



(11) **EP 3 124 583 A1**

(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 153(4) EPC

(43) Date of publication:
01.02.2017 Bulletin 2017/05

(21) Application number: **15768985.2**

(22) Date of filing: **23.03.2015**

(51) Int Cl.:
C10M 173/02 (2006.01) **C10M 129/08** (2006.01)
C10M 129/16 (2006.01) **C10M 129/32** (2006.01)
C10M 129/40 (2006.01) **C10M 135/26** (2006.01)
C10M 145/26 (2006.01) **C10N 30/06** (2006.01)
C10N 40/20 (2006.01) **C10N 40/22** (2006.01)

(86) International application number:
PCT/JP2015/058733

(87) International publication number:
WO 2015/146908 (01.10.2015 Gazette 2015/39)

(84) Designated Contracting States:
**AL AT BE BG CH CY CZ DE DK EE ES FI FR GB
GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO
PL PT RO RS SE SI SK SM TR**
Designated Extension States:
BA ME
Designated Validation States:
MA

(30) Priority: **28.03.2014 JP 2014070521**

(71) Applicant: **Idemitsu Kosan Co., Ltd**
Tokyo 100-8321 (JP)

(72) Inventors:
• **JIBIKI Yosuke**
Ichihara-shi
Chiba 299-0107 (JP)
• **TAKAGI Fumiaki**
Ichihara-shi
Chiba 299-0107 (JP)
• **KITAMURA Tomohiko**
Ichihara-shi
Chiba 299-0107 (JP)

(74) Representative: **Hoffmann Eitle**
Patent- und Rechtsanwälte PartmbB
Arabellastraße 30
81925 München (DE)

(54) **WATER-SOLUBLE METALWORKING FLUID, AND METALWORKING COOLANT**

(57) A water-soluble metalworking fluid of the invention contains: a component (A) that is a dicarboxylic acid including a sulfide structure; a component (B) that is a polyalkylene glycol; a component (C) that is polyhydric alcohol polyalkylene oxide adducts; and a component (D) that is a monocarboxylic acid.

EP 3 124 583 A1

Description

TECHNICAL FIELD

5 **[0001]** The present invention relates to a water-soluble metalworking fluid and a metalworking coolant provided by diluting the fluid with water.

BACKGROUND ART

10 **[0002]** A metalworking fluid used in metalworking is generally categorized into oil-type (oil-based) fluid and water-type (water-based) fluid, the latter of which is more frequently used because such water-based fluid is excellent in cooling capabilities and penetration capabilities and free from a risk of causing a fire.

[0003] Particularly, since cooling capabilities of the fluid is significant in grinding, a solution-type fluid not containing a mineral oil is frequently used (see, for instance, Patent Literature 1). The solution-type fluid exhibits favorable cooling capabilities and rot resistance, but exhibits inferior lubricity to those of non-water-type, emulsion-type and soluble-type fluids. An insufficient lubricity causes deterioration in roughness of a machined surface, a decrease in lifetime of a grinding stone, or grinding burn.

15 **[0004]** Accordingly, in order to add the lubricity to the soluble-type fluid, polyalkylene glycol (PAG) is sometimes blended with the fluid (see Patent Literatures 2 and 3).

20

CITATION LIST

PATENT LITERATURE(S)

25 **[0005]**

Patent Literature 1: JP-A-40-14480

Patent Literature 2: JP-A-10-324888

Patent Literature 3: JP-A-2010-70736

30

SUMMARY OF THE INVENTION

PROBLEM(S) TO BE SOLVED BY THE INVENTION

35 **[0006]** In the soluble-type fluids disclosed in Patent Literatures 2 and 3, a favorable lubricity is obtained by increasing an amount of PAG. However, even if a great amount of PAG is blended, improvement in the lubricity is limited. Accordingly, under severe machining conditions, a friction coefficient between a grinding stone and a ground material is increased to cause a decrease in lifetime of the grinding stone and grinding burn.

40 **[0007]** An object of the invention is to provide a water-soluble metalworking fluid exhibiting excellent lubricity and wear resistance even under severe machining conditions, and a metalworking coolant provided by diluting the water-soluble metalworking fluid with water.

MEANS FOR SOLVING THE PROBLEM(S)

45 **[0008]** The inventors found that the lubricity and the wear resistance could be improved by using a water soluble fluid containing all of a dicarboxylic acid having a sulfide structure, PAG, a polyalkylene oxide adduct of polyhydric alcohol such as pentaerythritol, and a monocarboxylic acid. The invention has been reached based on this finding.

[0009] Specifically, the invention provides a water-based metalworking fluid and a metalworking coolant as follows.

50 **[0010]** According to an aspect of the invention, a water-soluble metalworking fluid includes: a component (A) that is a dicarboxylic acid comprising a sulfide structure; a component (B) that is a polyalkylene glycol; a component (C) that is polyhydric alcohol polyalkylene oxide adducts; and a component (D) that is a monocarboxylic acid.

[0011] According to another aspect of the invention, a water-soluble metalworking coolant is provided by diluting the above-mentioned water-soluble metalworking fluid with water by 2 to 200 times in volume.

55 **[0012]** The water-soluble metalworking fluid (undiluted solution) of the invention exhibits favorable lubricity and wear resistance in a form of a metalworking coolant provided by diluting the fluid with water. Accordingly, when the metalworking coolant of the invention is used for grinding, the metalworking coolant is unlikely to cause deterioration in roughness of a machined surface even under severe machining conditions, so that grinding burn and a decrease in lifetime of the grinding stone can be sufficiently restrained.

