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(54) **AQUEOUS LUBRICATING COATING AGENT HAVING EXCELLENT CORROSION RESISTANCE AND WORKABILITY, AND METAL MATERIAL**

(57) Provided is a water-based lubricating coating agent from which a lubricating coating film which has excellent corrosion resistance, workability, and film removability in practical use is obtained.

A water-based lubricating coating agent character-

ized in that a water-soluble silicate (A) and at least one water-soluble inorganic salt (B) selected from the group consisting of a tungstate, a phosphate and a borate are blended such that the solid content mass ratio (B)/(A) falls within the range of 0.7 to 25.

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**Description**

## Technical Field

5 **[0001]** The present invention relates to a water-based lubricating coating agent which is applied when plastic working is performed to various types of metal materials, and a metal material with a coating film formed by applying the agent onto the metal material surface and drying the agent.

## Background Art

10 **[0002]** As lubricants for plastic working, so-called chemical conversion coating films are common which are composite coating films using phosphate coating films and soaps. However, the chemical conversion coating films have problems such as by-products associated with reactions with metal materials, effluent treatments of water such as water rinsing, and large spaces for the treatments, and in recent years, environmentally conscious water-based dry-in-place type one-pack lubricants have been developed.

15 **[0003]** Patent Literature 1 discloses a water-based lubricating coating agent for plastic working of metal materials, characterized in that the composition of (A) water-soluble inorganic salt and (B) a wax is dissolved or dispersed in water, and the solid content mass ratio (B)/(A) falls within the range of 0.3 to 1.5, and a method of forming a coating film therefrom.

20 **[0004]** Patent Literature 2 discloses a water-based lubricating coating agent for plastic working of metal materials, which contains an alkali metal borate (A), characterized in that the alkali metal borate (A) includes a lithium borate, the molar ratio of lithium to all of the alkali metals is 0.1 to 1.0 in the alkali metal borate (A), and the molar ratio (B/M) between a boric acid B and an alkali metal M is 1.5 to 4.0 in the alkali metal borate (A), and a method of forming a coating film therefrom. This technique is supposed to suppress the crystallization of the coating film, which is caused by moisture absorption of the coating film, thereby making it possible to form coating films with not only workability but also high corrosion resistance.

25 **[0005]** Patent Literature 3 discloses a non-phosphorus aqueous lubricant for plastic working, which contains A component: inorganic solid lubricant, B component: wax, and C component: water-soluble inorganic metal salt, characterized in that the solid content mass ratio (A component/B component) is 0.1 to 5 between the A component and the B component, and the solid content mass ratio (C component/(A component + B component + C component)) of the C component is 1 to 30% to the total amount of the A component, B component, and C component. This technique is directed to a lubricant containing no phosphorus, and supposed to be able to achieve corrosion resistance comparable to that of chemical conversion coating films.

30 **[0006]** Patent Literature 4 discloses a water-based lubricating coating agent including a water-soluble inorganic salt (A), a lubricant (B) selected from molybdenum disulfide and graphite, and a wax (C) dissolved or dispersed in water, where the ratio (B)/(A) is 1.0 to 5.0 in terms of solid content weight ratio, and the ratio (C)/(A) is 0.1 to 1.0 in solid content weight ratio, and a method of forming a coating film therefrom. This technique is supposed to achieve the same level of high workability as that of chemical conversion coating films by blending a conventional water-based lubricating coating agent with molybdenum disulfide or graphite.

35 **[0007]** Patent Literature 5 discloses a film forming agent containing a silicate (A), a polycarboxylate (B), a water-affinity polymer and/or a water-affinity organic lamellar structure (C), and a molybdate and/or tungstate (D), where the mass ratios between the respective components are: B/A = 0.02 to 0.6, C/A = 0.05 to 0.6, and D/A = 0.05 to 0.6.

