(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 3 305 882 A1

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

(43) Date of publication:
11.04.2018 Bulletin 2018/15

(21) Application number: **16802886.8**

(22) Date of filing: **24.03.2016**

(51) Int Cl.:

C10M 173/00 *(2006.01)*	***C23C 22/83*** *(2006.01)*
C10M 101/02 *(2006.01)*	***C10M 101/04*** *(2006.01)*
C10M 103/06 *(2006.01)*	***C10M 105/24*** *(2006.01)*
C10M 107/04 *(2006.01)*	***C10M 107/06*** *(2006.01)*
C10M 109/00 *(2006.01)*	***C10M 129/40*** *(2006.01)*
C10N 10/02 *(2006.01)*	***C10N 10/04*** *(2006.01)*
C10N 10/12 *(2006.01)*	***C10N 20/00*** *(2006.01)*
C10N 20/06 *(2006.01)*	***C10N 30/00*** *(2006.01)*
C10N 30/06 *(2006.01)*	***C10N 40/20*** *(2006.01)*

(86) International application number:
PCT/JP2016/059437

(87) International publication number:
WO 2016/194447 (08.12.2016 Gazette 2016/49)

(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 MD

(30) Priority: **29.05.2015 JP 2015109579**

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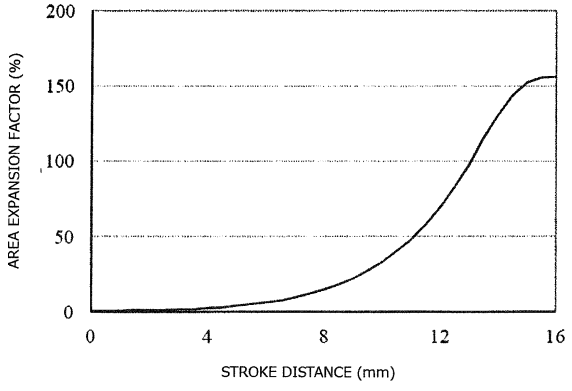
(54) WATER-CONTAINING LUBRICATING FILM AGENT, SURFACE TREATED METALLIC MATERIAL, AND METHOD FOR FORMING WATER CONTAINING-LUBRICATING FILM OF METALLIC MATERIAL

(57) Provided are a lubricant coating agent which can reduce industrial waste (environmental conservation), and impart excellent lubricity in a water-containing state even in the case of carrying out no forced drying after a lubrication treatment step (drying at room temperature, leaving at room temperature), or even to metallic products in shapes that are difficult to dry completely, e.g., the inner surfaces of steel pipes, as well as techniques related thereto.

A water-containing lubricant coating agent, on use in metal plastic working carried out in a water-containing state with a water content of 3 to 50 mass%, characterized in that at least one lipophilic lubricating component (A) and/or at least one solid lubricant (B) with cleavability are dispersed in water, and furthermore, at least one water-soluble lubricating component (C) selected from the group consisting of fatty acid components having 12 to 20 carbon atoms is dissolved in a water-phase side at a mass ratio of (C)/[(A) + (B)] = 0.05 to 0.5.

FIG. 3

[Fig. 3]



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Description

Technical Field

[0001] The present invention relates to a water-containing lubricant coating agent for imparting excellent lubricity to a metal material surface , in particular, such as iron and steel, stainless steel, and aluminum, and a surface-treated metal material with a lubricant coating formed with the use of the agent, as well as techniques related thereto. More particularly, the present invention relates to a lubricant coating agent for imparting excellent lubricity in plastic working such as forging, wire drawing, tube drawing, heading of the metal material, and press forming of a plate, and techniques related thereto.

Background Art

[0002] In general, in plastic working of metal materials such as iron and steel and stainless steels, for the purposes of preventing from seizure and galling caused by metal contact between materials to be worked and tools, and imparting corrosion resistance, coatings that have lubricity and corrosion resistance are provided on the metal material surfaces. Such coatings include two types: a reactive type of forming, on a metal material surface, a chemical conversion coating by chemical reaction, and then further forming a lubricant thereon; and a non-reactive type of physically forming a lubricant on a metal material surface.

[0003] In the case of the former reactive type, lubricant coatings that have a two-layer structure obtained by forming, on a metal material surface, a chemical conversion coating such as a phosphate coating or an oxalate coating that has a role as a carrier, and then further applying a lubricant such as a lime soap, a molybdenum disulfide, or an oil; and lubricant coatings that have a three-layer structure (chemical conversion coating /metal soap coating /unreacted soap coating) obtained by providing a chemical conversion coating, and then reactive-coating with a reactive soap such a sodium stearate are widely used. In particular, the latter lubricant coatings that have the three-layer structure are known to be capable of producing excellent lubricity in a stable manner even in heavy working regions.

[0004] However, the chemical conversion treatment with the chemical reaction and the reactive soap require solution management, temperature management for controlling the chemical reaction, removal and disposal of sludge as a reaction by-product, and disposal and renewal due to solution deterioration. For the purpose of global environmental conservation in recent years, the reduction of industrial waste has become a great problem. To that end, lubricant coating agents and treatment methods which produce no waste have been desired.

[0005] As a lubricant coating agent for solving the problem mentioned previously, Patent Literature 1 discloses an aqueous lubricant composition for plastic working of metal materials, which contains: (a) at least one water-soluble resin selected from the group consisting of a water-soluble polyether compound and water-soluble polyester compound with specific strength and elongation; (b) at least one water-soluble inorganic salt selected from the group consisting of a phosphate, a vanadate, a borate, a silicate, and a tungstate; and water, where the solid content meets (b)/(a) = 0.1 to 5 in weight ratio. This lubricant coating agent is a non-reactive coating-type lubricant without the generation of sludge unlike the chemical conversion treatment with the chemical reaction and the reactive soap, and without solution deterioration. However, lubricant coatings containing a water-soluble inorganic salt as main component are not capable of exhibiting favorable lubricity under the condition that the lubricant coatings contain water, and there is thus a need to dry the lubricant coating forcibly with an oven, a jet heater, or the like after lubrication treatment steps. Furthermore, even when the lubricant coatings are dried completely, the lubricant coatings containing a water-soluble inorganic salt as main component absorb moisture of water vapor in the atmosphere, thereby decreasing the lubricity, and there is thus a need to dry the coatings again before working, or control the humidity in the plants to keep the humidity low. In addition, depending on the shape of the metal material (for example, in the case of forming a lubricant coating on the inner surface of a steel pipe), the lubricant coating may be difficult to dry completely.

Citation List

Patent Literature

[0006] Patent Literature 1: JP 5224251

Non Patent Literature

[0007] Non Patent Literature 1: Shinobu KOMIYAMA et al.: Technical report/Nihon Parkerizing Co., Ltd., (2014), p. 3 to 10

Summary of Invention

Technical Problem

[0008] To deal with the problems of the prior art mentioned previously, a main object of the present invention is to provide a lubricant coating agent which can reduce industrial waste (environmental conservation), and impart excellent lubricity in a water-containing state even in the case of carrying out no forced drying after a lubrication treatment step (drying at room temperature, leaving at room temperature), or even to metallic products in shapes that are difficult to dry completely, e.g., the inner surfaces of steel pipes, as well as techniques related thereto.

Solution to Problem

[0009] The inventors have found, as a result of earnest studies for solving the problem mentioned previously, that the problem can be solved by a lubricant coating agent that has a lipophilic lubricating component and/or a solid lubricant dispersed in water, where a water-soluble lubricating component that has a specific structure and property is dissolved in a water-phase side at a predetermined ratio, thereby leading to the completion of the present invention.

[0010] More specifically, the present invention provides an agent for water-containing lubricant coating (referred to as "water-containing lubricant coating agent" hereinafter) on use in metal plastic working carried out in a water-containing state with a water content of 3 to 50 mass%, where at least one lipophilic lubricating component (A) and/or at least one solid lubricant (B) with cleavability are dispersed in water, and furthermore, at least one water-soluble lubricating component (C) selected from the group consisting of fatty acid components having 12 to 20 carbon atoms is dissolved in a water-phase side at a mass ratio of (C)/[(A) + (B)] = 0.05 to 0.5, more preferably 0.1 to 0.3. The upper limit of the water content is 50 mass% or less, preferably 30 mass% or less. The lower limit of the water content is 3 mass% or more, preferably 5 mass% or more, further preferably 7.5 mass% or more, further preferably 10 mass% or more, and further preferably 12.5 mass% or more, and the most preferred lower limit is 15 mass% or more.

[0011] The water-soluble lubricating component (C) is preferably at least one selected from the group consisting of sodium salts and potassium salts of straight-chain saturated fatty acids of a lauric acid (carbon number: 12), a tridecanoic acid (carbon number: 13), a myristic acid (carbon number: 14), a pentadecanoic acid (carbon number: 15), a palmitic acid (carbon number: 16), heptadecanoic acid (carbon number: 17), stearic acid (carbon number: 18), and arachidic acid (carbon number: 20).

[0012] The water-soluble lubricating component (C) is more preferably a sodium salt or a potassium salt of a straight-chain saturated fatty acid having 15 to 18 carbon atoms, and most preferably at least one selected from the group consisting of a sodium stearate and a potassium stearate that are straight-chain saturated fatty acid salts having 18 carbon atoms.

[0013] It is preferable to use, for the lipophilic lubricating component (A), at least one selected from the group consisting of an oil, an extreme-pressure agent, a metal soap and a wax, which preferably have a solubility parameter (SP value) of 10 or less, more preferably 9 or less. At least one selected from the group consisting of mineral oils, animal and plant oils and fats, and synthetic oils can be used as the oil. At least one selected from the group consisting of phosphorus-based extreme-pressure agents, sulfur-based extreme-pressure agents, organomolybdenum-based extreme-pressure agents, and organozinc-based extreme-pressure agents can be used as the extreme-pressure agent. At least one selected from the group consisting of metal salts other than sodium salts and potassium salts of fatty acids having 12 to 20 carbon atoms can be used as the metal soap. At least one selected from the group consisting of a polyethylene wax, a polypropylene wax, a carnauba wax, and a microcrystalline wax can be used as the wax.

[0014] The solid lubricant (B) which can be used for the water-containing lubricant coating agent according to the present invention is not to be considered particularly limited as long as the lubricant has cleavability, but preferably has a layered clay mineral, further preferably carrier particles. At least one selected from the group consisting of natural products and synthetic products of a smectite group, a vermiculite group, a mica group, a brittle mica group, a pyrophyllite group, and a kaolinite group can be used as the layered clay mineral. The carrier particles refer to particles including the lipophilic lubricating component between particles of and/or between layers of the layered clay mineral. The inclusion amount of the lipophilic lubricating component in the carrier particles is preferably 5 mass% or more, and more preferably 8 mass% or more in mass ratio to the total mass of the carrier particles.

[0015] In addition, solid lubricants other than the layered clay mineral and the carrier particles include at least one poorly soluble crystalline inorganic salts selected from the group consisting of phosphates, carbonates, oxalates, sulfates, metal hydroxides, and metal oxides, other than sodium salts and potassium salts.

[0016] The average particle size (volumetric basis) of the solid lubricant (B), which is obtained by a laser diffraction method, is preferably 30 μm or less, more preferably 20 μm or less, and further preferably 10 μm or less.

[0017] The water-containing lubricant coating agent according to the present invention can contain, as a binder, at least one selected from the group consisting of a water-soluble inorganic salt, a water-soluble organic salt, and a water-

based resin.

[0018] The problem mentioned previously can be also solved by a water-containing lubricant coating formed on a metal material surface with the use of the water-containing lubricant coating agent according to the present invention, which is characterized by a water content of 3 to 50 mass%. The upper limit of the water content is 50 mass% or less, preferably 30 mass% or less. The lower limit of the water content is 3 mass% or more, preferably 5 mass% or more, further preferably 7.5 mass% or more, further preferably 10 mass% or more, and further preferably 12.5 mass% or more, and the most preferred lower limit is 15 mass% or more.

[0019] The problem mentioned previously can be also solved by a surface-treated metal material characterized in that a lubricant coating in a water-containing state, formed on the metal material surface with the water-containing lubricant coating agent according to the present invention, is formed such that the coating amount of the lubricant coating is 0.1 g/m^2 or more, preferably 3 g/m^2 or more, further preferably 5 g/m^2 or more.

[0020] The problem mentioned previously can be also solved by a method for forming a water-containing lubricant coating for a metal material, which includes a contact step of bringing the metal material into contact with the water-containing lubricant coating agent according to the present invention, characterized in that the metal material is brought into contact at a treatment temperature at which the water-soluble lubricating component (C) can be dissolved in a water-phase side of the water-containing lubricant coating at a mass ratio of (C)/[(A) + (B)] = 0.05 to 0.5, more preferably 0.1 to 0.3 in the contact step.

[0021] The problem mentioned previously can be also solved by the method for forming a water-containing lubricant coating for a metal material, characterized in that the method further includes, before the contact step, a chemical conversion treatment step where a chemical conversion coating is coated on the metal material surface.

Effects of Invention

[0022] According to the present invention, the previously mentioned water-containing lubricant coating agent, surface-treated metal material, and method for forming a water-containing lubricant coating for a metal material are applied, thereby making it possible to impart excellent lubricity even in the case of carrying out no forced drying in a drying furnace after a lubrication treatment step, in the case of having no choice but to carry out working with the lubricant coating in a water-containing state such as when metallic products have shapes that are difficult to dry completely, e.g., the inner surfaces of steel pipes, or in the case when the lubricant coating absorbs moisture in the atmosphere even after completely drying the coating.