DESCRIPTION OF EMBODIMENT(S)

[0013] A water-soluble metalworking fluid according to an aspect of the invention (hereinafter, also referred to as "the present fluid") is provided by blending: a component (A) that is a dicarboxylic acid comprising a sulfide structure; a component (B) that is a polyalkylene glycol; a component (C) that is polyhydric alcohol polyalkylene oxide adducts; and a component (D) that is a monocarboxylic acid. The present fluid is an undiluted solution and is diluted with water to provide a metalworking coolant according to another aspect of the invention. The present invention will be described in detail below.

Component (A)

[0014] A component (A) of the present fluid is a dicarboxylic acid including a sulfide structure and has an effect of improving lubricity.

[0015] As the component (A), a dicarboxylic acid represented by a formula (1) below is particularly excellent in improvement in lubricity.



[0016] Herein, R^1 and R^2 each are a hydrocarbon group having 1 to 5 carbon atoms. n is an integer from 1 to 8. When R^1 and R^2 each contain 6 or more carbon atoms, water solubility may be deteriorated.

[0017] The total number of the carbon atoms in the dicarboxylic acid of the formula (1) is in a range from 4 to 12, however, is preferably in a range from 6 to 10 in terms of water solubility and lubricity. R^1 and R^2 each are preferably an alkylene group, examples of which include a methylene group, ethylene group, methylethylene group, propylene group, and butylene group. An ethylene group is particularly preferable in terms of water solubility and lubricity.

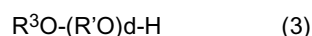
[0018] When n is 9 or more, the dicarboxylic acid becomes structurally unstable and may be decomposed. Accordingly, n is preferably 6 or less, more preferably 2 or less, further preferably 1.

[0019] Examples of the dicarboxylic acid include thiodipropionic acid, dithiodipropionic acid, thiodiacetate, thiodisuccinate, dithiodiacetate, and dithiodibutyrate.

[0020] A content of the component (A) is preferably in a range from 0.1 mass% to 14 mass% based on the total amount of the undiluted solution, more preferably from 1 mass% to 10 mass%, further preferably from 2 mass% to 5 mass%. When the content of the component (A) is excessively large, rust resistance of the present fluid (undiluted solution) diluted with water may be decreased.

Component (B)

[0021] A component (B) of the present fluid, which is polyalkylene glycol, contributes to improvement in lubricity in the same manner as the component (A) and further contributes to improvement in wear resistance. The component (B) is preferably at least one of polyalkylene glycol represented by formulae (2) and (3) below in terms of improvement in lubricity and wear resistance.



[0022] In the formula (2), EO denotes an ethylene oxide unit and PO denotes a propylene oxide unit. a and c each independently are an integer from 1 to 30. b is an integer from 5 to 100. The total number of an EO structure in the formula (2) is preferably in a range from 10 to 30. The total number of a PO structure in the formula (2) is preferably in a range from 10 to 50, more preferably in a range from 20 to 40. When the total number of the EO structure exceeds 60, lubricity of the present fluid diluted with water may be decreased. When the total number of the PO structure exceeds 100, water solubility may be decreased.

[0023] In the formula (3), R^3 is an alkyl group having 1 to 30 carbon atoms. When the number of the carbon atoms in R^3 exceeds 30, water solubility may be decreased. R'O denotes an oxide unit selected from PO and EO. A mixture of PO and EO may be used in R'O . It should be noted that a mole fraction of EO in R'O is preferably less than 1 in terms of antifoaming property of the present fluid diluted with water. d is an integer from 1 to 50. When the number of the carbon atoms in R^3 exceeds 30, water solubility may be decreased.

[0024] A mass average molecular weight of the component (B) is preferably 500 to 10000, more preferably 1000 to 5000. When the mass average molecular weight is less than 500 or more than 10000, lubricity of the present fluid diluted with water may be decreased.

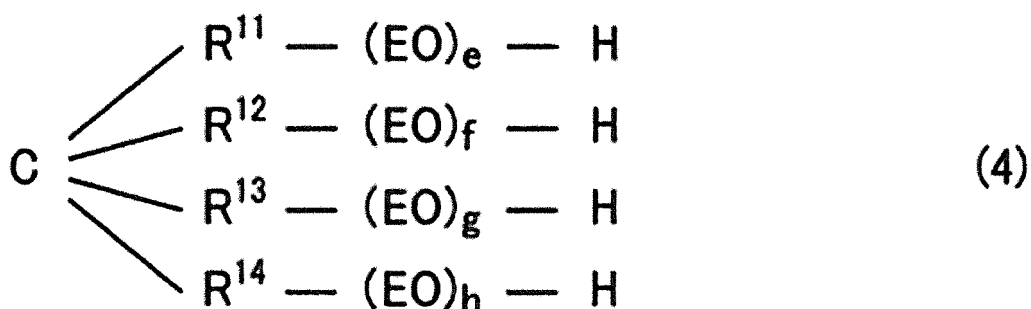
[0025] Polyalkylene glycol represented by the formulae (2) and (3) that is the component (B) may be used alone or in a mixture. Moreover, polyalkylene glycol represented by the formulae (2) and (3) may be in a mixture of polyalkylene glycol having various structures that are different in, for instance, the number of the units of the EO structure and PO structure.

