13 wherein the at least one ethylene oxide, propylene oxide co-polymer of component (e) is an ethylene oxide, propylene oxide block co-polymer.

15. A composition as claimed in claim 14 wherein component (e) is a mixture of ethylene oxide, propylene oxide block co-polymers.

16. A composition as claimed in any preceding claim which further comprises one or more of: a yellow metal inhibitor, a biocide, a dispersant/wetting agent, a chelating agent, and antifoam and a coolant conditioner.

17. A method of cold rolling a metal comprising applying the metalworking fluid composition according to claim 2 and/or a metalworking fluid comprising the additive package composition according to claim 1 to: (i) the interfaces between the metal to be rolled and each work roll; and/or (ii) the arc of contact between contacting rolls.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Frequency (Hz)
Load (kN)
Frequency (Hz)
Data Point
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30
40
0
50
100
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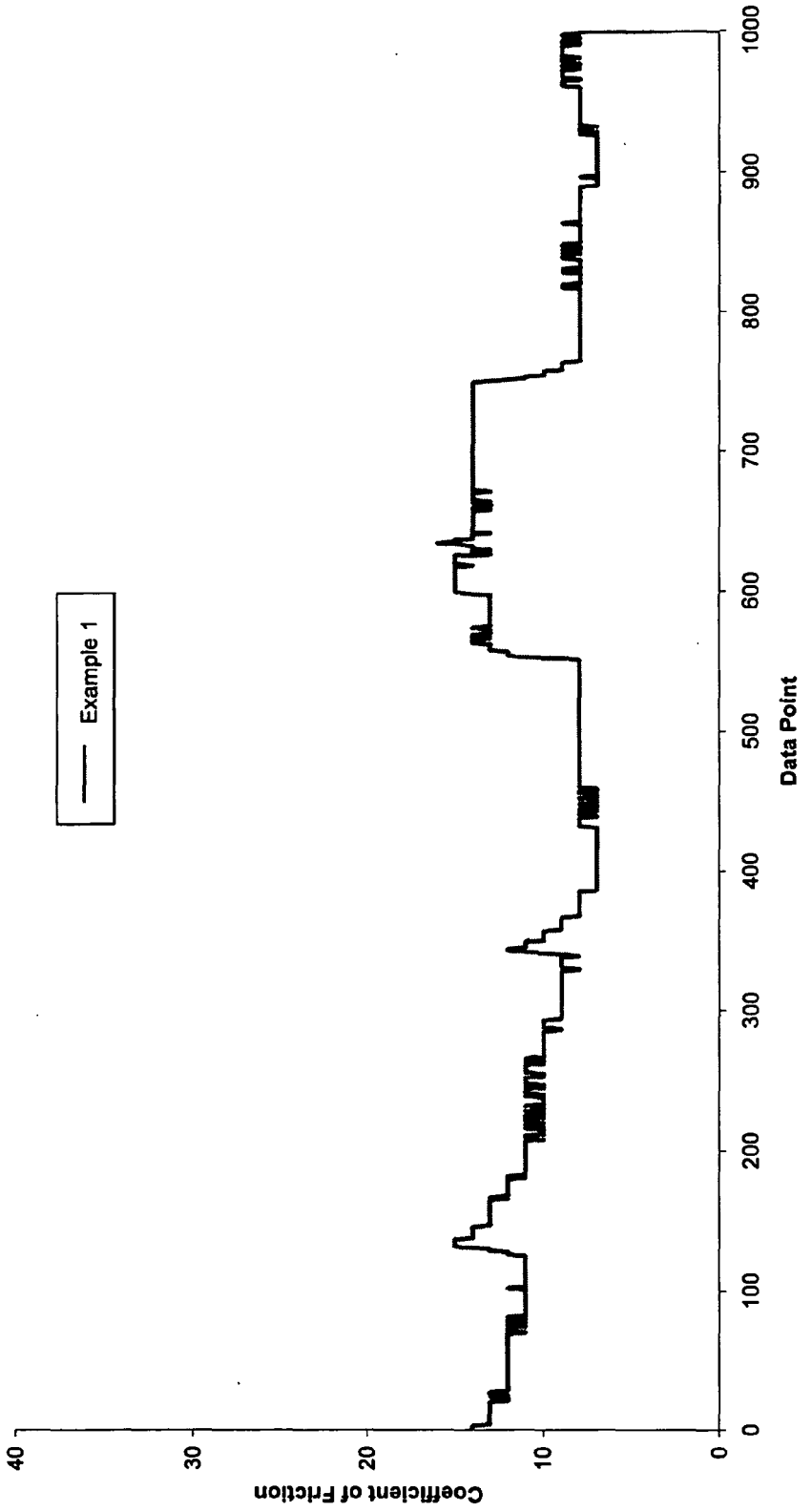
900
1000