Brief Description of Drawings

[0023]

Fig. 1 is a diagram illustrating a method for an upsetting-ball ironing tribo-test according to an example.

Fig. 2 is a diagram illustrating the shape of a surface subjected to an ironing process in the upsetting-ball ironing tribo-test in Fig. 1.

Fig. 3 is a graph showing the relationship between an ironing distance (stroke distance) and an area expansion ratio.

Description of Embodiments

[0024] The water-containing lubricant coating agent according to the present invention is one where at least one lipophilic lubricating component (A) and/or at least one solid lubricant (B) with cleavability are dispersed in water, and furthermore, characterized in that as a water-soluble lubricating component (C), a fatty acid component that has a specific structure is dissolved in a water-phase side at a mass ratio of (C)/[(A) + (B)] = 0.05 to 0.5, more preferably 0.1 to 0.3. A lubricant coating formed on a metal material surface with the use of the foregoing lubricant coating agent can exhibit excellent lubricity as long as the water content falls within the range of 3 to 50 mass%, even the lubricant coating is in a water-containing state. In the case of the coating-type lubricant coating agent containing, as its main component, a water-soluble inorganic salt as typified by Patent Literature 1 mentioned previously, when the lubricant coating is in a water-containing state, the followability of the lubricant coating with respect to area expansions during working may be deceased, thereby decreasing lubricity. In contrast, the water-containing lubricant coating agent according to the present invention is characterized in that the water-soluble fatty acid component is dissolved in the water-phase side of the lubricant coating agent at the predetermined ratio. In the water-containing lubricant coating formed with the lubricant coating agent, the water-soluble fatty acid component is condensed to a concentration nearly close to saturation in the water contained by the lubricant coating at the process of water evaporation in the lubricant coating after lubrication treatment, and furthermore, the excess water-soluble fatty acid component no longer dissolved will exist as a continuous coating (not granular) in the water-containing lubricant coating. The thus structured lubricant coating has excellent

followability with respect to area expansions during working, and exhibits favorable lubricity even with the lubricant coating in a water-containing state, as long as the water content falls within the range mentioned previously. In particular, the present invention is preferred when there is no drying furnace after lubrication treatment, and when complete drying is impossible, such as for the inner surfaces of steel pipes.

[0025] The upper limit of the water content in the water-containing lubricant coating according to the present invention is 50 mass% or less, preferably 30 mass% or less. The lower limit of the water content is 3 mass% or more, preferably 5 mass% or more, further preferably 7.5 mass% or more, further preferably 10 mass% or more, and further preferably 12.5 mass% or more, and the most preferred lower limit is 15 mass% or more. When the upper limit of the water content exceeds 50 mass%, the lubricant coating may become fragile, thereby decreasing the lubricity. The lower limit of the water content is preferably low from the perspective of lubricity, and may be less than 3 mass% without any problem. However, from the perspective of productivity, for example, shapes with poor drying performance like the inner surfaces of steel pipes have the problem of significantly decreased productivity, such as a drying time setting required to be extremely long in order to adjust the water content to less than 3 mass%, or an incidental facility required for accelerating drying performance by circulating hot air into the steel pipes with a jet heater or the like, and moreover, failure to achieve a water content of less than 3 mass% in some cases, e.g., in the case of high humidity in the plant. Therefore, from both aspects of lubricity and productivity, the lower limit of the water content is 3 mass% or more, preferably 5 mass% or more, further preferably 7.5 mass% or more, further preferably 10 mass% or more, and further preferably 12.5 mass% or more, and most preferably, 15 mass% or more.

[0026] The adjustment of the water content will be described. For example, when a metal material surface is brought into contact with the water-containing lubricant coating with the total solid content concentration of 15 mass%, water and the solid content are adhered to the metal material at a mass ratio of 85 : 15 immediately after lubricating treatment (no water evaporated yet), and the water content in this case is thus 85 mass%. With this water content, the lubricant coating is fragile, and favorable lubricity is thus not obtained. When the metal material is dried from this condition, the water content is decreased with water evaporation in the lubricant coating. The adjustment of the water content refers to an operation carried out from an initial state with a water content in excess of 50 mass% until the water content falls within the range of 3 to 50 mass%. More specifically, although the following suggestion is not necessarily appropriate because the evaporation rate of water in the water-containing lubricant coating varies depending on the shape of the metallic product, the temperature in the plant, and the humidity condition, the water content may be adjusted such that the water content is 50 mass% or less, more preferably 30 mass% or less, by setting the leaving time after lubrication treatment to be longer under the condition that is exposed in a high-humidity environment or that is less likely to be dried, such as at the inner surface of a steel pipe. When a forced drying step with an oven is provided after lubrication treatment, the water content can be adjusted to 50 mass% or less in a shorter time.

[0027] In addition, when the completely dried (water content: 0 mass%) lubricant coating is left in a high-humidity environment, the lubricant coating absorbs moisture, thereby turning into a water-containing lubricant coating, but as long as the water content is 3 to 50 mass%, the lubricity can be maintained at a practical level.

[0028] In addition, the water-containing lubricant coating according to the present invention is defined as one that is fixed without flowing on a metal material surface even in a water-containing state. For example, the water-containing lubricant coating is considered distinguished from a lubricant for use in liquid form like a water-soluble cutting agent. As long as the water-containing lubricant coating does not easily flow on metal material surface, the viscosity is not to be considered limited specifically, but for example, in the case of a lubricant coating with a water content within the range of 3 to 50 mass%, the viscosity at 20°C (B-type viscometer, JIS Z8803) is 250 mPa·s or more. As long as the water content in the lubricant coating is 50 mass% or less, the lubricant coating is fixed without flowing on the metal material surface. It is to be noted that the previously mentioned water-soluble cutting agent is not considered to form any lubricant coating, but in many cases, the water content of the water-soluble cutting agent is typically 90 mass% or more, and the kinematic viscosity thereof at 20°C is approximately 1 mPa·s.

[0029] There is a need for the water-soluble lubricating component (C) to be dissolved in a water-phase side of the water-containing lubricant coating agent at a mass ratio of (C)/[(A) + (B)] = 0.05 to 0.5, more preferably 0.1 to 0.3. When the proportion of the water-soluble lubricating component falls below 0.05, a continuous coating of the fatty acid component is made less likely to be formed in the water-containing lubricant coating, and the lubricity may be thus decreased. When the proportion of the water-soluble lubricating component (C) exceeds 0.5, the whole water-containing lubricant coating may become fragile, thereby decreasing the lubricity.

[0030] In the water-containing lubricant coating agent according to the present invention, a saturated fatty acid having 12 to 20 carbon atoms and/or a sodium salt or 9 potassium salt of an unsaturated fatty acid can be used as the water-soluble lubricating component (C). In addition, a water-solubilized adduct of the fatty acid having 12 to 20 carbon atoms with an ethylene oxide (EO) and/or a propylene oxide (PO) can be also used. In this case, the total addition molar number of EO and PO is not particularly limited, as long as water solubility can be ensured, but for example, 20 moles or more.

[0031] Specifically, for example, a sodium salt, a potassium salt, an EO adduct, or a PO adduct of at least one straight-chain saturated fatty acid selected from the group consisting of lauric acid (carbon number: 12), tridecanoic acid (carbon

number: 13), myristic acid (carbon number: 14), pentadecanoic acid (carbon number: 15), palmitic acid (carbon number: 16), heptadecanoic acid (carbon number: 17), stearic acid (carbon number: 18), and arachidic acid (carbon number: 20); a sodium salt, a potassium salt, an EO adduct, or a PO adduct of at least one branched-chain saturated fatty acid selected from the group consisting of isopalmitic acid (carbon number: 16) and isostearic acid (carbon number: 18); and a sodium salt, a potassium salt, an EO adduct, or a PO adduct of at least one unsaturated fatty acid selected from the group consisting of oleic acid (carbon number: 18), linoleic acid (carbon number: 18), and ricinolic (ricinoleic) acid (carbon number: 18) can be used. In order to further enhance the lubricity, the number of double bonds is preferably 2 or less in the unsaturated fatty acid component. In addition, the straight-chain fatty acid salt is more preferred in terms of lubricity than the branched-chain fatty acid salt. Furthermore, a sodium salt or a potassium, or an EO adduct or a PO adduct obtained from a natural fatty acid such as a beef tallow soap may be used as long as the carbon number falls within the range mentioned previously.

[0032] In these fatty acid components, it is more preferable to use a sodium salt or a potassium salt than an EO adduct and a PO adduct from the perspective of lubricity. The reasons of using a sodium salt or a potassium salt of the fatty acid are because of high solubility in water and excellent coating continuity in the water-phase side when a water-containing lubricant coating has been formed. More specifically, while the solubility in water varies depending on the type of the fatty acid component, it is because there is a temperature that can dissolve all of the fatty acid components mentioned previously in the proportion of (C)/[(A) + (B)] = 0.05 to 0.5 in the range of 20 to 90°C which is a common lubrication treatment temperature.

[0033] Among the fatty acid components mentioned previously, the sodium salts or potassium salts of straight-chain saturated fatty acids having 15 to 18 carbon atoms are more preferred from the perspective of lubricity, and the sodium salt or potassium salt of stearic acid is most preferred. The reason therefor will be mentioned below. While the more carbon number of the fatty acid is more advantageously for forming a continuous coating of the fatty acid component in the water-containing lubricant coating, the solubility in water decreases with increased carbon number of the fatty acid. More specifically, there is a trade-off relationship between the continuity as a coating of the fatty acid component in the water-containing lubricant coating and the saturated concentration in water. For this reason, among sodium salts or potassium salts of the fatty acids having 12 to 20 carbon atoms, the salts having 15 to 18 carbon atoms are more preferred, and the sodium salt or potassium salt of stearic acid having 18 carbon atoms is most preferred.

[0034] In the case of the previously mentioned fatty acid components having 11 or less carbon atoms, the continuity as a coating of the fatty acid component in the water-containing lubricant coating decreases, and therefore decreasing the lubricity. In the case of the carbon number of 21 or more, the solubility in water decreases, and therefore, also in this case, the continuity as a coating of the fatty acid component is often impaired.

[0035] Fatty acid salts of metals other than the sodium and potassium mentioned previously, for example, metal soaps such as zinc salts, calcium salts, aluminum salts, and magnesium salts of the fatty acids mentioned previously are all insoluble in water, and unsuitable for the water-soluble lubricating component (C) of the water-containing lubricant coating agent according to the present invention. The reason therefor is because the foregoing metal soaps are insoluble in water, and thus the saturated concentration in the water in the water-containing lubricant coating is nearly zero, and furthermore, because the excess metal soaps are granularly precipitated without forming any continuous coating. More specifically, for forming a coating of fatty acid component with continuity in the water-containing lubricant coating, the process, which leads from the condition that the water-soluble lubricating component is dissolved in the lubricant coating to the condition that the water-containing lubricant coating is formed through gradual water evaporation, is important and the salts that are irresolvable in the initial stage of the lubricant coating formation, like the metal soap mentioned previously will not turn into a continuous coating in the water-containing lubricant coating, or will not dissolve in the water in the water-containing lubricant coating. The thus structured water-containing lubricant coating poorly follows area expansions during working, thereby failing to achieve favorable lubricity.

[0036] The definition of "water-soluble (dissolved in water)" of the water-soluble lubricating component (C) according to the present invention will be described in more detail. The sodium salt, potassium salt, ethylene oxide (EO) adduct, and propylene oxide (PO) adduct of the fatty acids, which are water-soluble lubricating components, are all components that have surface-active properties, and in water, uniformly dissolved between water molecules, or present as a micelle with a hydrophilic group oriented outward, that is, a molecular assembly. Typically, the components dissolve uniformly between water molecules at low concentrations, but come to form micelles as a molecular assemblies when the concentrations are increased to exceed the critical micelle concentrations. In accordance with the present invention, the case of dissolving uniformly between water molecules and the case of forming micelles in water are both defined as "dissolved in water". The reason therefor is because the water-soluble lubricating component in the lubricant coating agent is capable of forming a water-containing lubricant coating with excellent lubricity, in each case of uniform dissolution and micellar state. On the other hand, in the case of water-insoluble fatty acid salts like metal soaps, metal soap particles themselves are not dissolved in water, and it is also impossible to turn into a molecular assembly such as a micelle. Accordingly, in accordance with the present invention, from the perspective of lubricity, the case of dissolving uniformly between water molecules and the case of forming micelles are defined as "dissolution in water", and the case of not

dissolving uniformly in water and forming no micelles is defined as "insoluble in water". In other words, the water-soluble lubricating component (C) according to the present invention refers to at least one component selected from the group consisting of fatty acid components having 12 to 20 carbon atoms, which is uniformly dissolved between water molecules or turned into a micelle.