[0026] A content of the component (B) is preferably in a range from 10 mass% to 60 mass% based on the total amount of the undiluted solution, more preferably from 20 mass% to 40 mass%, further preferably from 20 mass% to 30 mass%. When the content of the component (B) is excessively large, lubricity after being diluted at a typical dilution ratio may be excessively increased to decrease a biting performance of a grinding stone in grinding.

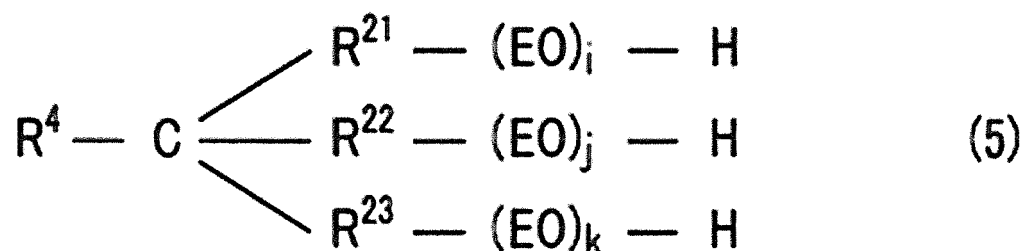
Component (C)

[0027] A component (C) of the present fluid is at least one of the compounds represented by the formulae (4) to (7). The component (C) contributes to improvement in wear resistance.

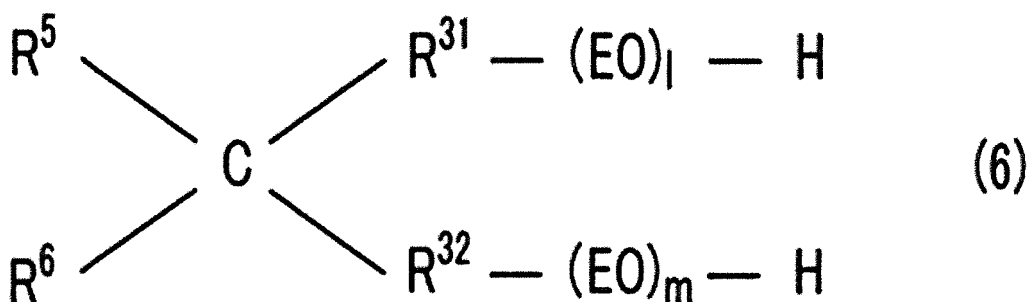
Formula 1



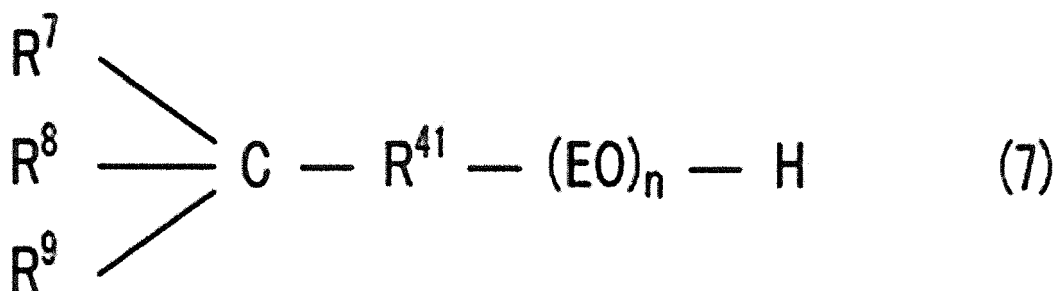
Formula 2



Formula 3



Formula 4



[0028] In the formula (4), R^{11} to R^{14} are each independently an alkylene group having 1 to 5 carbon atoms. e to h are each independently an integer from 1 to 30.

[0029] In the formula (5), R^4 is an alkyl group having 1 to 30 carbon atoms. R^{21} to R^{23} are each independently an alkylene group having 1 to 5 carbon atoms. i to k are each independently an integer from 1 to 30.

[0030] In the formula (6), R^5 and R^6 are each independently an alkyl group having 1 to 30 carbon atoms. R^{31} and R^{32} are each independently an alkylene group having 1 to 5 carbon atoms. 1 to m are each independently an integer from 1 to 30.

[0031] In the formula (7), R^7 to R^9 are each independently an alkyl group having 1 to 30 carbon atoms. R^{41} is an alkylene group having 1 to 5 carbon atoms. n is an integer from 1 to 30.

[0032] Among the above component (C), an EO adduct of pentaerythritol or an EO adduct of trimethylolpropane is preferable in terms of improvement in wear resistance.

[0033] A content of the component (C) is preferably in a range from 5 mass% to 30 mass% of the total amount of the present fluid in terms of wear resistance at a typical dilution ratio.

Component (D)

[0034] A component (D) of the present fluid, which is a monocarboxylic acid, contributes to improvement in lubricity and wear resistance. The monocarboxylic acid is preferably a so-called long-chain carboxylic acid, specifically a compound represented by a formula (8) below.



R^{10} is a hydrocarbon group having 11 or more carbon atoms. The hydrocarbon group may be linear or branched and saturated or unsaturated. Tall oil fatty acid is preferable in terms of lubricity and wear resistance.

[0035] Specific examples of the long-chain carboxylic acid include lauric acid, stearic acid, oleic acid, linolic acid, linolenic acid, erucic acid, palmitic acid, ricinoleic acid, hydroxy fatty acid (e.g., ricinoleic acid, 12-hydroxystearic acid), arachidic acid, behenic acid, melissic acid, isostearic acid, soy oil fatty acid extracted from fat and oil, coconut oil fatty acid, rape-seed oil fatty acid, and tall oil fatty acid (C18).

