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(54) WATER-SOLUBLE METALWORKING OIL, 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 and a component (B) that is a monocarboxylic acid, in which the fluid contains no polyalkylene glycol. A metalworking coolant of the invention is provided by diluting the above-described water-soluble metalworking fluid with water.

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Description

TECHNICAL FIELD

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

BACKGROUND ART

[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.

[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).

CITATION LIST

PATENT LITERATURE(S)

[0005]

Patent Literature 1: JP-A-40-14480
Patent Literature 2: JP-A-10-324888
Patent Literature 3: JP-A-2010-70736

SUMMARY OF THE INVENTION

PROBLEM(S) TO BE SOLVED BY THE INVENTION

[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.

[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)

[0008] The inventors have found that a system including a dicarboxylic acid having a sulfide structure and a long-chain carboxylic acid is excellent in both of lubricity and wear resistance when PAG is preferably excluded from the system. 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.

[0010] According to an aspect of the invention, a water-soluble metalworking fluid contains a component (A) that is a dicarboxylic acid including a sulfide structure and a component (B) that is a monocarboxylic acid, in which the fluid contains no polyalkylene glycol.

[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.

[0012] Since the water-soluble metalworking fluid (undiluted solution) according to the above aspect of the invention contains the component (A) that is a dicarboxylic acid including a sulfide structure and the component (B) that is a monocarboxylic acid but does not contain a polyalkylene glycol, the water-soluble metalworking fluid 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 according to the above aspect 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] Exemplary embodiment(s) of the invention will be described in detail below.

[0014] A water-soluble metalworking fluid in an exemplary embodiment of the invention (hereinafter, also referred to as "the present fluid") is an undiluted solution provided by blending a component (A) that is a dicarboxylic acid including a sulfide structure and a component (B) that is a monocarboxylic acid, in which the present fluid contains no polyalkylene glycol. The present fluid and a metalworking coolant provided by diluting the present fluid with water will be described in detail below.

Component (A)

[0015] A component (A) of the present fluid is a dicarboxylic acid including a sulfide structure and provides lubricity. As the component (A), a dicarboxylic acid represented by a formula (1) below is particularly excellent in lubricity.

$$HOOC\text{-}R^1\text{-}S_n\text{-}R^2\text{-}COOH \quad (1)$$

[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 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 (2) below.

$$R^3\text{-}COOH \quad (2)$$

[0022] R^3 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.

[0023] 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 (C 18).

[0024] A content of the component (B) 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.

[0025] The present fluid is provided in a form of the undiluted solution obtained by blending the above components (A) and (B) with water, but does not contain a polyalkylene glycol (PAG). However, the invention encompasses an instance where a polyalkylene glycol is mixed as an impurity at a slight amount as low as the polyalkylene glycol does not damage the advantages of the invention.

[0026] In the present fluid (undiluted solution), a total content of the components (A) and (B) is preferably in a range from 4 mass% to 40 mass% of the total amount of the present fluid, more preferably from 5 mass% to 15 mass%.

[0027] When the total content of the components (A) and (B) is less than 4 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) and (B) exceeds 40 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.

[0028] Water for preparing the undiluted solution is preferably 20 mass% to 75 mass% of the total amount of the present fluid. When water is less than 20 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.

[0029] 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

[0030] It is preferable that the present fluid further contains a nonion-based surfactant as a component (C). 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.

[0031] An acethylene glycol surfactant is particularly preferable as the component (C) 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.

[0032] A content of the component (C) 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 (C) is excessively large, antifoaming performance of the present fluid after being diluted is deteriorated.

[0033] It is preferable that the present fluid further contains alkanolamine as a component (D). Alkanolamine reacts with the component (A) or the component (B) to form alkanolamine carboxylate, thereby improving lubricity. Moreover, alkanolamine also serves as a rust inhibitor.

[0034] 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.

[0035] 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.

[0036] 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.

[0037] 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.

[0038] A content of the component (D) 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 (D) 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 (D) exceeds 55 mass%, the stability of the undiluted solution is lowered.

[0039] 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 (D). 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.

[0040] 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.

[0041] 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.

[0042] 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.

[0043] 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).

[0044] 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.

[0045] The fungicide is exemplified by 2-pyridylthio-1-oxide salt. Examples of the fungicide are 2-pyridylthio-1-oxide sodium, zinc bis(2-pyridyldithio-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.

[0046] 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.

[0047] 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.

[0048] 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).

[0049] 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

[0050] Next, the invention will be described in detail with reference to Examples, but is not limited at all by the Examples.

Examples 1 to 2, Comparatives 1 to 6

[0051] 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

[0052]

Test machine: block-on-ring test machine (manufactured by Marubishi Engineering Co., Ltd.)
Load: 100N
Rotation rate: 500 rpm (53m/min)
Time: 10 min
Ring: SAE 4620STEEL
Block: S45C

Evaluation Items (Evaluation Method)

Lubricity

[0053] Standards of the evaluation based on a friction force (N) are as follows.