## Prior Art Documents

45 Patent Literature

**[0008]**

50 Patent Literature 1: WO 02/012420 A  
 Patent Literature 2: JP 2011-246684 A  
 Patent Literature 3: JP 2013-209625 A  
 Patent Literature 4: WO 02/012419 A  
 Patent Literature 5: JP 2002-363593 A

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## Summary of Invention

## Technical Problem

**[0009]** However, even the use of the water-based lubricating coating agents according to Patent Literatures 1 to 5 has the problem of being unable to form a coating film that has a combination of high corrosion resistance (in particular, long-term rust prevention property) and workability for strong working at the same time, as comparable to those of chemical conversion coating films in actual environments. In addition, when a water-based lubricating coating agent is used which contains a silicate, defective film removal may be caused, thereby causing defective plating or defective peeling of oxidized scale.

## Solution to Problem

**[0010]** The inventors have found, as a result of earnestly studying in order to solve the problems mentioned above, that the formation of a coating film by combining a water-soluble silicate and a specific water-soluble inorganic salt at a specific ratio provides high corrosion resistance (in particular, long-term rust prevention property), workability and adequate film removability which have not been able to be achieved in any way by the single components, thereby achieving the present invention.

**[0011]** The present invention (1) is a water-based lubricating coating agent characterized in that a water-soluble silicate (A) and at least one water-soluble inorganic salt (B) selected from a tungstate, a phosphate and a borate are blended such that the solid content mass ratio (B)/(A) falls within the range of 0.7 to 25.

**[0012]** The present invention (2) is the water-based lubricating coating agent according to the invention (1), which is characterized in that the agent includes a resin component (C), and the solid content mass ratio (C)/{(A) + (B)} is 0.01 to 3.

**[0013]** The present invention (3) is the water-based lubricating coating agent according to the invention (2), characterized in that the resin component (C) is at least one selected from the group consisting of a vinyl resin, an acrylic resin, an epoxy resin, an urethane resin, a phenolic resin, a cellulose derivative, a polymaleic acid, a polyolefin, and a polyester.

**[0014]** The present invention (4) is the water-based lubricating coating agent according to the inventions (1)-(3), characterized in that the agent includes a lubricant (D), and the solid content mass ratio (D)/{(A) + (B)} is 0.01 to 6.

**[0015]** The present invention (5) is the water-based lubricating coating agent according to the invention (4), characterized in that the lubricant (D) is at least one selected from the group consisting of a wax, polytetrafluoroethylene, a fatty acid soap, a fatty acid metal soap, a fatty acid amide, molybdenum disulfide, tungsten disulfide, graphite, melamine cyanurate, an amino acid compound of layered structure, and a layered clay mineral.

**[0016]** The present invention (6) is a metal material with a lubricating coating film of 0.5 to 40 g/m<sup>2</sup> as coating weight, which is formed on a metal material surface by applying and drying the water-based lubricating coating agent for plastic working according to the inventions (1)-(5), which is excellent in plastic workability.

## Advantageous Effects of Invention

**[0017]** The use of the water-based lubricating coating agent according to the present invention provides a lubricating coating film which is excellent in corrosion resistance, workability and film removability in practical use. In addition, the agent is significantly superior as compared with conventional water-based lubricating coating films in that all of these performances have a level comparable or superior to those of chemical conversion coating films. Metal materials where the coating film with the previously mentioned great characteristics is formed on the metal material surfaces can be obtained by applying and drying the water-based lubricating coating agent according to the present invention.

## Brief Description of Drawings

**[0018]** Fig. 1 is indications of the evaluation in an upsetting-ball ironing tribo-test (seizure resistance evaluation).