[0036] A content of the component (D) is preferably in a range from 1 mass% to 20 mass% of the total amount of the present fluid in terms of lubricity and wear resistance at a typical dilution ratio.

[0037] The present fluid is provided in a form of the undiluted solution obtained by blending the above components (A) to (D) with water. In the present fluid (undiluted solution), a total content of the components (A) to (D) is preferably in a range from 40 mass% to 90 mass% of the total amount of the present fluid, more preferably from 60 mass% to 80 mass%.

[0038] When the total content of the components (A) to (D) is less than 40 mass%, a decrease in lubricity (an increase in a friction coefficient) may occur if the present fluid is diluted with water at an excessively high dilution ratio at a working site. On the other hand, when the total content of the components (A) to (D) exceeds 90 mass%, stability of the undiluted solution may be decreased. The stability of the undiluted solution means that uniformity of the undiluted solution is lost due to phase separation, undissolved mass or precipitation of solid content and the like.

[0039] Water for preparing the undiluted solution is preferably 15 mass% to 75 mass% of the total amount of the present fluid. When water is less than 15 mass%, dissolution of the components (A) and (B) becomes difficult and preparation of the undiluted solution becomes complicated. When water for preparing the undiluted solution exceeds 75 mass%, an excessive amount of the undiluted solution has to be stored or transported, thereby lowering handleability.

[0040] The fluid (undiluted solution) may be directly used, but, is preferably diluted with water at a ratio (volume ratio) of 2 to 200 times, preferably 5 to 100 times to be used as a metalworking coolant.

Other Components

[0041] It is preferable that the present fluid further contains a nonion-based surfactant as a component (E). By blending such a surfactant, wettability of the present fluid is improved, so that the present fluid easily penetrates between the grinding stone and a ground material.

[0042] An acethylene glycol surfactant is particularly preferable as the component (E) in terms of the effects. As the acethylene glycol surfactant, for instance, acethylene glycol and an alkylene oxide adduct thereof disclosed in JP-A-2011-12249 are suitably usable. For instance, an acethylene glycol EO adduct is suitable. Examples of a commercially available acethylene glycol surfactant include Dynol 604, Surfynol 420 and Surfynol 465 which are manufactured by Air Products and Chemicals, Inc.

[0043] A content of the component (E) is preferably in a range from 0.1 mass% to 20 mass% of the total amount of the undiluted solution, more preferably from 1 mass% to 10 mass%. When the content of the component (E) is excessively large, antifoaming performance of the present fluid after being diluted is deteriorated.

[0044] It is preferable that the present fluid further contains alkanolamine as a component (F). Alkanolamine reacts with the component (A) or the component (D) to form alkanolamine carboxylate, thereby improving lubricity. Moreover, alkanolamine also serves as a rust inhibitor.

[0045] The kind of alkanolamine is not particularly limited. A combination of primary, secondary and tertiary amines is usable. However, when only the primary amine is used, since volatility of the primary amine is high, working environments may be deteriorated because of odor generation. Accordingly, when the primary amine is used, it is preferable to combine the secondary amine and/or tertiary amine with the primary amine. The tertiary amine is preferable in terms of odor generation.

[0046] Examples of the primary amine are 1-amino-2-propanol, 2-amino-2-methyl-1-propanol, 1-amino-2-butanol, 2-amino-1-propanol, and 3-amino-2-butanol. Among the above, in view of the rust resistance for iron, 1-amino-2-propanol and 2-amino-2-methyl-1-propanol are particularly preferable. In the present fluid, one of the above components may be used alone, or two or more thereof may be used.

[0047] Examples of the secondary amine include diethanolamine, di(n-propanol)amine, diisopropanolamine, N-methylmonoethanolamine, N-ethylmonoethanolamine, N-cyclomonoethanolamine, N-n-propylmonoethanolamine, N-i-propylmonoethanolamine, N-n-butylmonoethanolamine, N-i-butylmonoethanolamine, and N-t-butylmonoethanolamine. In the present fluid, one of the above components may be used alone, or two or more thereof may be used.

[0048] Examples of the tertiary amine include N-methyldiethanolamine, N-ethyldiethanolamine, triethanolamine, N-cyclohexyldiethanolamine, N-n-propyldiethanolamine, N-i-propyldiethanolamine, N-n-butyldiethanolamine, N-i-butyldiethanolamine, and N-t-butyldiethanolamine. One of the above components may be used alone, or two or more thereof may be used.

[0049] A content of the component (F) is preferably in a range from 20 mass% to 55 mass% of the total amount of the present fluid (undiluted solution). When the content of the component (F) is less than 20 mass%, rust resistance may be decreased if the present fluid is diluted with water at an excessively high dilution ratio at a working site. On the other hand, when the content of the component (F) exceeds 55 mass%, the stability of the undiluted solution is lowered.

[0050] Herein, in order to improve the rust resistance, it is preferable to use carboxylic acid containing no sulfur as the rust inhibitor together with the component (F). In view of antifoaming capabilities and hard water stability, preferable examples of the carboxylic acid include: a monocarboxylic acid such as caproic acid, nonane acid, isononane acid, trimethylhexanoic acid, neodecanoic acid and decane acid having 8 to 10 carbon atoms; and a dicarboxylic acid such as nonane diacid, undecanoic diacid, sebacic acid, dodecanoic diacid having 9 to 12 carbon atoms.