[0037] Next, details of the lipophilic lubricating component will be described. At least one selected from the group consisting of mineral oils, animal and plant oils and fats, and synthetic oils can be used as the oil. More specifically, for example, naphthenic mineral oil or paraffinic mineral oil-based machine oils, turbine oils, spindle oils, and the like can be used as the mineral oils. For example, palm oil, rapeseed oils, coconut oils, castor oils, beef tallow, pork oils, whale oils, fish oils, or these components with ethylene oxide (EO) added thereto (for example, polyoxyethylene castor oils (EO adducts)) can be used as the animal and plant oils and fats. However, in the case of adding EO, the EO is preferably 1 mol or less because the lipophilicity decreases as the molar number of the added EO increases. Ester oils (for example, esters of polyalcohols such as ethylene glycol and trimethylolpropane and fatty acids such as stearic acid, oleic acid, and linoleic acid (e.g., trimethylolpropane trioleate)), silicone oils (for example, polydimethylsiloxane and polydiphenylsiloxane), and the like can be used as the synthetic oils. Hydrophobic organic compounds (for example, organic ammonium compounds, organic phosphonium compounds, organic sulfonium compounds, organic amine compounds) can be also used as synthetic oils for the lipophilic lubricating component according to the present invention. The naphthenic mineral oils are preferred as the mineral oils, the palm oils, the castor oils, and the oils with ethylene oxide added thereto (polyoxyethylene plant oils (ethylene oxide adducts)) are preferred as the animal and plant oils and fats, and the ester oils (trimethylolpropane trioleate) are preferred as the synthetic oils.

[0038] An agent that effectively develops an extreme-pressure effect at the friction surface between a metal material and a tool during working is preferred as the extreme-pressure agent. Examples of such an extreme-pressure agent can include sulphurized olefins, sulfurized esters, sulphites, thiocarbides, phosphate ester, phosphite ester, molybdenum dithiocarbamate (MoDTC), molybdenum dithiophosphate (MoDTP), zinc dithiophosphate (ZnDTP), and tricresyl phosphate, and the phosphates (tricresyl phosphate) are preferred. According to the present invention, the use of the extreme-pressure agent in combination with the oil mentioned previously is more advantageous than the use of the extreme-pressure agent alone, for achieving higher lubricity. The preferred ratio between the oil and the extreme-pressure agent falls within the range of 1 : 0.03 to 1 : 1 in mass ratio. When the ratio of the extreme-pressure agent falls below 1 : 0.03, the effect of the extreme-pressure agent is reduced, thereby leading to no significant difference from the case of the oil alone. In addition, while there is no problem even when the ratio exceeds 1 : 1, the extreme-pressure action is nearly saturated, which is not economical.

[0039] In the case of using the oil and/or the extreme-pressure agent as the lipophilic lubricating component, a viscosity index improver may be blended for the purpose of achieving higher lubricity. Specifically, at least one viscosity index improver selected from polymethacrylates, olefin copolymers, and polyisobutylenes can be used. The viscosity index (JIS K2283) is preferably 100 or more, and more preferably 200 or more.

[0040] Fatty acid salts having 12 to 20 carbon atoms can be used as the metal soap. The metal species is not particularly limited as long as the metal is any metal other than sodium and potassium, but from the perspective of lubricity, the metal soap preferably has a melting point of 100 to 250°C. The metal soap corresponding to the foregoing is at least one metal soap selected from zinc salts, calcium salts, aluminum salts, lithium salts, magnesium salts, and the like of the fatty acids mentioned previously, and a metal soap of stearic acid is most preferred.

[0041] The wax is not to be considered particularly specified in terms of structure and type, but preferably has a melting point of 70 to 150°C, because the wax melts by heat generated during working, thereby developing lubricity. Waxes that have a melting point in this range include, for example, microcrystalline waxes, polyethylene waxes, polypropylene waxes, and carnauba waxes, and polyethylene waxes are preferred.

[0042] In the case of the lipophilic lubricating component, parameters that indicate lipophilicity include a solubility parameter (SP value, unit $(cal/cm^3)^{1/2}$). The solubility parameter refers to a parameter for solubility or compatibility in a two-component system. The solubility or compatibility is supposed to be better as the solubility parameters of the components are closer in value to each other. Various methods are disclosed for the measurement method. For example, methods such as a method of evaluation from solubility in a solvent with a known SP value, a Fedors method based on theoretical calculation, and a turbidimetric titration method are typical measurement methods. The turbidimetric titration method devised by K. WSuh, et al. was adopted as the method for measuring the SP value according to the present invention (J. Appl. Polym. Sci., 12, 2359 (1968)). In accordance with the turbidimetric titration method, the SP value of the lipophilic lubricating component can be evaluated by dissolving the lipophilic lubricating component in a good solvent with a known SP value, followed by carrying out turbidimetric titration with a poor solvent that is higher in SP value than the good solvent and a poor solvent that is lower in SP value than the good solvent. The SP value of water is approximately 23, and as the SP value of a target component is lower than that of water, the lipophilicity is higher.

[0043] The lipophilic lubricating component for use in the present invention preferably has an SP value of 10 or less, and further preferably 9 or less. When the SP value of the lipophilic lubricating component exceeds 10, the water content of the water-containing lubricant coating tends to increase due to decreased lipophilicity. In addition, the lower limit of

the SP value of the lipophilic lubricating component is not to be considered particularly specified, but for example, 7 or more.

[0044] Next, the solid lubricant with cleavability will be described. According to Solid Lubrication Handbook (Japanese Society of Tribologists: Yokendo Co. Ltd. (2009) 53), the solid lubricant refers to a substance interposed between two objects for purposes such as friction reduction, seizure prevention, and improved mold life when the objects cause relative movement. In general, the solid lubricant is used as a component of lubricant coating for plastic working, sliding members, press forming, and the like, and specifically, layered clay minerals, poorly soluble crystalline inorganic salts such as phosphates (for example, zinc phosphate, calcium phosphate, zinc calcium phosphate, iron phosphate, manganese phosphate, lithium phosphate, and the like), carbonates (for example, zinc carbonate, magnesium carbonate, calcium carbonate, and the like), oxalates (for example, iron oxalate, calcium oxalate, and the like), sulfates (for example, calcium sulfate, and the like), metal hydroxides (for example, calcium hydroxide, magnesium hydroxide, and the like), and metal oxides (for example, calcium oxide, magnesium oxide, and the like), other than sodium salts and potassium salts, and the like are applied as the solid lubricant, and can be also used in the present invention. It is to be noted that the previously mentioned term "poorly soluble" means that the solubility in water at 20°C is 0.5 g/100 g or less.

[0045] Among solid lubricants mentioned previously, the layered clay mineral is more preferable in the water-containing lubricant coating agent according to the present invention. Specifically, examples thereof can include a smectite group of natural products and synthetic products, a vermiculite group of natural products and synthetic products, a mica group of natural products and synthetic products, a brittle mica group of natural products and synthetic products, a pyrophyllite group of natural products and synthetic products, and a kaolinite group of natural products and synthetic products. These layered clay minerals may be each used alone, or more than one thereof may be used in combination.

[0046] The layered clay mineral will be described in more detail. Clay minerals are main-component minerals constituting clay. Layered silicate minerals (phyllosilicate minerals), calcite, dolomite, feldspars, quartz, boiling stones (zeolite), and others, minerals that have chain-like structures (such as attapulgite, sepiolite), minerals that have no clearly crystalline structure (allophane), and the like are referred to as clay minerals, and in general, layered silicate minerals among the clay minerals are referred to as layered clay minerals.

[0047] The layered clay mineral forms a crystal structure that has two-dimensional layers of positive and negative ions stacked parallel and bonded, and this layered structure has therein two structural units: one unit of a tetrahedral layer composed of Si^{4+} and O^{2-} surrounding it; the other of an octahedral layer composed of Al^{3+} (or Mg^{2+}, Fe^{2+}, or the like) and $(OH)^-$ surrounding it.

[0048] In the tetrahedral layer, O located at four vertexes of the tetrahedron and Si located in the center form tetrahedrons of Si-O, which are linked to each other at the three vertexes to a two-dimensional extent, thereby forming a layer lattice that has a composition of Si_4O_{10}. The Si^{4+} is often substituted with Al^{3+}.

[0049] In the octahedral layer, octahedrons formed by (OH) or O located at six vertexes of the octahedron and Al, Mg, Fe, or the like located in the center are linked at each vertex to a two-dimensional extent, thereby forming a layer lattice that has a composition of $Al_2(OH)_6$, $Mg_3(OH)_6$, or the like.

[0050] The octahedral layers include: a 3-octahedral type that has lattice points all occupied with a divalent cation (such as Mg^{2+}) at the lattice point of cation surrounded by six anions; and a 2-octahedral type that has 2/3 lattice points occupied with a trivalent cation (such as Al^{3+}) at the lattice point of cation, and 1/3 lattice points remaining vacant.

[0051] There are two types on combinations of tetrahedral layers and octahedral layers: one of the combinations is a 2 : 1 type structure that has, as a unit, a linkage of two tetrahedral layers and one octahedral layer sandwiched therebetween; and the other is a 1 : 1 type structure that has, as a unit, a linkage of one tetrahedral layer and one octahedral layer. The smectite group, vermiculite group, mica group, and pyrophyllite group mentioned previously refer to layered clay minerals that have the 2 : 1 type structure, whereas the kaolinite group refers to layered clay minerals that have the 1 : 1 type structure.

[0052] With regard to the relationship between the hydrophilicity of the layered clay mineral and the crystal structure, for example, as for kaolin, the layered clay mineral has the 1 : 1 crystal structure, which is believed to exhibit hydrophilicity because octahedrons having hydrophilic groups (such as OH) are orientated at the surface. On the other hand, in the case of the 2 : 1 crystal structure, there is believed to be a strong tendency to be lower in hydrophilicity than the 1 : 1 structure, because tetrahedrons having hydrophobic groups (SiO) are orientated at the surface.

[0053] To explain layered clay minerals that belong to the respective groups in more detail, the smectite group includes montmorillonite, beidellite, nontronite, saponite, iron saponite, hectorite, sauconite, and stevensite, the vermiculite group includes di.vermiculite and tri.vermiculite, the mica group includes muscovite, palagonite, illite, phlogopite, biotite, and lepidolite, the brittle mica group includes margarite and clintonite, the pyrophyllite group includes pyrophyllite and talc, and the kaolinite group includes kaolinite, dickite, nacrite, halloysite, chrysotile, lizardite, and antigorite. Among these minerals, particularly preferred is at least one selected from the two layered clay minerals that belong to the pyrophyllite group mentioned above. The reason therefor is because the layered clay minerals that belong to the pyrophyllite group have the lowest Mohs hardness of 1, and thus have the effect of reducing working loads, and excellent followability to area expansions during working. The Mohs hardness is preferably 2 or less, and further preferred Mohs hardness is 1.

[0054] Next, the most preferred solid lubricant in the water-containing lubricant coating agent according to the present invention is carrier particles where the lipophilic lubricating component is included between particles of and/or between layers of the layered clay mineral. The carrier particles refer to particles that allows the lipophilic lubricating component to more efficiently follow, through utilizing cleavability of the layered clay mineral. More specifically, the lipophilic lubricating component is included between the particles and/or between the layers corresponding to cleavage faces of the layered clay mineral with cleavability, thereby making it possible to further increase the cleavability of the layered clay mineral, and furthermore, cause the lipophilic lubricating component to more efficiently follow area expansions during working. To explain in more detail, the layered clay mineral refers to particles of two-dimensional layered crystals stacked parallel and bonded. According to the present invention, the spaces between surfaces of the layered crystals are defined as interlayer spaces. Furthermore, when the previously mentioned layered crystals stacked parallel and bonded are regarded as primary particles, multiple primary particles may further aggregate (agglomerate) into larger secondary particles (the layered clay mineral that forms the secondary particles is referred to as an "aggregated layered clay mineral"), and in this case, the spaces between the particles are defined as inter-particle spaces. Both the interlayer spaces and the inter-particle spaces are loosely bonded in a layered form, which are cleavage faces that are capable of including a lipophilic lubricating component according to the present invention. The inclusion of the lipophilic lubricating component between the particles of and/or between the layers of the layered clay mineral with cleavability allows the layered clay mineral and the lipophilic lubricating component to follow at the same time, that is, to take a role as carrier particles, even in working which is high in working load and high in the area expansion ratio of the worked surface, such as cold plastic working, thereby imparting slidability along with the prevention of galling, and thus making it possible to improving lubricity. It is to be noted that the "inclusion" herein refers to the situation that the lipophilic lubricating component is trapped between the particles of and/or between the layers of the layered clay mineral. More specifically, in the carrier particles according to the present invention, when the layered clay mineral is not cleaved, the lipophilic lubricating component is held between the particles of and/or between the layers of the layered clay mineral, and this condition is referred to as an "inclusion" condition according to the present invention. On the other hand, when the layered clay mineral is cleaved during working, the lipophilic lubricating component included between the particles of and/or between the layers of the layered clay mineral exudes to the worked surface, and the exuded lipophilic lubricating component follows along with the layered clay mineral so as to wet the worked surface.

[0055] The inclusion amount of the lipophilic lubricating component is preferably 5 mass% or more, and further preferably 8 mass% or more in mass ratio to the total mass of the carrier particles. While the particles act as carrier particles even when the inclusion amount falls below 5 mass%, the significant difference from the lubricity of a water-containing lubricant coating in the case of using the layered clay mineral alone can be further increased when the inclusion amount is adjusted to 5 mass% or more. The upper limit on the inclusion amount of the lipophilic lubricating component is not to be considered particularly limited, but for example, 50 mass% or less.

