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Applicant: **NIHON PARKERIZING CO., LTD.**
15-1, 1-Chome, Nihonbashi
Chuo-ku Tokyo 103(JP)

Inventor: **Fujii, Hiroyuki, c/o Nippondenso**
Co.,Ltd.
1-1 Showa-Cho
Kariya-City, Alchi-Pref, 448(JP)
Inventor: **Mizutani, Takanori, c/o Nippondenso**
Co.,Ltd.
1-1 Showa-Cho
Kariya-City, Alchi-Pref, 448(JP)
Inventor: **Shirai, Tokuo, c/o Nippondenso**
Co.,Ltd.
1-1 Showa-Cho

Kariya-City, Alchi-Pref, 448(JP)
Inventor: **Nagae, Yoshio, c/o Nihon**
Parkerizing Company, Ltd.
15-1 Nihonbashi 1-chome, Chuo-ku
Tokyo(JP)

Inventor: **Kaburaki, Kouji, c/o Nihon**
Parkerizing Company,Ltd
15-1 Nihonbashi 1-chome, Chuo-ku
Tokyo(JP)

Inventor: **Hetsugi, Kouji, c/o Nihon Parkerizing**
Company, Ltd
15-1 Nihonbashi 1-chome, Chuo-ku
Tokyo(JP)
Inventor: **Tanizawa, Yasuo, c/o Nihon**
Parkerizing Company,Ltd
15-1 Nihonbashi 1-chome, Chuo-ku
Tokyo(JP)

Representative: **Hale, Stephen Geoffrey et al**
J.Y. & G.W. Johnson Furnival House 14/18
High Holborn
London WC1V 6DE(GB)

Aqueous lubrication treatment liquid for cold plastic working metallic materials.

An aqueous lubrication treatment liquid for a cold plastic working of a metallic material comprises 4 to 160 g/l of a metallic soap, 50 to 400 g/l of a solid lubricant, 0.5 to 40 g/l of a dispersing surfactant for the metallic soap and the solid lubricant, and optionally a colloidal titanium compound in an amount of 10 ppm or more in terms of titanium and 5 to 150 g/l of a binder.

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AQUEOUS LUBRICATION TREATMENT LIQUID FOR COLD PLASTIC WORKING METALLIC MATERIALS

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to an aqueous lubrication treatment liquid for cold plastic working metallic materials.

More particularly, this invention relates to an aqueous lubrication treatment liquid for a cold plastic working (forging, tube drawing, wire drawing, etc.) of metallic materials, for example, steel, stainless steels, titanium-based alloys, copper, copper-based alloys, aluminum, aluminum-based alloys, etc. (hereinafter referred to as an aqueous lubrication treatment liquid).

2. Description of the Related Arts

As aqueous lubrication treatment liquids currently used for the cold plastic working of a metallic material, liquids which comprise a solid lubricant, for example, molybdenum disulfide or graphite, at least one member selected from inorganic binders and organic binders, and a surfactant are known.

When a cold working is carried out at a relatively small reduction, a method in which an aqueous lubrication treatment liquid is brought directly into contact with a surface of a metallic material free from grease, followed by drying to form a solid lubricant film thereon, is known.

In a high reduction cold working, a method is employed of forming a solid lubricant film over a chemical conversion coating where a metallic material surface, after the formation of the chemical conversion coating, is brought into contact with an aqueous lubrication treatment liquid, followed by drying, or has a solid lubricant powder deposited thereon. Using a solid lubricant in a powder state, however, causes a problem of a deterioration of the working environment, and thus most preferably a lubricant in the form of an aqueous treatment liquid is used. In this case, however, a conventional aqueous lubricant treatment liquid has a drawback in that it has an unstable and insufficient lubricating property and causes rusting of the treated or formed metallic material when left to stand after the lubricating treatment or a plastic working.

In the above cases, the currently used treatment agents cannot provide a stable and desired lubricity, which often results in the problems of seizing and galling.

SUMMARY OF THE INVENTION

An object of the present invention is to provide an aqueous lubrication treatment liquid for cold plastic working metallic materials, which liquid does not have the above-mentioned disadvantages of conventional aqueous lubrication treatment liquids and exhibits a high stability and an excellent lubricating property, without causing a rusting of the metallic materials.

The above-mentioned object can be attained by the aqueous lubrication treatment liquid of the present invention for cold plastic working metallic materials, which comprises 4 to 160 g/l of a metallic soap, 50 to 400 g/l of a solid lubricant, 0.5 to 40 g/l of a surfactant for uniformly dispersing the metallic soap and the solid lubricant, and water.

The aqueous lubrication treatment liquid of the present invention optionally further comprises a colloidal titanium compound in an amount of 10 ppm or more, in the terms of titanium.