[0051] Particularly, the above-mentioned trimethylhexanoic acid is excellent in reducing solid substances being formed on a surface of the present fluid (hard water stability) when the present fluid (undiluted solution) is diluted with water.

[0052] In view of rot resistance, the alkyl group that is a main chain of the carboxylic acid preferably has a branched structure. For the carboxylic acid, although dibasic acids are excellent in rust resistance as a salt, dibasic acids and monobasic acids are preferably mixed in use in view of stability (unlikeliness to be insoluble) of the undiluted solution.

[0053] The present fluid may be blended as necessary with publicly-known various kinds of additives as long as such addition is compatible with an object of the present invention. Examples of the additives include an extreme pressure agent, oiliness agent, fungicide (preservative), metal deactivator and antifoaming agent.

[0054] Examples of the extreme pressure agent include a sulfur-based extreme pressure agent, a phosphorus-based extreme pressure agent, an extreme pressure agent containing sulfur and metal, and an extreme pressure agent containing phosphorus and metal. One of the extreme pressure agents may be used alone or two or more thereof may be used in combination. The extreme pressure agent may be any extreme pressure agent, as long as the extreme pressure agent contains sulfur atoms or phosphorus atoms in its molecule and the extreme pressure agent can provide load bearing effects and wear resistance. Examples of the extreme pressure agent containing sulfur in its molecule include: sulfurized fat and oil, sulfurized fatty acid, ester sulfide, olefin sulfide, dihydrocarbyl polysulfide, a thiadiazole compound, an alkylthiocarbamoyl compound, a triazine compound, a thioterpene compound, a dialkylthiodipropionate compound

and the like. In view of blending effects, the extreme pressure agent is blended in the undiluted solution with a content of approximately 0.05 mass% to 0.5 mass% of the total amount of the final diluted fluid (coolant).

[0055] Examples of the oiliness agent include: an aliphatic compound such as aliphatic alcohol and fatty acid metal salt; and an ester compound such as polyol ester, sorbitan ester and glyceride. In view of blending effects, the oiliness agent is blended in the undiluted solution with a content of approximately 0.2 mass% to 2 mass% of the total amount of the coolant.

[0056] The fungicide is exemplified by 2-pyridylthio-1-oxide salt. Examples of the fungicide are 2-pyridylthio-1-oxide sodium, zinc bis(2-pyridylthio-1-oxide), and bis(2-sulfidepyridine-1-olato) copper. In view of blending effects, the fungicide is blended in the undiluted solution with a content of approximately 0.01 mass% to 5 mass% of the total amount of the coolant.

[0057] Examples of the metal deactivator include benzotriazole, benzotriazole derivative, imidazoline, pyrimidine derivative, and thiadiazole. One of the metal deactivator may be used alone or two or more thereof may be used in combination. In view of blending effects, the metal deactivator is blended in the undiluted solution with a content of approximately 0.01 mass% to 3 mass% of the total amount of the coolant.

[0058] Examples of the antifoaming agent include methyl silicone oil, fluorosilicone oil, polyacrylates and the like. In view of blending effects, the antifoaming agent is blended in the undiluted solution with a content of approximately 0.004 mass% to 0.08 mass% of the total amount of the coolant.

[0059] The water-soluble metalworking fluid according to the above aspect of the invention, which is diluted as necessary with water so that its concentration is adjusted suitably for the usage, is preferably applied in various metalworking fields such as grinding, cutting, polishing, squeezing, drawing, flatting and the like. Examples of the grinding include cylinder grinding, internal grinding, plane grinding, centerless grinding, tool grinding, honing grinding, super finishing, and special curve grinding (e.g., screw grinding, gear grinding, cum grinding, and roll grinding).

[0060] Herein, in the invention, the composition provided by blending the components (A) and (B) means not only a "composition containing the components (A) and (B)" but also a "composition containing a modified substance of at least one of the components (A) and (B) in place of the at least one of the components (A) and (B), and a "composition containing a reaction product obtained by reacting the component (A) with the component (B)."

Examples

[0061] Next, the invention will be described in detail with reference to Examples, but is not limited at all by the Examples.

Examples 1 to 5, Comparatives 1 to 6

[0062] After water-soluble metalworking fluids (undiluted solutions) were prepared according to blending compositions shown in Table 1, the undiluted solutions were respectively diluted with tap water by 20 times in volume to obtain sample oils. The sample oils were subjected to a block-on-ring test to evaluate lubricity and wear resistance. Testing conditions and evaluation items (evaluation method) are as follows. Results are shown in Table 1.

Block-On-Ring Test

[0063]

Test machine: block-on-ring test machine (manufactured by Marubishi Engineering Co., Ltd.)

Load: 100N

Rotation rate: 500 rpm (53m/min)

Time: 10min

Ring: SAE 4620STEEL

Block: S45C

Evaluation Items (Evaluation Method)

Lubricity

[0064] Standards of the evaluation based on a friction force (N) are as follows.

A: 13.5N or less

B: more than 13.5N

EP 3 124 583 A1

Wear Resistance

[0065] Standards of the evaluation based on a width of a wear track (μm) are as follows.