[0056] Next, an example of a method for inclusion of the lipophilic lubricating component between particles of and/or between layers of the layered clay mineral will be described in a method for manufacturing the carrier particles. Examples of the method include, in the case of an oil and an extreme-pressure agent that are liquid at room temperature, a method of adding the oil and the extreme-pressure agent in predetermined amounts to a powder of the layered clay mineral, and causing the mineral to include therein the oil and the agent while stirring. In addition, in the case of desiring the inclusion achieved in a short period of time and desiring the increased inclusion amount, it is preferable to apply a so-called reduced-pressure impregnation method of, not only simply the addition/stirring, but also blending the layered clay mineral, the oil, and the extreme-pressure agent in a decompression tank, followed by returning the pressure to the atmospheric pressure; a method of inclusion with the oil warmed and thus reduced in viscosity, or the like. On the other hand, methods for the inclusion of a metal soap or a wax that is solid at room temperature include a method of turning the soap or the wax into a liquid at a temperature equal to or higher than the melting point thereof, followed by blending the liquid with the layered clay mineral, thereby causing the layers to include the liquid therebetween; and a method of coating the lubricant on a metal material surface, followed by putting the material in an oven kept at a temperature equal to or higher than the melting point, thereby causing the layers to include the soap or the wax therebetween during the drying.

[0057] In addition, a layered clay mineral with an organic substance intercalated between layers of the layered clay mineral by the method described in the International Publication WO 2012/086564 A may be used as the layered clay mineral mentioned previously. Examples of the organic substance can include at least one cationic organic compound (organic group + cationic group) selected from organic ammonium compounds, organic phosphonium compounds, and organic sulfonium compounds. In this regard, the organic group of the organic compound is not particularly limited, but preferred are straight-chain, branched-chain, and cyclic (having a cyclic group) saturated hydrocarbon or unsaturated hydrocarbon groups having 1 to 30 carbon atoms. In addition, the hydrogen atoms bonded to the carbon atoms constituting the carbon chains or the carbon rings may be substituted with other substituent groups, some of the carbon atoms constituting the carbon chains or the carbon rings may be substituted with other atoms (such as O and S, for example), and furthermore, other bondings (for example, ester linkages, ether linkages) may be included between C-C chains.

Preferred is an organic ammonium compound composed of: an aliphatic hydrocarbon group (preferably having 1 to 30 carbon atoms) which is advantageous for friction reducing ability; and an ammonium group which is advantageous for interlayer fixing ability. In this regard, chlorides, bromides, iodides, nitrates, fluorides, hydroxides, and the like are preferred as organic salts which are used for intercalating the organic compound. Particularly preferred organic salts are quaternary ammonium chlorides from which by-product salts are easily removed by water rinsing (such as (capryl trimethyl ammonium chlorides, lauryl trimethyl ammonium chlorides, stearyl trimethyl ammonium chlorides, dicapryl dimethyl ammonium chlorides, dilauryl dimethyl ammonium chlorides, and distearyl dimethyl ammonium chlorides). Intercalating the foregoing organic substances between the layers of the layered clay mineral increases the interlayer distance, thus making it possible to decrease working loads. Furthermore, increasing the spaces between the layers of the layered clay mineral advantageously allows the lipophilic lubricating component to be more efficiently intercalated.

[0058] The solid lubricant for use in the present invention is preferably 1 to 30 μm, more preferably 1 to 20 μm, and further preferably 1 to 10 μm in average particle size, from the perspective of lubricity. When the average particle size exceeds 30 μm, the lubricity may be decreased. With the average particle size of less than 1 μm, the lubricity is favorable, but it is not possible to expect lubricity that is commensurate with the particle sizes, and the manufacturing cost of the solid lubricant is increased.

[0059] The average particle size of the solid lubricant can be measured by a laser diffraction method (volumetric basis). The average particle size of the layered clay mineral according to the present invention is directed to primary particles, and in order to keep as much as possible from being affected by secondary particles as aggregates of the primary particles, particle sizes are measured after enhancing redispersion (breaking secondary particles of the primary particles aggregated, thereby separating the secondary particles again into primary particles) with ultrasonic for approximately 3 to 5 minutes in advance. Thus, the average particle size for substantially primary particles can be measured by eliminating as much as possible the influence of secondary particles of the primary particles aggregated. Therefore, the average particle size of the layered clay mineral according to the present invention refers to an average value on a volumetric basis for the particle sizes on the primary particles of the layered clay mineral.

[0060] In the water-containing lubricant coating agent according to the present invention, the lipophilic lubricating component and the solid lubricant can be each used alone, but it is more preferable to use the component and the lubricant in combination, because the resistance to galling and the reduction in friction coefficient at a worked surface can be improved at the same time. In addition, as for the lubricity of the solid lubricant, the layered clay mineral alone is better than the crystalline inorganic salt, and the carrier particles with the lipophilic lubricating component included therein are more favorable than the layered clay mineral alone in terms of lubricity.

[0061] The water-containing lubricant coating agent according to the present invention can be blended with at least one binder selected from the group consisting of a water-soluble inorganic salt, a water-soluble organic salt, and a water-based resin, for the purpose of further enhancing the adhesion of the lipophilic lubricating component and/or the solid lubricant. Blending the foregoing components enables the lubricating component more strongly to adhere to metal material surfaces, thus making it possible to achieve higher lubricity.

[0062] Specifically, the water-soluble inorganic salt has at least one water-soluble inorganic acid salt selected from the group consisting of sulfates, silicates, borates, molybdates, vanadates, and tungstates, for example. The water-soluble organic salt has at least one water-soluble organic acid salt selected from the group consisting of malates, succinates, citrates, and tartrates, for example. The cations of these salts have at least one selected from the group consisting of a sodium ion, a potassium ion, a lithium ion, an ammonium ion, amines (such as ethylamine), and alkanolamines (such as monoethanolamine and diethanolamine).

[0063] As the water-based resin, that is, water-soluble or water-dispersible polymer resin, at least one can be selected from polymer resins of 1,000 to 1,000,000 in weight average molecular weight. In addition, the water-dispersible polymer resin is preferably 0.5 to 50 μm in average particle size (volumetric basis). The type of the polymer resin is not particularly limited as long as the polymer resin has coating formability, and stable solubility or dispersibility, but for example, polymer resins can be used, such as acrylic resins, urethane resins, epoxy resins, phenolic resins, hydroxyethyl cellulose, carboxymethyl cellulose, and polyvinyl alcohol. Furthermore, water-soluble polymer resins that have a combination of a binder action and lubricity, such as a polyethylene oxide and a polyethylene glycol, can be also used as the binder according to the present invention. It is to be noted that the weight average molecular weight of the polymer resin can be measured by a gel permeation chromatography method (GPC method). In addition, the average particle size of the water-dispersible polymer resin can be measured by a method that is similar to that for the average particle size of the layered clay mineral as mentioned previously.

[0064] The concentration of the binder mentioned previously preferably falls within the range of 3 to 20 mass% with respect to the total mass (including water) of the water-containing lubricant coating. When the concentration of the binder falls below 3 mass%, the binder action can be insufficiently achieved, and no significant improvement in lubricity can be expected as compared with a case without the binder. Alternatively, when the concentration of the binder exceeds 20 mass%, the water content of the water-containing lubricant coating may exceed 50 mass%, thereby decreasing the lubricity, in a case such as a short time period of leaving after lubrication treatment.

[0065] In the water-containing lubricant coating agent of the present invention, any of non-ionic surfactants, anionic surfactants, amphoteric surfactants, and cationic surfactants can be used as one which disperses, in water, the lipophilic lubricating component and/or the solid lubricant. The non-ionic surfactants include, but not particularly limited thereto, for example, polyoxyethylene alkyl esters obtained from polyoxyethylene alkyl ether, polyoxyalkylene (ethylene and/or propylene) alkyl phenyl ether, or polyethylene glycol (or ethylene oxide) and a higher fatty acid (for example, 12 to 18 carbon atoms); and polyoxyethylene sorbitan alkyl esters obtained from sorbitan, polyethylene glycol, and a higher fatty acid (for example, 12 to 18 carbon atoms), and the like. The anionic surfactants include, but not particularly limited thereto, for example, fatty acid salts, sulfate ester salts, sulfonate salts, phosphate ester salts, dithiophosphate ester salts, and the like. The amphoteric surfactants include, but not particularly limited thereto, for example, amino acid-type and betaine-type carboxylate salts, sulfate ester salts, sulfonate salts, phosphate ester salts, and the like. The cationic surfactants include, but not particularly limited thereto, for example, aliphatic amine salts, quaternary ammonium salts, and the like. These surfactants can be each used alone, or two or more of the surfactants can be used in combination.

[0066] A surface-treated metal material according to the present invention is characterized in that a water-containing lubricant coating (including water) obtained with the water-containing lubricant coating agent according to the present invention is formed to achieve a coating amount of 0.1 g/m^2 or more, preferably 3 g/m^2 or more, further preferably 5 g/m^2 or more (in a water-containing state). The setting of the coating amount may be determined appropriately depending on the working level required. More specifically, the coating amount of 5 g/m^2 or more is preferred for forging, wire drawing, and tube drawing, but the coating amount of 0.1 g/m^2 or more is enough in fields with low working degrees, such as plate press. However, when the coating amount falls below the lower limit mentioned previously, the lubricant coating may fail to fully coat a metal material surface depending on the roughness of the surface, and attention is thus required in terms of lubricity. In addition, the upper limit is not particularly specified, but for example, 40 g/m^2. When the water-containing lubricant coating is formed in excess of the upper limit of the coating amount, there is concern that the water content of the water-containing lubricant coating may exceed 50 mass% since dryability becomes worse, and attention is thus required in terms of lubricity. It is to be noted that as long as the coating amount falls within the range of up to the upper limit of 40 g/m^2, the lubricity of the water-containing lubricant coating increases as the coating amount increases.

[0067] The coating amount of the water-containing lubricant coating mentioned previously can be adjusted by the total solid content concentration (including no water) in the water-containing lubricant coating agent. Specifically, as long as the total solid content concentration falls within the range of 1 to 40 mass%, the coating amount of the water-containing lubricant coating falls within the range of approximately 0.1 to 40 g/m^2.

[0068] A method for forming a water-containing lubricant coating for a metal material according to the present invention includes at least a contact step of bringing a metal material into the water-containing lubricant coating agent mentioned previously. As mentioned previously, for the water-containing lubricant coating agent according to the present invention, there is a need to dissolve the water-soluble lubricating component (C) in the water-phase side at a mass ratio of (C)/[(A) + (B)] = 0.05 to 0.5, more preferably 0.1 to 0.3, and the solubility of the fatty acid component mentioned previously decreases as the carbon number increases, and also depends on temperature. Accordingly, an appropriate lubrication treatment temperature may be set within the range of 20 to 90°C, depending on the solubility of the hydrophilic lubricating component used. As an example, in the case of dissolving potassium stearate or sodium stearate at a ratio of (C)/[(A) + (B)] = 0.1 when the total solid content concentration of the water-containing lubricant coating agent is 15 mass%, none of the fatty acid components can be dissolved at the ratio under a lubrication treatment temperature of 20°C, but as long as the lubrication treatment temperature is set at 50°C for the potassium stearate, or 90°C for the sodium stearate, the components can be both dissolved at the ratio. Accordingly, an appropriate lubrication treatment temperature may be set in view of the solubility of the fatty acid component used.

[0069] The contacting method for bringing the metal material into the water-containing lubricant coating agent according to the present invention is not particularly limited, but examples of the method include a dipping method, a flow coating method, a spray method, and brush coating.

[0070] In order to improve the adhesion of the water-containing lubricant coating, it is preferable to clean up the metal material by at least one approach selected from the group consisting of shot blasting, sandblasting, alkaline degreasing, and acid cleaning (cleanup step) before the lubricant coating treatment (contact step). In this regard, the cleanup is intended to remove oxide scale grown by annealing or the like, and various types of contamination (e.g., oil). In particular, in recent years, reduced wastewater treatment burdens have been desired due to environmental concerns. In this case, the absence of wastewater can be achieved just by cleaning up the metal material surface with shot blasting, followed by carrying out the contact step with the use of the lubricant coating agent according to the present invention.

[0071] The water-containing lubricant coating agent according to the present invention is a non-reactive lubricant coating agent that involves no chemical conversion reaction, but after forming a chemical conversion coating in advance on the metal material surface (chemical conversion treatment step), the water-containing lubricant coating according to the present invention can be formed thereon. Components for such a chemical conversion coating include: a phosphate of at least one selected from Zn, Fe, Mn, Ni, Co, Ca, Mg, and Al (metal material: iron and steel, aluminum, and the like);

an iron oxalate (metal material: stainless steel); an aluminum fluoride (metal material: aluminum); and a zirconium oxide (metal material: iron and steel, aluminum, and the like). The application of the chemical conversion treatment further improves the lubricity, thereby making it possible to cope also with conditions with a severer working degree.

Examples

[0072] Effects of the present invention will be verified with reference to examples and comparative examples. The followings are details of the respective components for preparing water-containing lubricant coating agents for use in the examples and comparative examples.