Also, the aqueous lubrication treatment liquid of the present invention optionally further comprises 5 to 150 g/l of a binder.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The inventors of the present invention found for the first time that a lubricating film having an excellent lubricating activity not obtained by the conventional aqueous lubrication treatment liquid can be formed on a surface of a metallic article by applying a new type of aqueous lubrication treatment liquid comprising a metallic soap, a solid lubricant, and a surfactant.

Also, the inventors of the present invention further found that another new type of aqueous lubrication treatment liquid containing a colloidal titanium compound in addition to the above-mentioned component, is useful for forming a lubricating film having an excellent lubricating property and a superior resistance to rust on a surface of metallic article, for example, a cold plastic processed steel article.

Furthermore, the inventors of the present invention found that, in the above-mentioned aqueous lubrication treatment liquid, an addition of a binder to the metallic soap, solid lubricant, surfactant, and optionally, colloidal titanium compound is effective for further enhancing the lubricating property thereof, due to the synergistic effect of the binder with the other components, for example, the metallic soap and the colloidal titanium compound.

The present invention was completed based on the above-mentioned findings.

The aqueous lubrication treatment liquid of the present invention comprises, as principal components, 4 to 160 g/l of a metallic soap, 50 to 400 g/l of a solid lubricant, 0.5 to 40 g/l of a surfactant for uniformly dispersing the metallic soap and the solid lubricant in water, and water.

The metallic soap usable for the present invention comprises at least one member selected from salts of fatty acids and hydroxy-fatty acids having 12 to 22 carbon atoms with multivalent metals. The fatty acids and the hydroxy-fatty acids usable for the present invention include lauric acid, myristic acid, palmitic acid, stearic acid, behenic acid, and hydroxystearic acids. A preferable fatty acid is stearic acid. The multivalent metals usable for the present invention are selected from calcium, aluminum, magnesium, barium, and zinc.

A preferable metallic soap for the present invention is a wet state calcium stearate prepared in accordance with Japanese Examined Patent Publication No. 60-45680.

The metallic soap is contained in a dry content of 4 to 160 g/l, preferably 10 to 50 g/l in the aqueous lubrication treatment liquid. If the metallic soap is employed in an amount of less than 4 g/l, the resultant lubricating film on a metallic article exhibits an unsatisfactory lubricating effect. Also, even if the content of the metallic soap is increased to a level above 160 g/l, the lubricating effect of the resultant lubricating film on a metallic article is substantially not increased higher than that resulted from 160 g/l of the metallic soap; rather the lubricating effect of the solid lubricant is restricted by the large amount of the metallic soap.

The solid lubricant usable for the present invention comprises at least one member selected from, for example, molybdenum disulfide, graphite, tungsten disulfide, fluorinated graphite, boron nitride, and talc.

The content of solid lubricant in the treatment liquid is 50 to 400 g/l, preferably 150 to 250 g/l. A content of the solid lubricant of less than 50 g/l does not provide a sufficient formation of a solid lubricating film on the metallic article surface. If the content of the solid lubricant is more than 400 g/l, the lubrication effect becomes saturated so that no further improvement of the lubrication effect is obtained, and the cost of the aqueous lubrication liquid is increased.

In the aqueous lubrication treatment liquid of the present invention, when the metallic soap is employed in a mixing weight ratio of from 2:5 to 1:50 to the solid lubricant, the resultant lubricating film on the metallic article exhibits an excellent lubricating effect.

In the aqueous lubrication treatment liquid of the present invention, a surfactant is employed for dispersing the metallic soap and solid lubricant in water. There is no specific limitation of the type thereof.

Surfactants in general use include nonionic type surfactants, for example, polyoxyethylene alkyl ethers, polyoxyethylene alkylphenyl ethers, polyoxyethylene alkyl esters, and polyoxyethylene sorbitane alkyl esters; anionic type surfactants, for example, fatty acid salts, alkyl sulphates, alkyl sulphonate, alkyl phosphates and alkyl dithiophosphates; cationic type surfactants, for example, aliphatic amine salts, and quarternary ammonium salts; and amphoteric type surfactants, for example, amino acid type and betain type carboxylic acid salts, sulfuric ester salts, sulphonic ester salts, and phosphoric ester salts.

The content of the surfactant in the aqueous lubrication liquid of the present invention is 0.5 to 40 g/l, preferably 5 to 10 g/l. The content of the surfactant in the aqueous lubrication treatment liquid is preferably increased or decreased in response to the content of the solid lubricant. Where the content of surfactant is less than 0.5 g/l, the solid surfactant in the treatment liquid is insufficiently wetted, and a greater quantity than 40 g/l does not increase the dispersing effect of the surfactant to any significant degree.