5 A: 1000 μm or less
 B: more than 1000 μm and 1100 μm or less
 C: more than 1100 μm

Table 1

15

20

25

30

35

40

45

50

55

Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Comp. 1	Comp. 2	Comp. 3	Comp. 4	Comp. 5	Comp. 6
water	18.7	15.3	15.3	23.4	23.8	61.9	31.9	33.3	30.1	23.4
thiodipropionic acid	2.7	2.7	2.7	2.7	2.7	—	—	2.7	2.7	2.7
dodecanoic diacid	1.1	2.0	2.0	2.0	2.0	1.1	1.1	1.1	1.1	2.0
decanoic diacid	—	—	—	—	—	2.0	2.0	—	—	—
3,5,5-trimethylhexanoic acid	3.2	3.2	3.2	3.2	3.2	3.2	3.2	3.2	3.2	3.2
neodecanoic acid (C9)	—	—	—	—	—	3.4	3.4	3.4	—	—
lauric acid (C12)	—	—	—	—	—	—	—	—	4.0	—
tall oil fatty acid (C18) ¹⁾	5.4	5.4	5.4	5.4	5.4	—	—	—	—	5.4
1-amino-2-propanol	10.0	10.9	10.9	10.9	10.9	8.8	8.8	10.0	10.0	10.9
triethanolamine	20.0	21.6	21.6	14.4	14.4	17.5	17.5	19.4	20.0	14.4
cyclohexyldiethanolamine	—	—	—	9.1	9.1	—	—	—	—	9.1
HO(EO) _{8.5} -(PO) _{30.2} -(EO) _{8.5} H ²⁾	—	—	—	7.5	7.5	—	22.5	15.0	15.0	15.0
HO(EO) _{13.2} -(PO) ₃₀ -(EO) _{13.2} H ³⁾	7.5	7.5	7.5	5.0	5.0	—	7.5	5.0	5.0	5.0
MeO(PO)a((EO)b/(PO)c)(PO)dH ⁴⁾	—	—	—	—	—	—	—	—	—	—
pentaerythritol polyoxyethylene ether ⁵⁾	22.5	—	—	—	—	—	—	15.0	—	—
pentaerythritol polyoxyethylene ether ⁶⁾	—	22.5	—	7.5	7.5	—	—	—	—	—
trimethylolpropane tripolyoxyethylene ether ⁷⁾	—	—	22.5	—	—	—	—	—	—	—
oleyl alcohol	2.0	2.0	2.0	2.0	2.0	—	—	—	2.0	2.0
acethylene glycol surfactant ⁸⁾	4.8	4.8	4.8	4.8	4.8	—	—	4.8	4.8	4.8
other components ⁹⁾	2.1	2.1	2.1	2.1	2.1	2.1	2.1	2.1	2.1	2.1
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
block-on-ring test: friction force (N)	10.8	13.3	13.4	12.3	9.4	21.6	17.3	14.9	11.8	10.1
block-on-ring test: width of wear track (μ m)	801	846	846	979	991	1723	1415	1214	1222	1156
lubricity	A	A	A	A	A	B	B	B	A	A
wear resistance	A	A	A	A	A	C	C	C	C	C

1) Tall Oil Fatty Acid (C18)

2) HO(EO)_{8.5}-(PO)_{30.2}-(EO)_{8.5}H: manufactured by Sanyo Chemical Industries, Ltd.3) HO(EO)_{13.2}-(PO)₃₀-(EO)_{13.2}H: manufactured by Sanyo Chemical Industries, Ltd.4) CH₃O(PO)a((EO)b/(PO)c)(PO)dH: "BLENBER LUB82" manufactured by Sanyo Chemical Industries, Ltd.

5) Pentaerythritol polyoxyethylene ether: "PNT-60U" manufactured by Nippon Nyukazai Co., Ltd.

- 6) Pentaerythritol polyoxyethylene ether: "PNT-40" manufactured by Nippon Nyukazai Co., Ltd.
 7) Trimethylolpropane tripolyoxyethylene ether: "TMP-60" manufactured by Nippon Nyukazai Co., Ltd.
 8) Acethylene glycol surfactant: a mixture of Dynol 604, Surfynol 420 and Surfynol 465 which are manufactured by Air Products and Chemicals, Inc.
 9) Other components: 30-mass% aqueous solution of polyethyleneimine (molecular weight of 1000) being 0.3 mass%, benzotriazole being 1.0 mass%, 35-mass% aqueous solution of benzisothiazoline being 0.2 mass%, sodium pyrrhione being 0.2 mass%, and a silicone antifoaming agent being 0.4 mass%

Evaluation Results

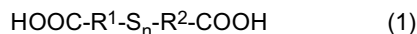
- [0066]** As each of coolants obtained by diluting the undiluted solutions of Examples 1 to 5 contains the components (A) to (D) of the invention, all the coolants are excellent in lubricity and wear resistance.
[0067] In contrast, as each of coolants obtained by diluting the undiluted solutions of Comparatives 1 to 6 does not contain one of the components (A) to (D), the coolants cannot simultaneously exhibit lubricity and wear resistance.

Claims

1. A water-soluble metalworking fluid comprising:

a component (A) that is a dicarboxylic acid comprising a sulfide structure;
 a component (B) that is a polyalkylene glycol;
 a component (C) that is polyhydric alcohol polyalkylene oxide adducts; and
 a component (D) that is a monocarboxylic acid.

2. The water-soluble metalworking fluid according to claim 1, wherein the component (A) is a compound represented by a formula (1) below,

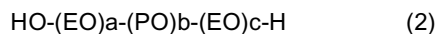


where:

R^1 and R^2 are each independently a hydrocarbon group having 1 to 5 carbon atoms, and
 n is an integer from 1 to 8.