[Lipophilic Lubricating Component]

[0073] The followings are lipophilic lubricating components used for tests. It is to be noted that the previously mentioned turbidimetric titration method was adopted as the method for measuring the solubility parameter (SP value).

<Oil>

[0074]

A-1 plant oil and fat: palm oil, SP value 8.5
A-2 plant oil and fat: castor oil, SP value 9.0
A-3 plant oil and fat: polyoxyethylene castor oil (product with 0.5 mol of ethylene oxide added), SP value 10.0
A-4 plant oil and fat: polyoxyethylene castor oil (product with 1 mol of ethylene oxide added), SP value 11.6
A-5 mineral oil: naphthenic mineral oil, SP value 8.3
A-6 synthetic oil: trimethylolpropane trioleate, SP value 8.7

<Extreme-Pressure Agent>

[0075] A-7 tricresyl phosphate, SP value 8.9

<Metal Soap>

[0076] A-8 zinc stearate, melting point 120°C, SP value 8.7

<Wax>

[0077] A-9 polyethylene wax, melting point 110°C, SP value 8.1

<Mixture of Oil and Extreme-Pressure Agent>

[0078]

A-10 (A-1) : (A-7) = 1 : 0.02 (mass ratio)
A-11 (A-1) : (A-7) = 1 : 0.03 (mass ratio)
A-12 (A-1) : (A-7) = 1 : 0.1 (mass ratio)
A-13 (A-1) : (A-7) = 1 : 1 (mass ratio)
A-14 (A-1) : (A-7) = 1 : 1.1 (mass ratio)

[Solid Lubricant]

[0079] The followings are solid lubricants used for tests. The average particle size of the solid lubricant was measured by a laser diffraction method on a volumetric basis under the following conditions after the redispersion of the solid lubricant into primary particles with ultrasonic in water for 3 minutes in advance.

Name of Measurement Machine: LA-920 from Horiba, Ltd.
Data Loading Frequency: 10 times
Calculation Frequency: 30 times
Ultrasonic Intensity: 7

Ultrasonic Time: 3 minutes
Dispersion Medium Circulation Speed: 3

<Crystalline Inorganic Salt>

[0080]

B-1 calcium carbonate: average particle size 3 μm , Mohs hardness 3
B-2 zinc phosphate: average particle size 3 μm, Mohs hardness 4

<Layered Clay Mineral>

[0081]

B-3 talc: average particle size 3 μm, Mohs hardness 1
B-4 kaolinite: average particle size 3 μm, Mohs hardness 2
B-5 synthetic mica: average particle size 3 μm, Mohs hardness 3
B-6 talc: average particle size 1 μm, Mohs hardness 1
B-7 talc: average particle size 10 μm, Mohs hardness 1
B-8 talc: average particle size 20 μm, Mohs hardness 1
B-9 talc: average particle size 30 μm, Mohs hardness 1
B-10 talc: average particle size 40 μm, Mohs hardness 1

<Carrier Particle>

[0082]

B-11 host: B-3, guest: A-12, inclusion amount: 8 mass%
B-12 host: B-3, guest: A-12, inclusion amount: 5 mass%
B-13 host: B-3, guest: A-12, inclusion amount: 4 mass%
B-14 host: B-3, guest: A-8, inclusion amount: 8 mass%
B-15 host: B-3, guest: A-9, inclusion amount: 8 mass%
host: layered clay mineral, guest: lipophilic lubricating component

[Water-Soluble Lubricating Component]

<Saturated Fatty Acid Salt (Straight Chain)>

[0083]

C-1 sodium caprate: carbon number 10
C-2 sodium laurate: carbon number 12
C-3 sodium myristate: carbon number 14
C-4 sodium palmitate: carbon number 16
C-5 sodium stearate: carbon number 18
C-6 potassium stearate: carbon number 18
C-7 potassium arachidate: carbon number 20
C-8 potassium behenate: carbon number 22

<Unsaturated Fatty Acid Salt>

[0084] C-9 sodium oleate: carbon number 18

<Saturated Fatty Acid Salt (Branched Chain)>

[0085] C-10 sodium isostearate: carbon number 18

<Natural Fatty Acid Salt>

[0086] C-11 beef tallow soap (sodium salt): carbon numbers 14 to 18

<Fatty Acid EO Adduct>

[0087] C-12 polyethylene glycol distearate (20 mol EO added)

[Surfactant]

D-1 polyoxyethylene sorbitol tetraoleate (60 mol EO added)

[Binder]

[0088]

E-1 potassium tetraborate
E-2 lithium citrate
E-3 water-based urethane resin: molecular weight 100000, average particle size 1.0 μm, solid content concentration 40 mass%
E-4 polyethylene glycol: molecular weight 20000, solid content concentration 100 mass%
E-5 polyethylene oxide: molecular weight 200000, solid content concentration 100 mass%

[Insoluble Metal Soap (For Comparison)]

[0089] F-1 calcium stearate: average particle size 3 μm

[Method for Inclusion of Lipophilic Lubricating Component between Particles and/or between Layers of Layered Clay Mineral]

[0090] As for the oil and extreme-pressure agent that are liquid at room temperature, the oil and the extreme-pressure agent were added to the layered clay mineral in proportions of an includable amount (1 : 1 in mass ratio) or more, and blended with the use of a mortar until being homogeneous in whole, thereby resulting in the lubricating component included between particles and/or between layers. The inclusion amount was adjusted by the blending time. Thereafter, the excess oil and extreme-pressure agent adhering to the layered clay mineral surface were removed by immersion in boiling water for 10 minutes, and the layered clay mineral was left to dry at room temperature for 24 hours. Alternatively, in the case of zinc stearate and wax that are poorly-soluble and solid at room temperature, the lubricating component turned into a liquid at a temperature equal to or higher than the melting points was added to the layered clay mineral (1 : 1 in mass ratio), and blended therewith in a mortar until becoming fully homogeneous, thereby resulting in the lubricating component included between particles and/or between layers. The inclusion amount was adjusted by the blending time. Thereafter, the wax (or zinc stearate) adhering to particle surfaces was removed by immersion for 10 minutes in an oil bath warmed to a temperature equal to the melting point of the wax (or zinc stearate) or higher, thereafter, the oil on the particle surfaces was removed by immersion in boiling water for 10 minutes, and thereafter, the layered clay mineral was left to dry at room temperature for 24 hours.

[Method for Measuring Inclusion Amount of Lipophilic Lubricating Component]

[0091] The inclusion amount of the lipophilic lubricating component was measured with the use of a total organic carbon meter (TOC-5000/SSM-5000A from Shimadzu Corporation) equipped with a solid sample burning system. The measuring method will be mentioned in detail below. First, a lipophilic lubricating component alone (lipophilic lubricating component itself) to be included was used and burned completely at a furnace temperature of 700°C, thereby creating a calibration curve of carbon intensity-lubricating component amount. Next, measured is the carbon intensity in carrier particles with the lipophilic lubricating component included between particles of and/or between layers of the layered clay mineral by the previously mentioned method under the same condition, and the obtained value is converted to the lubricating component amount.

$$\text{Inclusion Amount (\%)} = (\text{Mass of Lipophilic Lubricating Component/Total Mass of Carrier Particle}) \times 100$$

[Method for Measuring Coating Amount of Water-containing Lubricant Coating]

[0092] With the use of a commercially available degreasing agent (registered trademark: FINECLEANER E6400 from Nihon Parkerizing Co., Ltd.), under the conditions of concentration 20 g/L and temperature 60°C, a test piece with a water-containing lubricant coating formed was immersed for 30 minutes, thereby removing the lubricant coating, and the coating amount was determined from the mass difference between before and after the immersion.

$$\text{Coating Amount (g/m}^2\text{)} = (\text{Test Piece Mass before Removing - Test Piece Mass after Removing})/\text{Surface Area of Test Piece}$$

[Method for Measuring Water Content]

[0093] The water-containing lubricant coating was completely dried under the conditions of 110°C at 1 hour, and the coating amount of this lubricant coating was regarded as a completely dried coating amount. The water content was obtained from the following formula.

$$\text{Water Content (mass\%)} = [1 - (\text{Completely Dried Coating Amount/Coating Amount of Water-containing lubricant coating})] \times 100$$

[Lubrication Treatment Method]

<Step A>

[0094]

(1) Degreasing: a test piece (metal material) was immersed for 10 minutes in a commercially available degreasing agent (registered trademark: FINECLEANER E6400 from Nihon Parkerizing Co., Ltd., concentration: 20 g/L) warmed to 60°C.
(2) Water Rinsing: the degreased test piece was immersed for 10 seconds in tap water.
(3) Lubrication Treatment (Contact Step): the test piece rinsed with the water was immersed for 30 seconds in the lubricant coating agent for metal materials (see Tables 1 and 2), warmed to a predetermined temperature.
(4) Drying: a water-containing lubricant coating was formed by adjusting time such that the water content of the water-containing lubricant coating reaches a predetermined value at room temperature (20°C, relative humidity 80%RH).

<Step B>

[0095]

(1) Degreasing: a test piece (metal material) was immersed for 10 minutes in a commercially available degreasing agent (registered trademark: FINECLEANER E6400 from Nihon Parkerizing Co., Ltd., concentration: 20 g/L) warmed to 60°C.
(2) Water Rinsing: the degreased test piece was immersed for 10 seconds in tap water.
(3) Phosphate Treatment (Chemical Conversion Treatment Step): the test piece rinsed with the water was immersed for 10 minutes in a commercially available phosphate treatment solution (registered trademark: PALBOND 181X from Nihon Parkerizing Co., Ltd., concentration: 90 g/L) warmed to 80°C.
(4) Water Rinsing: the test piece subjected to the phosphate treatment was immersed for 30 seconds in tap water at room temperature.
(5) Lubrication Treatment (Contact Step): the test piece rinsed with the water was immersed for 30 seconds in the lubricant coating agent for metal materials (see Table 1), warmed to a predetermined temperature.
(6) Drying: a water-containing lubricant coating was formed by adjusting time such that the water content of the

water-containing lubricant coating reaches a predetermined value at room temperature (20°C, relative humidity 80%RH).

[Method for Adjustment of Water Content]

[0096] The water content of the water-containing lubricant coating was adjusted by the lubrication treatment temperature and the subsequent leaving time. To explain more specifically, the appropriate lubrication treatment temperature varies depending on the solubility of the target water-soluble lubricating component. First, a powder of the water-soluble lubricating component, corresponding to a predetermined concentration, is added into the water-containing lubricant coating agent at room temperature. Thereafter, the temperature at which particles of the water-soluble lubricating component were completely dissolved by gradually warming while stirring was regarded as the lubrication treatment temperature. It is to be noted that as can be seen from Table 1, for example, in the case of a straight-chain saturated fatty acid sodium salt, the solubility thereof deceases with carbon number increases. In order to compensate for this decreased solubility, the lubrication treatment temperature is set to be high. Next, after subjecting the metal material to a lubrication treatment at a set temperature, the metal material is left in the room temperature (20°C, relative humidity: 80%RH), and in the process of leaving the metal material, moisture gradually evaporates, thereby decreasing the water content in the water-containing lubricant coating with the leaving time. In this regard, the evaporation rate of moisture tends to be higher as the lubrication treatment temperature is higher. Accordingly, in order to adjusting to a predetermined water content, the water content was adjusted in view of the lubrication treatment temperature and the evaporation rate of moisture, in a way that the leaving time in the room temperature is set to be shorter when the lubrication treatment temperature is higher, whereas the leaving time is set to be longer when the lubrication treatment temperature is lower. It is to be noted that treated objects after the lubrication treatment were left as it were in the room at a forging test and a wire drawing test as described later, whereas steel pipes for use in a tube drawing test were left while venting to the inner surface of the steel pipes with the use of a blower such that the water contents in the inner surfaces of the steel pipes are equal to those in the outer surfaces thereof.