The aqueous lubrication treatment liquid of the present invention can be supplemented with another additive, for example, a high molecular dispersing agent, defoaming agent, and rust-preventive additive.

The aqueous lubrication treatment liquid of the present invention optionally contains a colloidal titanium compound in addition to the above-mentioned components.

The colloidal titanium compound is preferably in a state of a cloudy solution prepared, for example, by neutralizing a compound of sulphuric acid with titanium or of phosphoric acid with titanium, with an alkali, for example, caustic soda or the like. The content of colloidal titanium in the aqueous lubrication treatment liquid is 10 ppm or more, preferably 10 to 5000 ppm, more preferably 50 to 300 ppm, in terms of titanium.

When the colloidal titanium compound is employed in an amount of less than 10 ppm, the improvement

in the lubricating effect and the rust-preventing effect of the resultant lubricating film on the metallic article surface is not significant. When the colloidal titanium compound is added in an amount of 10 ppm or more, however, the improvement in the lubricating effect and the rust-preventing effect of the resultant lubricating film becomes significant and increases with an increase in the content thereof. Accordingly, the content of colloidal titanium compound in the aqueous lubrication liquid of this invention has no specific upper limit: it is possible to increase the content to a high level as long as the preparation of the aqueous lubrication treatment liquid is possible. Nevertheless, the colloidal titanium compound is usually employed in a content of from 10 to 5000 ppm.

The colloidal titanium compound usable for the present invention is in the form of colloidal particles consisting of negatively charged micelles. Accordingly, the colloidal titanium compound is definitely distinct from fine particles of titanium compounds, for example, titanium dioxide, usable for pigments, which particles are produced by finely pulverizing grains of the compounds, and the resultant particles do not have an electrical charge when dispersed in water.

The aqueous lubrication treatment liquid optionally contains a binder in addition to the above-mentioned components.

The binder comprises at least one member selected from inorganic and organic binder materials and is effective for further enhancing the lubricating effect of the resultant lubricating film on the metallic article surface.

The inorganic binder is not restricted to a specific type of binder and preferably comprises at least one member selected from the borates, phosphates, and silicates mentioned below.

a. Borates

Alkali metal salts, alkali earth metal salts and ammonium salts of HBO_2 , H_3BO_3 , $\text{H}_4\text{B}_2\text{O}_5$, $\text{H}_2\text{B}_4\text{O}_7$, HB_5O_8 , $\text{H}_2\text{B}_6\text{O}_{10}$, $\text{H}_2\text{B}_8\text{O}_{13}$, etc.

b. Phosphates

Alkali metal salts, alkali earth metal salts and ammonium salts of H_3PO_4 , HPO_3 , $\text{H}_4\text{P}_2\text{O}_6$, H_3PO_3 , $\text{H}_4\text{P}_2\text{O}_5$, HPO_2 , H_3PO_2 , $\text{H}_3\text{P}_3\text{O}_9$, and polyphosphoric acids, for example, $\text{H}_4\text{P}_2\text{O}_7$, $\text{H}_5\text{P}_3\text{O}_{10}$, $\text{H}_6\text{P}_{11}\text{O}_{13}$, etc.

c. Silicates

Those expressed by the general formula $\text{M}_2\text{O} \cdot \text{XSiO}_2$, where M denotes an alkali metal atom or alkali earth metal atom and x denotes a positive integer of 1 to 5.

The organic binder is not limited to a specific type of binder, and preferably comprises at least one member selected from water-soluble high molecular compounds, for example, natural high molecular substance such as starch, sea weeds, vegetable mucilages, animal proteins, and fermentation mucilages; semi-synthetic high molecular substances prepared from starch and cellulose; and synthetic polymers, for example, polyvinyl pyrrolidone, polyethylene glycol, and polyvinyl alcohol.

The binder is employed in a solid content of 5 to 150 g/l, preferably 10 to 50 g/l, in the aqueous lubrication treatment liquid of the present invention. This solid content is variable depending on the content of the solid lubricant. If the content of the binder is less than 5 g/l, the improvement in the bonding property of the resultant lubricating film to the metallic article surface is not satisfactory. Also, if the binder is employed in a too large content of more than 150 g/l, the resultant aqueous lubrication treatment liquid exhibits an undesirable high viscosity, and thus the amount of the aqueous lubrication treatment liquid adhered to the surface of the metallic article becomes too large. This large amount of the resultant lubricating film formed on the metallic article surface causes the metallic die, through/which the metallic article is cold plastic worked, to be clogged.

The aqueous lubrication treatment liquid of the present invention can be prepared by dispersing and dissolving the above-mentioned components in predetermined amounts in water in the same way as usually practiced.