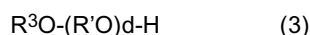
3. The water-soluble metalworking fluid according to claim 1 or 2, wherein
 a content of the component (A) is in a range from 0.1 mass% to 14 mass% of a total amount of the fluid.

4. The water-soluble metalworking fluid according to any one of claims 1 to 3, wherein
 the component (B) is at least one of a compound represented by a formula (2) below and a compound represented by a formula (3) below,



where:

EO denotes an ethylene oxide unit and PO denotes a propylene oxide unit,
 a and c each independently are an integer from 1 to 30, and
 b is an integer from 5 to 100,



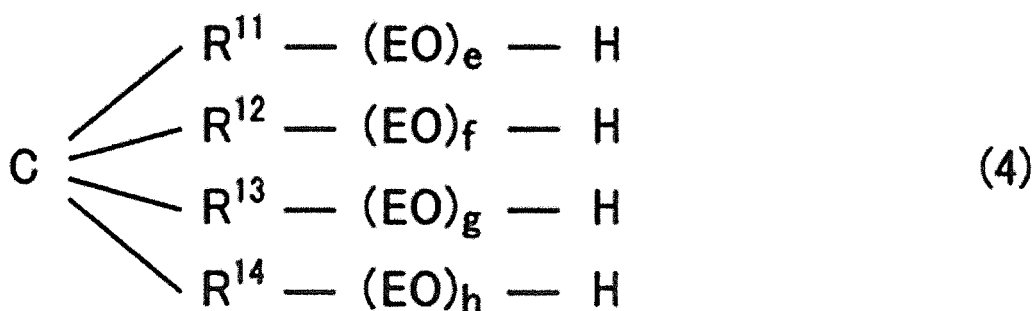
where:

R^3 is an alkyl group having 1 to 30 carbon atoms,
 R'O denotes an oxide unit selected from PO and EO, in which PO and EO are optionally used in mixture,

a mole fraction of EO in R'O is less than 1, and
d is an integer from 1 to 50.

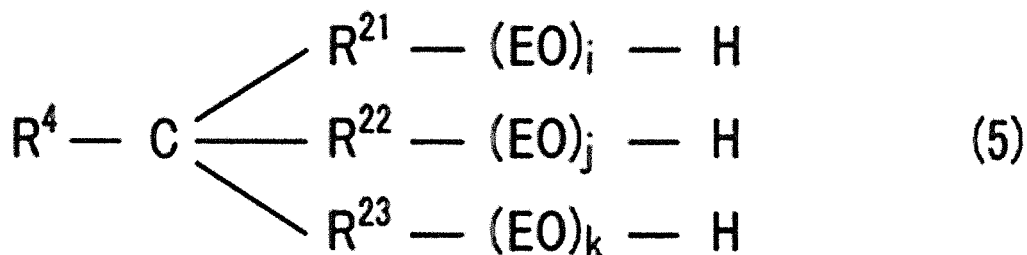
5. The water-soluble metalworking fluid according to any one of claims 1 to 4, wherein
a content of the component (B) is in a range from 10 mass% to 60 mass% of the total amount of the fluid.
6. The water-soluble metalworking fluid according to any one of claims 1 to 5, wherein
the component (C) is at least one of compounds represented by formulae (4) to (7) below,

Formula 1



where: R¹¹ to R¹⁴ are each independently an alkylene group having 1 to 5 carbon atoms, and e to h are each independently an integer from 1 to 30,

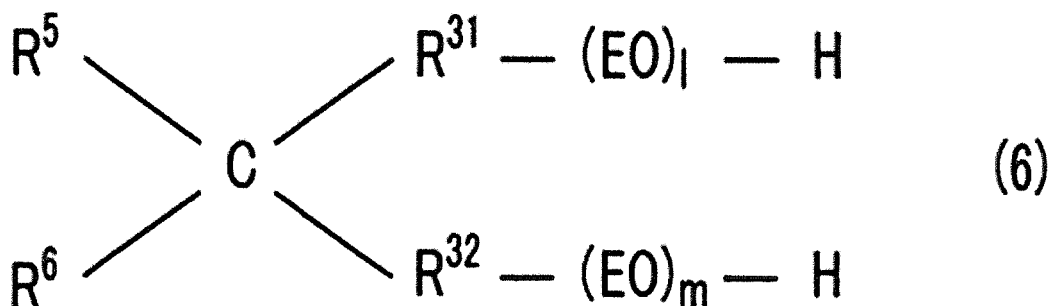
Formula 2



where:

R⁴ is an alkyl group having 1 to 30 carbon atoms,
R²¹ to R²³ are each independently an alkylene group having 1 to 5 carbon atoms, and i to k are each independently an integer of 1 to 30,

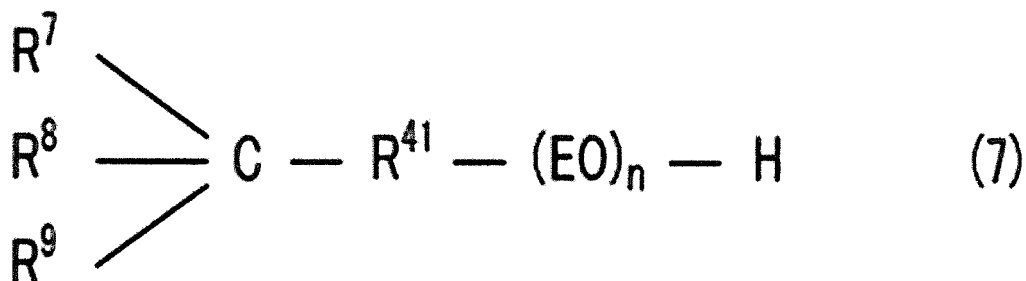
Formula 3



where:

R⁵ and R⁶ are each independently an alkyl group having 1 to 30 carbon atoms,
 R³¹ and R³² are each independently an alkylene group having 1 to 5 carbon atoms, and 1 to m are each
 independently an integer from 1 to 30,

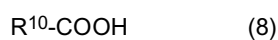
Formula 4



where:

R⁷ to R⁹ are each independently an alkyl group having 1 to 30 carbon atoms,
 R⁴¹ is an alkylene group having 1 to 5 carbon atoms, and
 n is an integer from 1 to 30.