[Table 1]

[0097]

[Table 1]

	composition of water-containing lubricant coating agent (1000 g in total)													lubrication treatment condition		water-containing lubricant coating		treatment step	parameter
	lipophilic lubricating component (A)		solid lubricant (B)		water-soluble lubricating component (C)		binder component (E)		surfactant (D)		water	(C)/[(A)+(B)]	total solid content concentration (mass%)	treatment temperature (°C)	drying time (min)	coating amount (g/m2)	water content (mass%)		
	type	blending amount (g)	type	blending amount (g)	type	blending amount (g)	type	blending amount (g)	type	blending amount (g)	blending amount (g)								
Example 1	A-12	87.9	B-11	43.9	C-2	13.2		0	D-1	5	850	0.10	15	20	60	10	30	Step A	Component C
Example 2	A-12	87.9	B-11	43.9	C-3	13.2		0	D-1	5	850	0.10	15	50	15	10	30	Step A	
Example 3	A-12	87.9	B-11	43.9	C-4	13.2		0	D-1	5	850	0.10	15	80	8	10	30	Step A	
Example 4	A-12	87.9	B-11	43.9	C-5	13.2		0	D-1	5	850	0.10	15	80	8	10	30	Step A	
Example 5	A-12	87.9	B-11	43.9	C-6	13.2		0	D-1	5	850	0.10	15	50	15	10	30	Step A	
Example 6	A-12	87.9	B-11	43.9	C-7	13.2		0	D-1	5	850	0.10	15	70	10	10	30	Step A	
Example 7	A-12	87.9	B-11	43.9	C-9	13.2		0	D-1	5	850	0.10	15	50	15	10	30	Step A	
Example 8	A-12	87.9	B-11	43.9	C-10	13.2		0	D-1	5	850	0.10	15	50	15	10	30	Step A	
Example 9	A-12	87.9	B-11	43.9	C-11	13.2		0	D-1	5	850	0.10	15	80	10	10	30	Step A	
Example 10	A-12	87.9	B-11	43.9	C-12	13.2		0	D-1	5	850	0.10	15	80	10	10	30	Step A	
Example 11	A-12	92.0	B-11	46.0	C-6	7.0		0	D-1	5	850	0.05	15	50	15	10	30	Step A	blending ratio
Example 12	A-12	74.4	B-11	37.2	C-6	33.5		0	D-1	5	850	0.30	15	80	10	10	30	Step A	
Example 13	A-12	64.5	B-11	32.2	C-6	48.3		0	D-1	5	850	0.50	15	80	8	10	30	Step A	
Example 14	A-1	87.9	B-11	43.9	C-6	13.2		0	D-1	5	850	0.10	15	50	15	10	30	Step A	Component A
Example 15	A-2	87.9	B-11	43.9	C-6	13.2		0	D-1	5	850	0.10	15	50	15	10	30	Step A	
Example 16	A-3	87.9	B-11	43.9	C-6	13.2		0	D-1	5	850	0.10	15	50	15	10	30	Step A	
Example 17	A-4	87.9	B-11	43.9	C-6	13.2		0	D-1	5	850	0.10	15	50	15	10	30	Step A	
Example 18	A-5	87.9	B-11	43.9	C-6	13.2		0	D-1	5	850	0.10	15	50	15	10	30	Step A	
Example 19	A-6	87.9	B-11	43.9	C-6	13.2		0	D-1	5	850	0.10	15	50	15	10	30	Step A	
Example 20	A-7	87.9	B-11	43.9	C-6	13.2		0	D-1	5	850	0.10	15	50	15	10	30	Step A	
Example 21	A-8	87.9	B-11	43.9	C-6	13.2		0	D-1	5	850	0.10	15	50	15	10	30	Step A	
Example 22	A-9	87.9	B-11	43.9	C-6	13.2		0	D-1	5	850	0.10	15	50	15	10	30	Step A	
Example 23	A-10	87.9	B-11	43.9	C-6	13.2		0	D-1	5	850	0.10	15	50	15	10	30	Step A	
Example 24	A-11	87.9	B-11	43.9	C-6	13.2		0	D-1	5	850	0.10	15	50	15	10	30	Step A	
Example 25	A-13	87.9	B-11	43.9	C-6	13.2		0	D-1	5	850	0.10	15	50	15	10	30	Step A	
Example 26	A-14	87.9	B-11	43.9	C-6	13.2		0	D-1	5	850	0.10	15	50	15	10	30	Step A	
Example 27	A-12	87.9	B-1	43.9	C-6	13.2		0	D-1	5	850	0.10	15	50	15	10	30	Step A	Component B
Example 28	A-12	87.9	B-2	43.9	C-6	13.2		0	D-1	5	850	0.10	15	50	15	10	30	Step A	
Example 29	A-12	87.9	B-3	43.9	C-6	13.2		0	D-1	5	850	0.10	15	50	15	10	30	Step A	
Example 30	A-12	87.9	B-4	43.9	C-6	13.2		0	D-1	5	850	0.10	15	50	15	10	30	Step A	
Example 31	A-12	87.9	B-5	43.9	C-6	13.2		0	D-1	5	850	0.10	15	50	15	10	30	Step A	
Example 32	A-12	87.9	B-6	43.9	C-6	13.2		0	D-1	5	850	0.10	15	50	15	10	30	Step A	
Example 33	A-12	87.9	B-7	43.9	C-6	13.2		0	D-1	5	850	0.10	15	50	15	10	30	Step A	
Example 34	A-12	87.9	B-8	43.9	C-6	13.2		0	D-1	5	850	0.10	15	50	15	10	30	Step A	
Example 35	A-12	87.9	B-9	43.9	C-6	13.2		0	D-1	5	850	0.10	15	50	15	10	30	Step A	
Example 36	A-12	87.9	B-10	43.9	C-6	13.2		0	D-1	5	850	0.10	15	50	15	10	30	Step A	
Example 37	A-12	87.9	B-12	43.9	C-6	13.2		0	D-1	5	850	0.10	15	50	15	10	30	Step A	
Example 38	A-12	87.9	B-13	43.9	C-6	13.2		0	D-1	5	850	0.10	15	50	15	10	30	Step A	
Example 39	A-12	87.9	B-14	43.9	C-6	13.2		0	D-1	5	850	0.10	15	50	15	10	30	Step A	
Example 40	A-12	87.9	B-15	43.9	C-6	13.2		0	D-1	5	850	0.10	15	50	15	10	30	Step A	
Example 41	A-12	77.9	B-11	38.9	C-6	13.2	E-1	15	D-1	5	850	0.11	15	50	15	10	30	Step A	Component E
Example 42	A-12	77.9	B-11	38.9	C-6	13.2	E-2	15	D-1	5	850	0.11	15	50	15	10	30	Step A	
Example 43	A-12	77.9	B-11	38.9	C-6	13.2	E-3	37.5	D-1	5	828	0.11	15	50	15	10	30	Step A	
Example 44	A-12	77.9	B-11	38.9	C-6	13.2	E-4	15	D-1	5	850	0.11	15	50	15	10	30	Step A	
Example 45	A-12	77.9	B-11	38.9	C-6	13.2	E-5	15	D-1	5	850	0.11	15	50	15	10	30	Step A	
Example 46	A-10	131.8		0.0	C-6	13.2		0	D-1	5	850	0.10	15	50	15	10	30	Step A	only Component A
Example 47	A-11	131.8		0.0	C-6	13.2		0	D-1	5	850	0.10	15	50	15	10	30	Step A	
Example 48	A-12	131.8		0.0	C-6	13.2		0	D-1	5	850	0.10	15	50	15	10	30	Step A	
Example 49	A-13	131.8		0.0	C-6	13.2		0	D-1	5	850	0.10	15	50	15	10	30	Step A	
Example 50	A-14	131.8		0.0	C-6	13.2		0	D-1	5	850	0.10	15	50	15	10	30	Step A	
Example 51		0.0	B-1	131.8	C-6	13.2		0	D-1	5	850	0.10	15	50	15	10	30	Step A	only Component B
Example 52		0.0	B-2	131.8	C-6	13.2		0	D-1	5	850	0.10	15	50	15	10	30	Step A	
Example 53		0.0	B-3	131.8	C-6	13.2		0	D-1	5	850	0.10	15	50	15	10	30	Step A	
Example 54		0.0	B-4	131.8	C-6	13.2		0	D-1	5	850	0.10	15	50	15	10	30	Step A	
Example 55		0.0	B-5	131.8	C-6	13.2		0	D-1	5	850	0.10	15	50	15	10	30	Step A	
Example 56		0.0	B-11	131.8	C-6	13.2		0	D-1	5	850	0.10	15	50	15	10	30	Step A	
Example 57		0.0	B-12	131.8	C-6	13.2		0	D-1	5	850	0.10	15	50	15	10	30	Step A	
Example 58		0.0	B-13	131.8	C-6	13.2		0	D-1	5	850	0.10	15	50	15	10	30	Step A	
Example 59		0.0	B-14	131.8	C-6	13.2		0	D-1	5	850	0.10	15	50	15	10	30	Step A	
Example 60		0.0	B-15	131.8	C-6	13.2		0	D-1	5	850	0.10	15	50	15	10	30	Step A	
Example 61	A-12	87.9	B-11	43.9	C-6	13.2		0	D-1	5	850	0.10	15	50	5	10	50	Step A	water content
Example 62	A-12	87.9	B-11	43.9	C-6	13.2		0	D-1	5	850	0.10	15	50	7	10	15	Step A	
Example 63	A-12	87.9	B-11	43.9	C-6	13.2		0	D-1	5	850	0.10	15	60	10	10	12.5	Step A	
Example 64	A-12	87.9	B-11	43.9	C-6	13.2		0	D-1	5	850	0.10	15	70	10	10	10	Step A	
Example 65	A-12	87.9	B-11	43.9	C-6	13.2		0	D-1	5	850	0.10	15	80	13	10	7.5	Step A	
Example 66	A-12	87.9	B-11	43.9	C-6	13.2		0	D-1	5	850	0.10	15	80	15	10	5	Step A	
Example 67	A-12	87.9	B-11	43.9	C-6	13.2		0	D-1	5	850	0.10	15	90	10	10	3	Step A	
Example 68	A-12	77.9	B-11	38.9	C-6	13.2	E-1	15	D-1	5	850	0.11	15	80	13	10	7.5	Step A	
Example 69	A-12	77.9	B-11	38.9	C-6	13.2	E-2	15	D-1	5	850	0.11	15	80	13	10	7.5	Step A	
Example 70	A-12	77.9	B-11	38.9	C-6	13.2	E-3	37.5	D-1	5	828	0.11	15	80	13	10	7.5	Step A	
Example 71	A-12	77.9	B-11	38.9	C-6	13.2	E-4	15	D-1	5	850	0.11	15	80	13	10	7.5	Step A	
Example 72	A-12	77.9	B-11	38.9	C-6	13.2	E-5	15	D-1	5	850	0.11	15	80	13	10	7.5	Step A	
Example 73	A-12	77.9	B-11	38.9	C-6	13.2	E-1	15	D-1	5	850	0.11	15	90	10	10	3	Step A	
Example 74	A-12	77.9	B-11	38.9	C-6	13.2	E-2	15	D-1	5	850	0.11	15	90	10	10	3	Step A	
Example 75	A-12	77.9	B-11	38.9	C-6	13.2	E-3	37.5	D-1	5	828	0.11	15	90	10	10	3	Step A	
Example 76	A-12	77.9	B-11	38.9	C-6	13.2	E-4	15	D-1	5	850	0.11	15	90	10	10	3	Step A	
Example 77	A-12	77.9	B-11	38.9	C-6	13.2	E-5	15	D-1	5	850	0.11	15	90	10	10	3	Step A	
Example 78	A-12	5.9	B-11	2.9	C-6	0.9		0	D-1	0.3	990	0.10	1	50	10	0.1	30	Step A	total solid content concentration /coating amount
Example 79	A-12	26.4	B-11	13.2	C-6	4.0		0	D-1	1.5	955	0.10	5	50	10	3	30	Step A	
Example 80	A-12	44.0	B-11	22.0	C-6	6.6		0	D-1	2.5	925	0.10	7.5	50	10	5	30	Step A	
Example 81	A-12	234.4	B-11	117.1	C-6	35.2		0	D-1	13.3	600	0.10	40	80	10	40	30	Step A	
Example 82	A-12	87.9	B-11	43.9	C-6	13.2		0	D-1	5	850	0.10	15	50	15	10	30	Step B	treatment step
Example 83	A-12	131.8		0.0	C-6	13.2		0	D-1	5	850	0.10	15	50	15	10	30	Step B	
Example 84		0.0	B-11	131.8	C-6	13.2		0	D-1	5	850	0.10	15	50	15	10	30	Step B	

[Comparative Example 1]

<Zinc Phosphate Treatment + Reactive Soap Treatment>

[0098]

(1) Degreasing: a test piece (metal material) was immersed for 10 minutes in a commercially available degreasing agent (registered trademark: FINECLEANER E6400 from Nihon Parkerizing Co., Ltd., concentration: 20 g/L) warmed to 60°C.
(2) Water Rinsing: the degreased test piece was immersed for 30 seconds in tap water at room temperature.
(3) Phosphate Treatment: the test piece rinsed with the water was immersed for 10 minutes in a commercially available phosphate treatment solution(registered trademark: PALBOND 181X from Nihon Parkerizing Co., Ltd., concentration: 90 g/L) warmed to 80°C.
(4) Water Rinsing: the test piece subjected to the phosphate treatment was immersed for 30 seconds in tap water at room temperature.
(5) Reactive Soap Treatment: the test piece rinsed with the water was immersed for 5 minutes in a commercially available reactive soap treatment solution (registered trademark: PALUBE 235 from Nihon Parkerizing Co., Ltd., concentration: 70 g/L) warmed to 80°C.
(6) Drying: the test piece subjected to the reactive soap treatment was dried for 3 minutes at 80°C.

[Comparative Example 2]

[0099] According to an example in Patent Literature 1, a lubricant coating agent of the following composition was prepared.

<Lubricant Composition>

[0100]

water-soluble polymer compound: ALKOX (Water-Soluble Polyether) 50 g from Meisei Chemical Works, Ltd.
sodium pyrophosphate: 50 g
water: 900 g

<Lubrication Treatment Condition>

[0101] The lubrication treatment was carried out in accordance with the step A mentioned previously. The treatment temperature was 50°C, the drying condition was of leaving for 20 minutes in an environment at 20°C and relative humidity 80%RH. The water content in this case was 30%.