When the total content of the components is relatively low, the resultant prepared liquid can be directly used as an aqueous lubrication treatment liquid. If the total content of the components is relatively high, the resultant prepared liquid is directly used or diluted with an additional amount of water and then used as an aqueous lubrication treatment liquid, in response to the type of metallic article, the type of cold plastic working, and the intensity of the working.

The metallic article to be treated by the aqueous lubrication treatment liquid is optionally subjected to a chemical conversion procedure before the lubrication treatment.

There is no specific restriction of the type of the chemical conversion layer on the metallic material, and, for example, zinc phosphate treatment, iron oxalate treatment, cuprous oxide treatment, aluminum fluoride treatment, and titanium fluoride treatment commonly used according to the type of metals, can be used.

The aqueous lubrication treatment liquid of the present invention is applied to a metallic material, usually by an immersion procedure wherein the temperature thereof is maintained at a level between room temperature and 80 °C.

When the aqueous lubrication treatment liquid is applied at a high temperature, the metallic article is also heated, and thus the layer of the aqueous lubrication treatment liquid formed on the metallic article surface can be dried at an enhanced drying efficiency. Nevertheless, if the temperature of the aqueous lubrication treatment liquid becomes too high, the viscosity and concentration of the aqueous lubrication treatment liquid is altered, and thus a complicated control becomes necessary to maintain the viscosity and concentration of the aqueous lubrication treatment liquid at a predetermined level by supplying water thereto.

The lubrication process using the aqueous lubrication treatment liquid of the present invention usually is carried out in the following sequence. The sequence is variable depending on the type of metallic article, surface condition, type of cold plastic working, and grade of reduction.

- ① Degreasing - water rinsing - lubrication treatment according to the present invention - drying
- ② Degreasing - water rinsing - pickling - water rinsing - lubrication treatment according to the present invention - drying (pickling is carried out to remove rust and scale)
- ③ Degreasing - water rinsing - pickling - water rinsing - chemical conversion treatment - water rinsing - lubrication treatment according to the present invention - drying
- ④ Degreasing - water rinsing - chemical conversion treatment - water rinsing - lubrication treatment according to the present invention - drying

The degreasing is optionally carried out when necessary. The pickling is carried out to remove rust and scale from the metallic article surface.

The metallic article is optionally surface-treated by a shot blast treatment or a sand blast treatment or by the above-mentioned chemical conversion procedure, before the lubrication treatment. The type of surface treatment can be chosen in consideration of the type and surface condition of the metallic article, and the type and intensity of the cold plastic working procedure.

By applying the specific aqueous lubrication treatment liquid of the present invention, the resultant solid lubricating film formed on the metallic article surface or on the chemical conversion layer exhibits an excellent lubricating effect and rust-preventive effect in comparison with that derived from the conventional aqueous lubrication treatment liquid.

The present invention offers an aqueous lubrication treatment liquid for cold plastic working of metallic articles by which the metallic articles can be given an excellent lubricating property that enables a satisfactory high reduction of a cold plastic working without seizure and galling, with a high workability, and giving the thus processed products a high rust resistance.

EXAMPLES

The present invention will be further explained by way of Examples and Comparative Examples, which in no way limit this invention.

Examples 1 - 21 and Comparative Examples 1 - 11

In each of these examples and comparative Examples, a bar consisting of a carbon steel (JIS G4051) and having a diameter of 30 mm was subjected to the following procedures.

Degreasing → water rinsing → pickling → water rinsing → chemical conversion treatment → water rinsing → lubrication treatment - drying

In the degreasing stage, the carbon steel bar was treated in a solution containing 20 g/l of Fine Cleaner 4360 (trademark of degreasing agent, a product of Nihon Parkerizing Co.) at 70 °C for 10 min.

In each water rinse stage, the carbon steel bar was treated with running city water at room temperature for 60 sec.

The pickling procedure was carried out by using an Ivit 700 A (trademark: made by Asahi Kagaku K.K.) in an amount of 0.05 g/l at room temperature for 10 minutes.

The chemical conversion procedure was carried out by immersing the carbon steel bar in an aqueous solution containing a zinc phosphate type chemical conversion film-forming agent (trademark: PB181X, made by Nihon Parkerizing K.K.) in an amount of 90 g/l. An accelerator for the chemical conversion film-forming agent (trademark: AC131, made by Nihon Parkerizing K.K.) was applied in an amount of 0.3 g/l at a

temperature of 80 °C for 15 minute, except for Examples 7, 8, 20, and 21 and Comparative Examples 1 and 7, wherein the chemical conversion was not applied.

The lubrication treatment was carried out by immersing the carbon steel bar in the aqueous lubrication treatment liquid having the composition as shown in Table 1 at a temperature of 80 °C for 3 minutes, except for Comparative Examples 6 and 11, and the treatment was carried out at a temperature of 70 °C for 3 minutes.