7. The water-soluble metalworking fluid according to any one of claims 1 to 6, wherein
 a content of the component (C) is in a range from 5 mass% to 30 mass% of the total amount of the fluid.
8. The water-soluble metalworking fluid according to any one of claims 1 to 7, wherein
 the component (D) is a compound represented by a formula (8) below,



where: R¹⁰ is a hydrocarbon group having 11 or more carbon atoms.

9. The water-soluble metalworking fluid according to any one of claims 1 to 8, wherein
 a content of the component (D) is in a range from 1 mass% to 20 mass% of the total amount of the fluid.
10. The water-soluble metalworking fluid according to any one of claims 1 to 9, further comprising:
 a component (E) that is an acethylene glycol surfactant.
11. The water-soluble metalworking fluid according to claim 10, wherein
 the component (E) is an acethylene glycol ethylene oxide adduct.
12. The water-soluble metalworking fluid according to claim 10 or 11, wherein
 a content of the component (E) is in a range from 1 mass% to 15 mass% of the total amount of the fluid.
13. The water-based metalworking fluid according to any one of claims 1 to 12, wherein
 the water-based metalworking fluid is in a form of an undiluted solution comprising water in a range from 15 mass%
 to 75 mass%.
14. A metalworking coolant provided by diluting the water-based metalworking fluid according to any one of claims 1 to
 13 with water by 2 to 200 times in volume.
15. The metalworking coolant according to claim 14, wherein
 the metalworking coolant is used for grinding.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2015/058733

A. CLASSIFICATION OF SUBJECT MATTER

C10M173/02(2006.01)i, C10M129/08(2006.01)n, C10M129/16(2006.01)n, C10M129/32(2006.01)n, C10M129/40(2006.01)n, C10M135/26(2006.01)n, C10M145/26(2006.01)n, C10N30/06(2006.01)n, C10N40/20(2006.01)n, C10N40/22(2006.01)n

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C10M173/02, C10M129/08, C10M129/16, C10M129/32, C10M129/40, C10M135/26, C10M145/26, C10N30/06, C10N40/20, C10N40/22

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho 1922-1996 Jitsuyo Shinan Toroku Koho 1996-2015
Kokai Jitsuyo Shinan Koho 1971-2015 Toroku Jitsuyo Shinan Koho 1994-2015

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
CAplus/REGISTRY (STN)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 2010-70736 A (Idemitsu Kosan Co., Ltd.), 02 April 2010 (02.04.2010), claims; 0001, 0023; examples & US 2011/0147645 A1 & WO 2010/021299 A1 & CN 102124090 A & TW 201022430 A	1-15
Y	JP 2013-53227 A (Idemitsu Kosan Co., Ltd.), 21 March 2013 (21.03.2013), claims; 0037 & US 2014/0296117 A1 & WO 2013/031894 A1 & EP 2752480 A1 & CN 103781888 A	1-15
Y	JP 2001-140080 A (Nippon Steel Corp.), 22 May 2001 (22.05.2001), claims; 0037 & US 6479152 B1 & EP 1099485 A2	10-15

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search
02 June 2015 (02.06.15)

Date of mailing of the international search report
16 June 2015 (16.06.15)

Name and mailing address of the ISA/
Japan Patent Office
3-4-3, Kasumigaseki, Chiyoda-ku,
Tokyo 100-8915, Japan

Authorized officer

Telephone No.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2015/058733

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 6-145559 A (Nihon Parkerizing Co., Ltd., Nippon Steel Corp.), 24 May 1994 (24.05.1994), claims; 0027 (Family: none)	10-15
A	JP 10-110181 A (Elf Atochem Japan Kabushiki Kaisha, Mec International Corp.), 28 April 1998 (28.04.1998), claims; examples (Family: none)	1-15
A	JP 2002-3881 A (Atofina), 09 January 2002 (09.01.2002), claims; examples & US 2002/0006880 A1 & EP 1156100 A1 & FR 2809117 A & CA 2348130 A & TW 524851 B	1-15
A	JP 2006-96826 A (Nicca Chemical Co., Ltd., Denso Corp.), 13 April 2006 (13.04.2006), claims; examples (Family: none)	1-15
A	JP 1-139694 A (Nippon Steel Corp., The Nisshin Oil Mills, Ltd.), 01 June 1989 (01.06.1989), claims; synthesis examples; examples (Family: none)	1-15
P, X	JP 2014-172949 A (Idemitsu Kosan Co., Ltd.), 22 September 2014 (22.09.2014), claims; examples (Family: none)	1-15

Form PCT/ISA/210 (continuation of second sheet) (July 2009)

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- JP 4014480 A [0005]
- JP 10324888 A [0005]
- JP 2010070736 A [0005]
- JP 2011012249 A [0042]