FIGURE 1

FIGURE 2


Example 1
Coefficient of Friction
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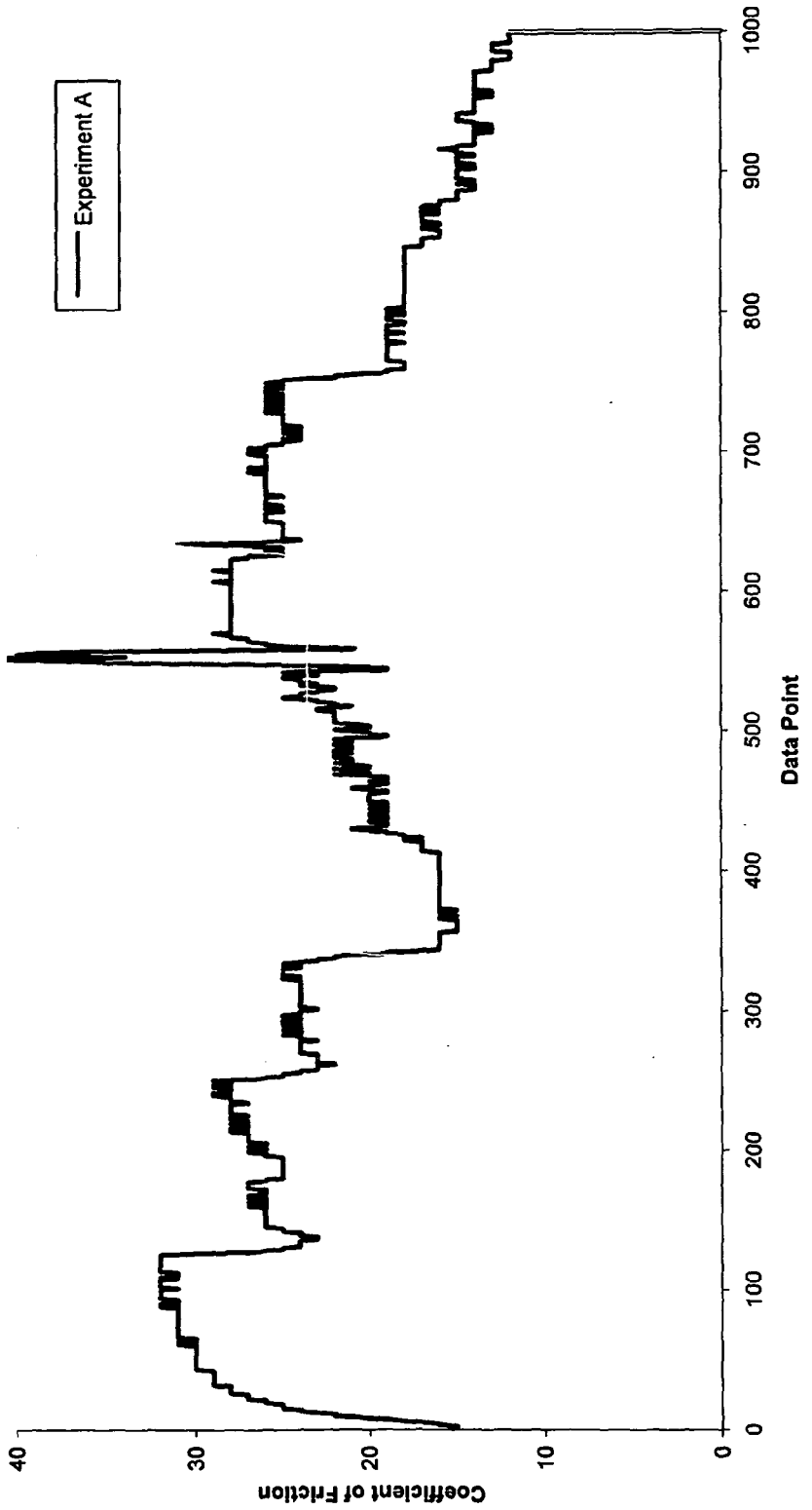
800
900
1000
Data Point

FIGURE 3


Experiment A
Coefficient of Friction
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20
30
40
0
100
200
300
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1000
Data Point

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EUROPEAN SEARCH REPORT

Application Number
EP 08 25 1963

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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	5 February 2009	Kazemi, Pirjo

CATEGORY OF CITED DOCUMENTS

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

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