The drying procedure was carried out by blowing hot air at a temperature of 120 °C for 10 minutes. Usually, the drying procedure can be carried out by leaving the treated metallic article to stand in the ambient atmosphere.

The resultant lubrication treated carbon steel bar was subjected to the cold forging test (cold backward cup extrusion test) as indicated in Table 2.

The lubricating effect was evaluated by measuring a largest depth of a good inner surface of the extruded cup which could be formed without generating galling or fouling in the form of vertical lines on the inside wall surface of the extruded cup. The greater the deepest depth of the good inner surface of the cup, the better the lubricating effect of the resultant lubricating film on the bar surface.

The test results are indicated in Table 1.

Also, the lubrication treated carbon steel bar was subjected to the rust-resistance test as indicated in Table 3. The rust-resistance was evaluated in the following four classes.

Class	Evaluation
4	No rust generated.
3	Rust generated in total area corresponding to less than 20% of entire area of surface of specimen.
2	Rust generated in total area corresponding to 20% to 50% of entire area of surface of specimen.
2	Rust generated in total area corresponding to more than 50% of entire area of surface of specimen.

The test results are indicated in Table 1.

Table 1

Example No.	Item	Composition of aqueous lubrication treatment liquid								Test results	
		Appli- cation of chemical conver- sion	Metallic soap (*)1 (g/l)	Solid lubricant		Colloidal titanium compound (*)5 (ppm)	Binder		Surfac- tant (*)9 (g/l)	Cup depth of good inner surface (mm)	Rust- resist- ance
				Type	Amount (g/l)		Type	Amount (g/l)			
1	Example	yes	40	(*)2	200	-	-	-	5	32	1
2		"	20	"	70	-	(*)6	20	2	38	1
3		"	20	"	300	-	"	20	7	34	1
4		"	60	"	200	-	(*)7	5	5	42	2
5		"	60	(*)3	200	-	(*)6	20	5	48	2
6		"	60	(*)4	200	-	"	20	5	42	2
7		no	60	(*)2	200	-	"	20	5	34	2
8		no	60	(*)4	200	-	"	20	5	30	2
9		yes	10	(*)2	70	50	-	-	1	36	4
10		"	10	"	100	10	-	-	1	44	3
11		"	20	"	200	50	-	-	1	40	4
12		"	150	"	400	100	-	-	5	48	4
13		"	20	(*)4	100	50	-	-	1	46	4
14		"	20	(*)3	200	50	-	-	5	42	4
15		"	20	(*)2	100	30	(*)8	5	1	50	3
16		"	20	"	100	10	"	20	1	48	3

Table 1 (Continued)

Item	Appli- cation of chemical conver- sion	Composition of aqueous lubrication treatment liquid							Test results		
		Metallic soap (*)1 (g/l)	Solid lubricant		Colloidal titanium compound (*)5 (ppm)	Binder		Surfac- tant (*)9 (g/l)	Cup depth of good inner surface (mm)	Rust- resist- ance	
			Type	Amount (g/l)		Type	Amount (g/l)				
Example	No.										
Example	17	yes	10	(*)2	100	50	(*)8	20	1	44	3
	18	"	10	"	70	50	"	20	1	40	3
	19	"	50	"	200	100	"	20	5	54	4
	20	no	20	"	200	50	-	-	5	36	4
	21	no	20	"	200	100	(*)8	20	5	36	4
Compar-	1	no	-	"	200	-	(*)6	20	5	16	1
ative	2	yes	-	"	30	-	-	-	1	16.	1
Example	3	"	-	"	200	-	(*)6	20	5	26	1
	4	"	1	"	200	-	"	3	5	22	1
	5	"	-	"	200	-	-	-	5	20	1
	6	"	(*)10							30	2
	7	no		(*)2	40	10	(*)8	20	1	16	3
	8	yes		"	100	4	"	20	1	28	1
	9	"		"	100	10	"	20	1	28	3
	10	"		"	100	4	"	20	1	20	1
	11	"	(*)10							32	2

Note:

- (*)₁ Metallic salt consisting of wet state calcium stearate (30% by dry solid weight) prepared in accordance with Japanese Examined Patent Publication No. 60-45680.
- (*)₂ Molybdenum disulfide.
- (*)₃ Tungsten disulfide.
- (*)₄ Graphite.
- (*)₅ Neutralization product of titanium phosphate solution with caustic soda, having pH of 8.
- (*)₆ Trisodium phosphate.
- (*)₇ Carboxymethylcellulose.
- (*)₈ Polyvinyl pyrrolidone.
- (*)₉ Polyoxyethylenenonylphenoether, HLB 15, made by Daiichi Kogyo Seiyaku K.K., trademark: Noigen EA150.
- (*)₁₀ ... Sodium soap type lubricant, (trademark: LUB-4601, made by Nihon Parkerizing K.K.), in an content of 70 g/l.