[Table 2]

[0102]

[Table 2]

	composition of water-containg lubricant coating agent (1000 g in total)											lubrication treatment condition		water-containing lubricant coating		treatment step	parameter
	lipophilic lubricating component (A)		solid lubricant (B)		water-soluble lubricating component (C)		surfactant (D)		water	(C)/[(A)+(B)]	total solid content concentration (mass%)	treatment temperature (°C)	drying time (min)	coating amount (g/m2)	water content (mass%)		
	type	blending amount (g)	type	blending amount (g)	type	blending amount (g)	type	blending amount (g)	blending amount (g)								
Comparative Example 3	A-12	87.9	B-11	43.9	C-1	13.2	D-1	5	850	0.10	15	50	15	10	30	Step A	Component C
Comparative Example 4	A-12	131.8		0.0	C-1	13.2	D-1	5	850	0.10	15	50	15	10	30	Step A	
Comparative Example 5		0.0	B-11	131.8	C-1	13.2	D-1	5	850	0.10	15	50	15	10	30	Step A	
Comparative Example 6	A-12	87.9	B-11	43.9	C-8	13.2	D-1	5	850	0.10	15	50	15	10	30	Step A	
Comparative Example 7	A-12	131.8		0.0	C-8	13.2	D-1	5	850	0.10	15	50	15	10	30	Step A	
Comparative Example 8		0.0	B-11	131.8	C-8	13.2	D-1	5	850	0.10	15	50	15	10	30	Step A	
Comparative Example 9	A-12	87.9	B-11	43.9	C-8	13.2	D-1	5	850	0.10	15	50	3	10	80	Step A	water content
Comparative Example 10	A-12	87.9	B-11	43.9	C-8	13.2	D-1	5	850	0.10	15	90	120	10	0	Step A	
Comparative Example 11	A-12	83.0	B-11	46.5	C-8	5.6	D-1	5	850	0.04	15	50	15	10	30	Step A	blending ratio
Comparative Example 12	A-12	80.4	B-11	30.2	C-8	54.4	D-1	5	850	0.80	15	80	8	10	30	Step A	
Comparative Example 13	A-12	86.7	B-11	48.3		0.0	D-1	5	850	0.00	15	80	8	10	30	Step A	no Component C
Comparative Example 14	A-8	86.7	B-11	48.3		0.0	D-1	5	850	0.00	15	80	8	10	30	Step A	
Comparative Example 15	A-12+F-1	87.9+13.2	B-11	43.9		0.0	D-1	5	850	0.00	15	80	8	10	30	Step A	

[Evaluation Method]

[0103] Effects of the lubricant coating agent for metal materials according to the present invention were verified by the following evaluations.

(1) Upsetting-Ball Ironing Tribo-Test (Comprehensive Lubricity Evaluation)
(2) Various Tests for Lubricity (Forgeability, Wire Drawability, Tube Drawability)
(3) Operability Applicability Test

[Upsetting-Ball Ironing Tribo-Test (Comprehensive Lubricity Evaluation)]

[0104] The upsetting-ball ironing tribo-test in Non Patent Literature 1 was conducted as a comprehensive lubricity evaluation for different working modes, such as forgeability, wire drawability, tube drawability, and slidability. Details of the lubricity test will be described below. First, as a first step, a cylindrical test piece is compressed at an upsetting ratio of 45%, thereby preparing a barrel-shaped test piece. This test piece is subjected to a predetermined lubrication treatment, and then, as a second step, the side surface part protruded in the barrel shape is subjected to ironing with the use of a ball (steel ball) (see Fig. 1). The surface subjected to the ironing process has a shape as shown in Fig. 2, and as the ironing process proceeds from the process start position, the lubricant coating is stretched, and when the followability of the lubricant coating reaches its limit, galling is caused. Furthermore, the area expansion ratio at each site from the process start position to the process end position can be calculated by FEM analysis, thereby providing the relationship between the ironing distance (stroke distance) and the area expansion ratio (Fig. 3). From the galling start position obtained from the surface subjected to the ironing in Fig. 2 and the relationship of ironing distance/area expansion ratio shown in Fig. 3, the limited area expansion ratio, which indicates the followability of the lubricant coating, can be calculated. The area expansion ratio of a worked surface in cold plastic working varies depending on respective product shapes, and it becomes typically several times to 100 times for a forged product, and several times to several tens of times for wire drawing and tube drawing. The maximum area expansion ratio in this test exceeds 150 times (process end position), which can cover almost all of the plastic working field, and the test is most appropriate as a comprehensive lubricity evaluation. The evaluation was made for the absolute value of the limited area expansion ratio for the lubricant coating, and the limited area expansion ratio of 10 times or more was regarded as a practical level.

<Working Conditions>

[0105]

Test Material: SWRM10K (13.96 mmφ $\times$ 32mm)
Upsetting Ratio: 45% (32 mm $\rightarrow$ 17.6 mm)
Ball for Use: SUJ-2 (10 mmφ bearing ball)
Working Speed: 60 mm/sec

[Forgeability Test]

<Spike Test>

[0106]

Test Material: S45C spheroidize-annealed material (25 mmφ $\times$ 30 mm)
Test Method: the test was carried out under the condition of die gap: 4.5 mm in accordance with the invention in JP 3227721. For the evaluation, the lubricant coating which follows protrusions of the test piece were evaluated visually. The followings are evaluation criteria. It is to be noted that the level B or higher was regarded as a practical level.

Evaluation Criteria:

[0107]

S: the coating which followed fully to the protrusion tip (almost no metallic luster)
A: the coating which followed to the protrusion tip
B: the coating which followed to the protrusion top
C: the coating which followed to the protrusion center
D: the coating which followed to the protrusion bottom

[Wire Drawability Test]

[0108]

Test Material: S45C, φ3.0 mm, 50000 mm in length
Test Method: wire drawing was conducted under the condition of an area reduction 10% with the use of an R die. The evaluations were made in accordance with the following criteria. It is to be noted that the level B or higher was regarded as a practical level.

Evaluation Criteria:

[0109]

S: almost no metallic luster, adequate following of lubricant coating, no galling
A: slight metallic luster observed, adequate followability of lubricant coating, no galling
B: a lot of metallic luster observed, but no galling
C: a lot of metallic luster observed, and galling observed
D: a lot of galling observed

[Tube Drawability Test]

[0110]

Test Material: STKM17A, φ25.4 mm × 2.5 mmt, 2000 mm in length
Test Method: test was carried out under the conditions of tube drawing speed 20 m/min and area reduction 20% with the use of an R die and a cylindrical plug in a drawing machine (a draw bench). The evaluations were made in accordance with the criteria. It is to be noted that the level B or higher is regarded as a practical level.

Evaluation Criteria:

[0111]

S: almost no metallic luster, adequate followability of lubricant coating, no galling
A: slight metallic luster observed, adequate followability of lubricant coating, no galling
B: a lot of metallic luster observed, but no galling
C: a lot of metallic luster observed, and galling observed
D: a lot of galling observed

[Operability Evaluation]

[0112] The performance in line operation was evaluated by a treatment load test (sludge generation test). In this test, with respect to 1 L of the lubricant coating agent, a test material was continuously treated until reaching a treatment load of 0.3 m^2, evaluation was made with the presence or absence of sludge generated. It is to be noted that the level B or higher is regarded as a practical level in the following evaluation criteria.
Test Material: Iron Steel Material; SPCC-SD, 70 mm × 150 mm × 0.8 mmt

Evaluation Criteria:

[0113]

A: no sludge generated
B: sludge slightly generated (generation amount: less than 3 g/L)
C: sludge generated (generation amount: 3 g/L or more)

[0114] Tables 3 and 4 show the results of the upsetting-ball ironing tribo-test (comprehensive lubricity evaluation).

[Table 3]

[0115]

[Table 3]

	limited area expansion ratio (%)		limited area expansion ratio (%)		limited area expansion ratio (%)
Example 1	**35**	Example 29	**30**	Example 57	**35**
Example 2	**37**	Example 30	**27**	Example 58	**25**
Example 3	**47**	Example 31	**25**	Example 59	**40**
Example 4	**50**	Example 32	**30**	Example 60	**40**
Example 5	**50**	Example 33	**30**	Example 61	**30**
Example 6	**40**	Example 34	**27**	Example 62	**50**
Example 7	**35**	Example 35	**25**	Example 63	**53**
Example 8	**35**	Example 36	**23**	Example 64	**55**
Example 9	**40**	Example 37	**45**	Example 65	**60**
Example 10	**30**	Example 38	**35**	Example 66	**65**
Example 11	**45**	Example 39	**50**	Example 67	**70**
Example 12	**50**	Example 40	**50**	Example 68	**70**
Example 13	**45**	Example 41	**60**	Example 69	**70**
Example 14	**40**	Example 42	**60**	Example 70	**70**
Example 15	**40**	Example 43	**60**	Example 71	**75**
Example 16	**37**	Example 44	**65**	Example 72	**75**
Example 17	**35**	Example 45	**65**	Example 73	**80**
Example 18	**40**	Example 46	**10**	Example 74	**80**
Example 19	**40**	Example 47	**13**	Example 75	**80**
Example 20	**40**	Example 48	**13**	Example 76	**85**
Example 21	**40**	Example 49	**13**	Example 77	**85**
Example 22	**40**	Example 50	**13**	Example 78	**15**

(continued)

	limited area expansion ratio (%)		limited area expansion ratio (%)		limited area expansion ratio (%)
Example 23	**47**	Example 51	**15**	Example 79	**30**
Example 24	**50**	Example 52	**15**	Example 80	**40**
Example 25	**50**	Example 53	**20**	Example 81	**50**
Example 26	**50**	Example 54	**18**	Example 82	**80**
Example 27	**21**	Example 55	**16**	Example 83	**35**
Example 28	**21**	Example 56	**40**	Example 84	**60**

[Table 4]

[0116]

[Table 4]

	limited area expansion ratio		limited area expansion ratio		limited area expansion ratio
Comparative Example 1	**90**	Comparative Example 6	**8**	Comparative Example 11	**8**
Comparative Example 2	**8**	Comparative Example 7	**5**	Comparative Example 12	**8**
Comparative Example 3	**8**	Comparative Example 8	**3**	Comparative Example 13	**2**
Comparative Example 4	**5**	Comparative Example 9	**8**	Comparative Example 14	**2**
Comparative Example 5	**3**	Comparative Example 10	**70**	Comparative Example 15	**2**

[0117] Table 5 shows the results (forgeability, wire drawability, tube drawability) of the various lubricity tests.

[Table 5]

[0118]

[Table 5]

	forgeability	wire drawability	tube drawability
Example 4	**A**	**A**	**A**
Example 5	**A**	**A**	**A**
Example 48	**B**	**B**	**B**
Example 56	**B**	**B**	**B**
Comparative Example 1	**S**	**S**	**S**

(continued)

	forgeability	wire drawability	tube drawability
Comparative Example 2	**C**	**C**	**C**

[0119] Table 6 shows the results of the operability evaluation.

[Table 6]

[0120]

[Table 6]

	operability		operability		operability
Example 1	**A**	Example 30	**A**	Example 59	**A**
Example 2	**A**	Example 31	**A**	Example 60	**A**
Example 3	**A**	Example 32	**A**	Example 61	**A**
Example 4	**A**	Example 33	**A**	Example 62	**A**
Example 5	**A**	Example 34	**A**	Example 63	**A**
Example 6	**A**	Example 35	**A**	Example 64	**A**
Example 7	**A**	Example 36	**A**	Example 65	**A**
Example 8	**A**	Example 37	**A**	Example 66	**A**
Example 9	**A**	Example 38	**A**	Example 67	**A**
Example 10	**A**	Example 39	**A**	Example 68	**A**
Example 11	**A**	Example 40	**A**	Example 69	**A**
Example 12	**A**	Example 41	**A**	Example 70	**A**
Example 13	**A**	Example 42	**A**	Example 71	**A**
Example 14	**A**	Example 43	**A**	Example 72	**A**
Example 15	**A**	Example 44	**A**	Example 73	**A**
Example 16	**A**	Example 45	**A**	Example 74	**A**
Example 17	**A**	Example 46	**A**	Example 75	**A**
Example 18	**A**	Example 47	**A**	Example 76	**A**
Example 19	**A**	Example 48	**A**	Example 77	**A**
Example 20	**A**	Example 49	**A**	Example 78	**A**
Example 21	**A**	Example 50	**A**	Example 79	**A**
Example 22	**A**	Example 51	**A**	Example 80	**A**
Example 23	**A**	Example 52	**A**	Example 81	**A**
Example 24	**A**	Example 53	**A**	Example 82	**A**
Example 25	**A**	Example 54	**A**	Example 83	**A**
Example 26	**A**	Example 55	**A**	Example 84	**A**
Example 27	**A**	Example 56	**A**	Comparative Example 1	**C**
Example 28	**A**	Example 57	**A**	Comparative Example 2	**A**
Example 29	**A**	Example 58	**A**		

[0121] As can be seen from Table 1, Examples 1 to 84 according to the present invention have achieved the practical levels (the limited area expansion ratio of 10% or more in the upsetting-ball ironing tribo-test, and ratings of B or higher in various lubricity tests) for all of the evaluation items.

[0122] In contrast, at the level of the phosphate + reactive soap listed in Comparative Example 1, the lubricity has achieved the practical level, but the operability applicability has been rated as C. In addition, at the level (corresponding to the example in Patent Literature 1) listed in Comparative Example 2, the lubricity has all failed to reach the practical level.