A: 13.5N or less
B: more than 13.5N

Wear Resistance

[0054] Standards of the evaluation based on a width of a wear track (μm) are as follows.

A: 1100 μm or less
B: more than 1100 μm

Table 1

		Ex. 1	Ex. 2	Comp. 1	Comp. 2	Comp. 3	Comp. 4	Comp. 5	Comp. 6
Blending Composition of Stock Solution (mass%)	water	43.4	44.8	61.9	31.9	33.3	33.3	30.1	23.4
	thiodipropionic acid	2.7	2.7	—	—	2.7	2.7	2.7	2.7
	dodecanoic diacid	2.0	2.0	1.1	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
	neodecanoic acid (C9)	—	—	3.4	3.4	3.4	3.4	—	—
	lauric acid (C12)	—	4.0	—	—	—	—	4.0	—
	tall oil fatty acid (C18) [1]	5.4	—	—	—	—	—	—	5.4
	1-amino-2-propanole	10.9	10.9	8.8	8.8	10.0	10.0	10.0	10.9
	triethanolamine	14.4	14.4	17.5	17.5	19.4	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]	—	—	—	22.5	15.0	—	15.0	15.0
	$HO(EO)_{13.2}-(PO)_{30}-(EO)_{13.2}H$ [3]	—	—	—	7.5	5.0	5.0	5.0	5.0
	$MeO(PO)a((EO)b/(PO)c)(PO)Dh$ [4]	—	—	—	—	—	—	—	—
	pentaerythritol polyoxyethylene ether [5]	—	—	—	—	—	15.0	—	—
	oleyl alcohol	2.0	2.0	—	—	—	—	2.0	2.0
	acethylene glycol surfactant [6]	4.8	4.8	—	—	4.8	4.8	4.8	4.8
	other components [7]	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
Evaluation Results	block-on-ring test: friction force	10.4	12.2	21.6	17.3	14.9	13.8	11.8	10.1
	block-on-ring test: width of wear track	1031	1054	1723	1415	1214	1081	1222	1156
	lubricity	A	A	B	B	B	B	A	A
	wear resistance	A	A	B	B	B	A	B	B

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) $CH_3O(PO)a((EO)b/(PO)c)(PO)dH$: "BLENBER LUB82" manufactured by Sanyo

Chemical Industries, Ltd.

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

6) Acethylene glycol surfactant: a mixture of Dynol 604, Surfynol 420 and Surfynol 465 which are manufactured by Air Products and Chemicals, Inc.

7) 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 pyrithione being 0.2 mass%, and a silicone antifoaming agent being 0.4 mass%

Evaluation Results

[0055] As each of coolants obtained by diluting the undiluted solutions of Examples 1 to 2 contains the components (A) and (B) of the invention but does not contain PAG, all the coolants are excellent in lubricity and wear resistance.

[0056] 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) and (B) or contains PAG, 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; and
a component (B) that is a monocarboxylic acid, wherein

the water-soluble metalworking fluid comprises no polyalkylene glycol.

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

$$HOOC\text{-}R^1\text{-}S_n\text{-}R^2\text{-}COOH \quad (1)$$

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 a compound represented by a formula (2) below,

$$R^3\text{-}COOH \quad (2)$$

where: R^3 is a hydrocarbon group having 11 or more carbon atoms.

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 1 mass% to 20 mass% of the total amount of the fluid.

6. The water-soluble metalworking fluid according to any one of claims 1 to 5, further comprising:

a component (C) that is an acethylene glycol surfactant.

7. The water-soluble metalworking fluid according to claim 6, wherein a content of the component (C) is in a range from 1 mass% to 15 mass% of the total amount of the fluid.

8. The water-based metalworking fluid according to any one of claims 1 to 7, 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%.

9. A metalworking coolant provided by diluting the water-based metalworking fluid according to any one of claims 1 to 8 with water by 2 to 200 times in volume.

10. The metalworking coolant according to claim 9, wherein
the metalworking coolant is used for grinding.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2015/058734

A. CLASSIFICATION OF SUBJECT MATTER
C10M173/02(2006.01)i, *C10M129/08*(2006.01)n, *C10M129/32*(2006.01)n, *C10M129/40*(2006.01)n, *C10M135/26*(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, C10M129/32, C10M129/40, C10M135/26, 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.
X Y	JP 10-110181 A (Elf Atochem Japan Kabushiki Kaisha, Mec International Corp.), 28 April 1998 (28.04.1998), claims; examples (Family: none)	1-5,8-10 6-10
X Y	JP 2002-3881 A (Atofina), 09 January 2002 (09.01.2002), claims; 0001; examples & US 2002/0006880 A1 & EP 1156100 A1 & FR 2809117 A & CA 2348130 A & TW 524851 B	1-5,8-10 6-10

☒ 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
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"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	Date of mailing of the international search report
01 June 2015 (01.06.15)	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.

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

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2015/058734

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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