Table 2

Cold Backward Cup Extrusion Test			
Testing machine	Cold forging press machine MSF200 (trademark) made by Fukui Kikai K.K.		
Test condition	Test piece	S20C • SUS410L 30 mm ϕ x 18 - 43 mm (cylinder)	
	Temperature	Room temperature	
	Working speed	30 spm	
	Reduction of area	50%	
	Tool	Punch Die	20.2 ϕ SKH53 30.0 ϕ SKD11

Table 3

Rust-Resistance Test	
Testing condition	Constant temperature of 50 °C constant humidity of 95% Time: 24 hours
Testing machine	Program constant temperature constant humidity vessel GLMP-62 (Trademark) made by K.K. Futaba Kagaku
Specimen	Length: 50 mm Diameter: 30 mm

In view of Table 1, in Examples 1 to 8 wherein the lubrication treatment liquid comprised the metallic soap, solid lubricant and surfactant and was free from the colloidal titanium compound, the resultant cup depth of the good inner surface was in the range of 30 to 48 mm and greater than that of Comparative Examples 1 to 5, in which the content of the metallic soap was at a low level of 4 g/l or less and in Comparative Examples 2 and 6 in which the content of the solid lubricant was less than 50 g/l. Accordingly, it is clear that the aqueous lubricant treatment liquids of the present invention free from the colloidal titanium compound provide an excellent lubricating effect on the metallic article, which effect was not obtained by the conventional aqueous lubrication treatment liquids.

In Examples 2 to 6, in which the aqueous lubrication treatment liquids contained 5 g/l or more of a binder, the resultant cup depth of the good inner surface was in the range of 34 to 38 mm and larger than the 32 mm of that in Example 1, in which no binder was employed. Therefore, it is clear that the addition of the binder effectively further enhances the lubricating effect of the aqueous lubrication treatment liquid of the present invention.

In Examples 7 and 8, in which no chemical conversion layer was formed on the carbon steel rod before the lubrication treatment, the resultant cup depth of the good inner surface was 30 to 34 mm, which was a little lower than that in Examples 2 to 6 in which the chemical conversion treatment was applied, and was similar to or a little higher than that in Comparative Example 6, in which a conventional aqueous lubrication treatment liquid was used.

In Examples 9 to 21 in which the aqueous lubrication treatment liquids contained a colloidal titanium compound, the resultant cup depth of the good inner surface was in the range of 36 to 54 mm, which is larger than that of the 30 to 48 mm in Examples 1 to 8 in which the colloidal titanium compound was not employed. Therefore, it is clear that the addition of the colloidal titanium compound effectively enhances the lubricating effect of the aqueous lubrication treatment liquid of the present invention.

In Comparative Examples 7 to 11, in which the solid lubricant is in a low content of less than 50 g/l, and in Comparative Examples 8 to 32 in which the metallic soap or colloidal titanium compound is in the low content of less than 4 g/l or less than 10 ppm, the resultant cup depth of the good inner surface was in the range of 16 to 32 mm, and was unsatisfactory.

Further, in Examples 15 to 19, in which a binder was employed, the resultant cup depth of the good inner surface was 40 to 54 mm, which was larger than the 36 to 4 mm in Examples 9 to 14 in which no binder was employed. Therefore, it is clear that the addition of a binder effectively enhances the lubricating effect of the aqueous lubrication treatment liquid of the present invention.

In Examples 20 and 21, in which the chemical conversion was not applied, the resultant lubricating effect was a little lower than that in Examples 15 and 16 in which the chemical conversion was applied, but was higher than that in Comparative Example 11 in which a conventional aqueous lubrication treatment liquid was employed.

In Examples 1 to 8 and Comparative Examples 1 to 6, in which the colloidal titanium compound was not employed, the resultant rust resistance was unsatisfactory (class 1 or 2), whereas in Examples 9 to 21 in which the colloidal titanium compound was employed, the resultant rust resistance was satisfactory (class 3 or 4). Accordingly, it is clear that the addition of the colloidal titanium compound effectively enhances the rust-preventive effect of the aqueous lubrication treatment liquid of the present invention.

Examples 22 to 28 and Comparative Examples 12 to 18

In each of Examples 22 to 28 and Comparative Examples 12 to 18, the same procedures as those in Example 1 were carried out, with the following exceptions.

The metallic article to be treated was a 13Cr stainless steel bar (SUS 410L, JIS G4303) having a diameter of 30 mm.

5 The pickling was carried out by using an aqueous solution of 7% of HNO₃ and 3% of HF at room temperature for 10 minutes.