[0123] Among the comparative examples related to the present invention, Comparative Examples 3 to 8 with the carbon numbers outside the range of 12 to 20 as the water-soluble lubricating component have all failed to achieve lubricity at the practical level.

[0124] Among the comparative examples regarding the water content, Comparative Example 9 with the water content in excess of 50 mass% has failed to achieve lubricity the practical level. In addition, Comparative Example 10 subjected to complete drying has understandably achieved lubricity at the practical level, and Example 5 and Examples 61 to 67 of the water-containing lubricant coatings corresponding to the same lubricant composition as the foregoing have also lubricity at the practical level as well.

[0125] Comparative Example 11 and Comparative Example 12 with the proportions of the water-soluble lubricating component outside the predetermined range, and furthermore, Comparative Examples 13 to 15 including no water-soluble lubricating component have all failed to reach the practical level for lubricity.

[0126] From the foregoing results, the present invention can be considered to have a greater deal of potential in industry, as compared with the prior art, because favorable lubricity can be achieved even when no lubricant coating can be dried completely, or in a poor environment with high humidity.

Claims

1. A water-containing lubricant coating agent, on use in metal plastic working carried out in a water-containing state with a water content of 3 to 50 mass%, wherein at least one lipophilic lubricating component (A) and/or at least one solid lubricant (B) with cleavability are dispersed in water, and furthermore, at least one water-soluble lubricating component (C) selected from the group consisting of fatty acid components having 12 to 20 carbon atoms is dissolved in a water-phase side at a mass ratio of (C)/[(A) + (B)] = 0.05 to 0.5.

2. The water-containing lubricant coating agent according to claim 1, wherein the water-soluble lubricating component (C) comprises at least one selected from the group consisting of sodium salts and potassium salts of lauric acid, tridecanoic acid, myristic acid, pentadecanoic acid, palmitic acid, heptadecanoic acid, stearic acid, and arachidic acid.

3. The water-containing lubricant coating agent according to claim 1, wherein the water-soluble lubricating component (C) comprises sodium stearate and/or potassium stearate.

4. The water-containing lubricant coating agent according to any one of claims 1 to 3, wherein the lipophilic lubricating component (A) has a solubility parameter (SP value) of 10 or less, and the lipophilic lubricating component (A) comprises at least one selected from the group consisting of an oil (A1), an extreme-pressure agent (A2), a metal soap (A3), and a wax (A4) as follows.

   an oil (A1): at least one selected from the group consisting of mineral oils, animal and plant oils and fats, and synthetic oils;
   an extreme-pressure agent (A2): at least one selected from the group consisting of phosphorus-based extreme-pressure agents, sulfur-based extreme-pressure agents, organomolybdenum-based extreme-pressure agents, and organozinc-based extreme-pressure agents;
   a metal soap (A3): at least one selected from the group consisting of metal salts other than sodium salts and potassium salts of fatty acids having 12 to 20 carbon atoms;
   a wax (A4): at least one selected from the group consisting of polyethylene waxes, polypropylene waxes, carnauba waxes, and microcrystalline waxes.

5. The water-containing lubricant coating agent according to any one of claims 1 to 4, wherein the solid lubricant (B) comprises at least one selected from the group consisting of the following layered clay mineral (B1), carrier particles (B2), and poorly soluble crystalline inorganic salt (B3).

   layered clay mineral (B1): at least one selected from natural products and synthetic products of a smectite group, a vermiculite group, a mica group, a brittle mica group, a pyrophyllite group, and a kaolinite group;

carrier particles (B2): particles including the lipophilic lubricating component (A) between particles of and/or between layers of the layered clay mineral (B1);
poorly soluble crystalline inorganic salt (B3): at least one selected from the group consisting of phosphates, carbonates, oxalates, sulfates, metal hydroxides, and metal oxides, other than sodium salts and potassium salts.

6. The water-containing lubricant coating agent according to claim 5, wherein an inclusion amount of the lipophilic lubricating component (A) in the carrier particles (B2) is 5 mass% or more in mass ratio to a total mass of the carrier particles (B2).

7. The water-containing lubricant coating agent according to any one of claims 1 to 6, wherein the solid lubricant (B) is 30 μm or less in average particle size.

8. The water-containing lubricant coating agent according to any one of claims 1 to 7, which further comprises, as a binder, at least one selected from the group consisting of a water-soluble inorganic salt, a water-soluble organic salt, and a water-based resin.

9. A water-containing lubricant coating formed on/over a metal material surface with the use of the water-containing lubricant coating agent according to any one of claims 1 to 8, wherein a water content is 3 to 50 mass%.

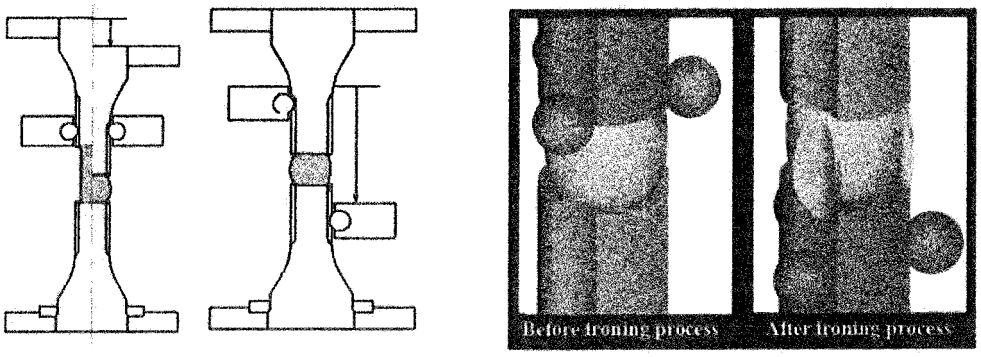
10. A surface-treated metal material, wherein the water-containing lubricant coating according to claim 9 is formed on/over a metal material surface to be 0.1 g/m^2 or more as a coating amount in a water-containing state.

11. A method for forming a water-containing lubricant coating for a metal material, the method comprising a contact step of bringing the metal material into contact with the water-containing lubricant coating agent according to any one of claims 1 to 8, wherein the metal material is brought into contact at a treatment temperature at which the water-soluble lubricating component (C) can be dissolved in a water-phase side of the water-containing lubricant coating agent at a mass ratio of (C)/[(A) + (B)] = 0.05 to 0.5 in the contact step.

12. The method for forming a water-containing lubricant coating for a metal material according to claim 11, the method further comprising, prior to the contact step, a chemical conversion treatment step of coating a surface of the metal material with a chemical conversion coating.

FIG. 1

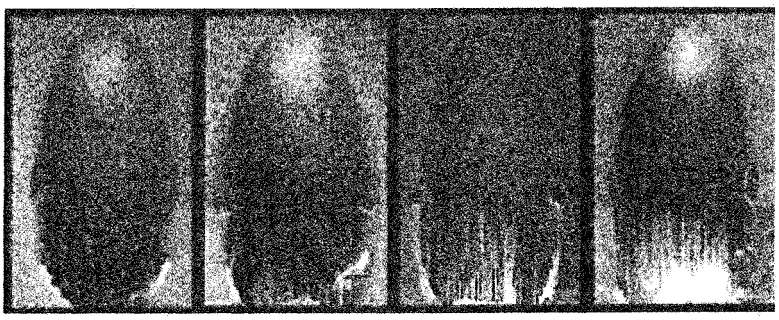
[Fig. 1]



UPSETTING BALL IRONING APPEARANCES BEFORE AND AFTER IRONING PROCESS

FIG. 2

[Fig. 2]



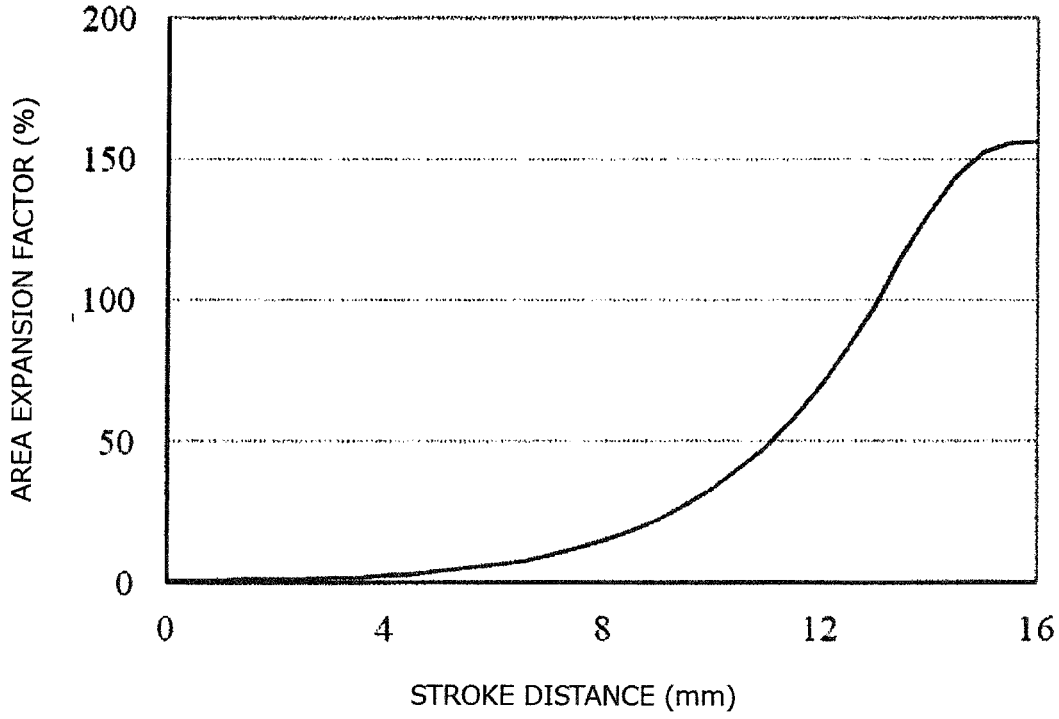
←PROCESS START POSITION
(STROKE DISTANCE: 0 mm)

←PROCESS END POSITION
(STROKE DISTANCE: 16 mm)

SUPERIOR ← LUBRICITY → INFERIOR

FIG. 3

[Fig. 3]


200
150
100
50
0
AREA EXPANSION FACTOR (%)
0
4
8
12
16
STROKE DISTANCE (mm)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2016/059437

A. CLASSIFICATION OF SUBJECT MATTER
See extra sheet.

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)
C10M173/00, C23C22/83, C10M101/02, C10M101/04, C10M103/06, C10M105/24, C10M107/04, C10M107/06, C10M109/00, C10M129/40, C10N10/02, C10N10/04, C10N10/12, C10N20/00, C10N20/06, C10N30/00, C10N30/06, C10N40/20

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 1996-2016
Kokai Jitsuyo Shinan Koho 1971-2016 Toroku Jitsuyo Shinan Koho 1994-2016

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
Japio-GPG/FX & Keyword: lubrication, metal working, carboxylate, sodium stearate and related terms,

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	WO 2012/133454 A1 (Nihon Parkerizing Co., Ltd.), 04 October 2012 (04.10.2012), claims; paragraphs [0001] to [0058]; example 10 & US 2014/0162917 A1 claims; paragraphs [0001] to [0161] & WO 2012/133453 A1 & EP 2692838 A1 & CN 103443254 A & KR 10-2013-0130054 A & CN 103517970 A	1-5,7-11 12

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

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
06 June 2016 (06.06.16)	14 June 2016 (14.06.16)
Name and mailing address of the ISA/ Japan Patent Office 3-4-3,Kasumigaseki,Chiyoda-ku, Tokyo 100-8915,Japan	Authorized officer Telephone No.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2016/059437

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Form PCT/ISA/210 (continuation of second sheet) (January 2015)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2016/059437

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	JP 2013-104125 A (Nippon Steel & Sumitomo Metal Corp.), 30 May 2013 (30.05.2013), claims; paragraphs [0001] to [0058]; examples (Family: none)	1-12
A	JP 2007-229743 A (Kobe Steel, Ltd.), 13 September 2007 (13.09.2007), claims; paragraphs [0001] to [0083]; examples (Family: none)	1-12

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2016/059437

Continuation of A. CLASSIFICATION OF SUBJECT MATTER
(International Patent Classification (IPC))

C10M173/00(2006.01)i, *C23C22/83*(2006.01)i, *C10M101/02*(2006.01)n, *C10M101/04*(2006.01)n, *C10M103/06*(2006.01)n, *C10M105/24*(2006.01)n, *C10M107/04*(2006.01)n, *C10M107/06*(2006.01)n, *C10M109/00*(2006.01)n, *C10M129/40*(2006.01)n, *C10N10/02*(2006.01)n, *C10N10/04*(2006.01)n, *C10N10/12*(2006.01)n, *C10N20/00*(2006.01)n, *C10N20/06*(2006.01)n, *C10N30/00*(2006.01)n, *C10N30/06*(2006.01)n, *C10N40/20*(2006.01)n

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

Continuation of B. FIELDS SEARCHED
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

JDreamIII & Keyword: JUNKATSU, KINZOKU KAKO, KARUBONSAN'EN, SUTEARINSAN Na (in Japanese) and related terms

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REFERENCES CITED IN THE DESCRIPTION

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- Solid Lubrication Handbook. Japanese Society of Tribologists: Yokendo Co. Ltd, 2009, 53 **[0044]**