The chemical conversion treatment was carried out by immersing the stainless steel bar in an aqueous solution containing 40 g/l of an oxalate type chemical conversion film-forming agent (trademark: FBA1, made by Nihon Parkerizing K.K.), 20 g/l of an oxalate type chemical conversion film-forming additive
10 (trademark: FBA2, made by Nihon Parkerizing K.K.), and 1 g/l of an oxalate type chemical conversion film-forming accelerator (trademark: AC-16, made by Nihon Parkerizing K.K.) at a temperature of 90 °C for 15 minutes.

The lubrication treatment was carried out by immersing the stainless steel bar in an aqueous lubrication treatment liquid having the composition as shown in Table 4, at a temperature of 80 °C for 3 minutes,
15 except that in Comparative Examples 14 and 18 the immersion treatment was carried out at a temperature of 70 °C for 3 minutes.

The treated stainless steel bar was subjected to the cold forging test as indicated in Table 2.

The test results are shown in Table 4.

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Table 4

Item Example No.	Composition of aqueous lubrication treatment liquid							
	Metallic soap (*)1 (g/l)	Solid lubricant		Colloidal titanium compound (*)5 (ppm)	Binder		Surfac- tant (*)9 (g/l)	Cold forging test Depth of good inner surface of cup (mm)
		Type	Amount (g/l)		Type	Amount (g/l)		
Example 22	20	(*)2	300	-	(*)6	20	7	38
23	60	(*)3	200	-	"	20	5	54
24	60	(*)4	200	-	"	20	5	48
25	10	(*)2	100	10	-	-	1	46
26	20	"	200	50	-	-	1	44
27	20	(*)3	200	50	-	-	5	54
28	50	(*)2	200	100	(*)8	20	5	58
Compar- ative	-	"	200	-	(*)6	20	5	28
13	1	"	200	-	"	3	5	28
Example 14 (*)10								32
15	0.5	(*)2	100	4	(*)8	20	1	32
16	-	"	100	10	"	20	1	32
17	-	"	100	4	"	20	1	28
18	(*)10							32

Note: (*)1 - (*)10 Same as defined above.

In Examples 22 to 24 in accordance with the present invention and free from the colloidal titanium compound, the depth of the good inner surface of cup was 38 to 54 mm, which is larger than the 28 to 32 mm in Comparative Examples 12 to 14. Accordingly, it is clear that, when applied to a stainless steel article, the aqueous lubrication treatment liquid of the present invention exhibits an excellent lubricating effect not obtained by the conventional lubrication treatment liquid.

In Examples 25 to 28 in which the colloidal titanium compound was employed, the depth of the good inner surface of cup was 44 to 58 mm, which is larger than the 28 to 32 mm in Comparative Examples 15 to 18 in which the contents of the metallic soap and solid lubricant fall outside of the scope of the present invention.

5 Also, it is clear that the lubricating effect of the aqueous lubrication treatment liquids in Examples 25 to 28, in which the colloidal titanium compound was added, is higher than that in Examples 22 to 24 in which the colloidal titanium compound was not employed.

10 Examples 29 to 32 and Comparative Examples 19 to 22

In each of Examples 29 to 32 and Comparative Examples 19 to 22, the same procedures as those in Example 1 were carried out, with the following exceptions.

The metallic article to be treated was a titanium wire (Second type, JIS H4600) having a diameter of 3
15 mm.

The pickling was carried out by using an aqueous solution containing 7% of HNO_3 and 3% of HF at room temperature for 10 minutes.

The chemical conversion treatment was carried out by immersing the titanium wire in an aqueous solution containing 36 g/l of a fluoride type chemical conversion film-forming agent (trademark: MET-3851,
20 made by Nihon Parkerizing K.K.) at a temperature of 60°C for 3 minutes.

The lubrication treatment was carried out by immersing the titanium wire in an aqueous lubrication treatment liquid having the composition as indicated in Table 5 at a temperature of 80°C for 3 minutes, except that, in Comparative Example 22, the treatment temperature was 70°C.

The resultant treated titanium wire was subjected to the cold wire drawing test as indicated in Table 6.

25 The test results are shown in Table 5.

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Table 5

Item	Composition of aqueous lubrication treatment liquid						Cold drawing test				
	Metallic soap (*)1 (g/l)	Solid lubricant		Colloidal titanium compound (*)5 (ppm)	Binder (*)8 (g/l)	Surfactant (*)9 (g/l)	Pass (*)11				
		Type	Amount (g/l)				1-st	2-nd	3-rd	4-th	5-th
Example No.											
Example 29	10	(*)2	100	10	-	1	good	good	good	good	good
30	20	"	100	50	-	1	"	"	"	"	"
31	20	(*)3	200	50	-	5	"	"	"	"	"
32	50	(*)2	200	100	20	5	"	"	"	"	"
Comparative	0.5	"	100	-	20	1	"	"	"	"	bad
20	-	"	100	10	20	1	"	"	"	"	"
Example 21	-	"	100	-	20	1	"	"	"	"	"
22	(*)10						"	"	"	"	"

Note: (*)₁ - (*)₁₀ Same as defined above.

(*)₁₁ Evaluation

Good: No galling formed during drawing procedure.

Bad: Galling formed.

Table 6

Wire Drawing Test			
Testing machine	Single head type wire drawing machine		
Test condition	Test piece		Titanium (second type) 3 mm $\varnothing$ x 12 mm
	Temperature		Room temperature
	Drawing speed		50 mm/min
	Pass condition	1-pass 2-pass 3-pass 4-pass 5-pass	Die diameter 2.7 mm $\varnothing$, Reduction 19.0% Die diameter 2.4 mm $\varnothing$, Reduction 21.0% Die diameter 1.15 mm $\varnothing$, Reduction 19.7% Die diameter 1.9 mm $\varnothing$, Reduction 21.7% Die diameter 1.7 mm $\varnothing$, Reduction 19.9%

Table 5 clearly indicates that, in Examples 29 to 32 in accordance with the present invention, the resultant lubrication treated titanium wires exhibited a high resistance to galling even after five passes of the cold drawing test whereas, in Comparative Examples 19 to 22, the resultant lubrication treated titanium wire had galls at the fifth pass of the cold drawing test.

Claims

1. An aqueous lubrication treatment liquid for cold plastic working metallic materials, comprising 4 to 160 g/l of a metallic soap, 50 to 400 g/l of a solid lubricant, 0.5 to 40 g/l of a surfactant for uniformly dispersing the metallic soap and the solid lubricant, and water.
2. The aqueous lubrication treatment liquid as claimed in claim 1, wherein the metallic soap comprises at least one member selected from salts of calcium, aluminum, magnesium, barium and zinc with fatty acids and hydroxy fatty acids having 12 to 22 carbon atoms.
3. The aqueous lubrication treatment liquid as claimed in claim 2, wherein the acids for the metallic soap are selected from the group consisting of lauric acid, myristic acid, palmitic acid, stearic acid, behenic acid and hydroxy stearic acid.
4. The aqueous lubrication treatment liquid as claimed in any one of the preceding claims, wherein the metallic soap is in a weight ratio of from 2:5 to 1:50 to the solid lubricant.
5. The aqueous lubrication treatment liquid as claimed in any one of the preceding claims, wherein said solid lubricant comprises at least one member selected from the group consisting of molybdenum disulfide, graphite, tungsten disulfide, fluorinated graphite, boron nitride and talc.
6. The aqueous lubrication treatment liquid as claimed in any one of the preceding claims which further comprises a colloidal titanium compound in an amount of 10 ppm or more in terms of titanium.
7. The aqueous lubrication treatment liquid as claimed in claim 6, wherein the colloidal titanium compound is in an amount of from 10 to 5000 ppm in terms of titanium.
8. The aqueous lubrication treatment liquid as claimed in claim 6 or claim 7, wherein the colloidal titanium compound is prepared by neutralizing at least one member selected from the group consisting of compound of sulfuric acid with titanium and of phosphoric acid with titanium.
9. The aqueous lubrication treatment liquid as claimed in any one of the preceding claims, which further comprises 6 to 150 g/l of a binder.
10. The aqueous lubrication treatment liquid as claimed in claim 9, wherein the binder comprises at least one member selected from the group consisting of inorganic borates, phosphates and silicates and water-soluble organic high molecular substances.



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EUROPEAN SEARCH REPORT

Application Number

EP 90 30 8707

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	DE-A-1 030 495 (METALLGESELLSCHAFT AG) * Claims 1-8; column 3, lines 6-43 * - - -	1-3,9,10	C 10 M 173/02 // (C 10 M 173/02 C 10 M 125:00
A	FR-A-2 102 283 (SOC. CONTINENTALE PARKER) * Claim * - - -	1-3,9,10	C 10 M 125:02 C 10 M 125:10 C 10 M 125:22
A	EP-A-0 261 438 (LONZA) * Claims 1-5; column 2, line 7 - column 3, line 9 * - - -	1,5,9,10	C 10 M 125:26 C 10 M 129:40) (C 10 N 10/00 C 10 N 40:24)
A	EP-A-0 270 836 (NIHON PARKERIZING) * Claims 1-5; page 7, line 4 * - - -	1-3,6-8	
P,X	DE-A-3 922 464 (NIPPON DENSO) * Claims 1-3 * - - - - -	1-10	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C 10 M
The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of search 20 November 90	Examiner RO TSAERT L.D.C.
CATEGORY OF CITED DOCUMENTS X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons ----- &: member of the same patent family, corresponding document			