## Description of Embodiments

**[0019]** The present invention will be described in detail below in the following order.

- Water-based Lubricating Coating Agent (Components or Raw Materials, Compositions, etc.)
- Method for Manufacturing Water-based Lubricating Coating Agent
- Application of Water-based Lubricating Coating Agent
- Method for Using Water-based Lubricating Coating Agent

## «Water-based Lubricating Coating Agent»

**[0020]** A water-based lubricating coating agent according to the present invention is obtained by blending a water-soluble silicate (A) (hereinafter, referred to as a silicate (A)) and at least one water-soluble inorganic salt (B) (hereinafter, referred to as an inorganic salt (B)) selected from a tungstate, a phosphate and a borate such that the solid content mass ratio (B)/(A) falls within the range of 0.7 to 25. The blend in the range can form a coating film with high corrosion resistance and workability and adequate film removability which have not been able to be achieved by the silicate (A) or inorganic salt (B) itself. It is to be noted that the term "water-soluble" in the Claims and the Specification means that the solubility in water at room temperature (25°C) {the mass (g) of a solute dissolved in 100 g of water} is at least 1 g, and preferably 10 g or more.

**[0021]** When the silicate (A) and the inorganic salt (B) are combined to provide a coating film, the inorganic salt (B) will be incorporated finely and homogeneously in a network structure formed by the silicate (A). As a result, the fragile coating film of the silicate (A) is made flexible to improve the workability. In addition, the incorporation of the inorganic salt (B) in the network structure of the silicate (A) makes the coating film denser, thereby enhancing the barrier performance, and thus improving the corrosion resistance (in particular, long-term rust prevention property). In addition, the network structure of the silicate (A) is appropriately blocked by the inorganic salt (B), thereby improving the film removability.

**[0022]** The ratio between the silicate (A) and the inorganic salt (B) is important for delivering the performances mentioned above. The performances are delivered at a solid content mass ratio (B)/(A) within the range of 0.7 to 25, but preferably in the range of 0.9 to 10.0, and more preferably 1.1 to 3.0. The ratio (B)/(A) below 0.7 results in failure to achieve sufficient corrosion resistance and workability, and also provides a coating film which is inferior in film removability. This is due to a rigid network structure formed by the relatively increased amount of the silicate. The ratio (B)/(A) in excess of 25 results in failure to achieve sufficient corrosion resistance, and also results in a coating film which is inferior in adhesion and uniformity. This is due to the fact that the relatively excessively small amount of the silicate results in failure to build an adequate network structure, thereby degrading the barrier performance, and degrading the adhesion and uniformity of the coating film.

**[0023]** In addition, in particular, when the silicate is combined with a tungstate, the corrosion resistance is significantly improved by the formation of a passivation film that has a self-repairing function unique to tungsten. In addition, because of having the self-repairing function, stable corrosion resistance can be achieved even when the coating film becomes defective, e.g., due to steels in contact with each other. For this reason, stable corrosion resistance is likely to be produced even in the case of processing large amounts of materials simultaneously, such as mass processing and coil processing of wire rods with the use of barrels for use in lubricating agents for cold forging.

**[0024]** Examples of the silicate (A) for use in the coating agent according to the present invention include, for example, lithium silicates, sodium silicates, and potassium silicates. These may be used singly, or two or more thereof may be combined. In particular, it is preferable to use lithium silicates and/or sodium silicates.

**[0025]** Types of the inorganic salt (B) for use in the coating agent according to the present invention will be specifically provided. Tungstates include, for example, lithium tungstates, sodium tungstates, potassium tungstates, and ammonium tungstates. Phosphates include, for example, ammonium phosphates, lithium phosphates, sodium phosphates, and potassium phosphates. Further, the phosphates include salts of condensed phosphoric acids such as a triphosphoric acid, a metaphosphoric acid, and a pyrophosphoric acid. Borates include, for example, sodium borates (e.g., sodium tetraborate), potassium borates (e.g., potassium tetraborate), and ammonium borates (e.g., ammonium tetraborate). These may be used singly, or two or more thereof may be combined.

**[0026]** Next, the resin component (C) will be described. The resin component (C) is blended for purpose of providing binder action, improving the adhesion between the base material and the coating film, providing leveling property by thickening action, stabilizing the dispersing component, and improving barrier property. Examples of the resin component (C) which has such functions and properties include, for example, vinyl resins, acrylic resins, epoxy resins, urethane resins, phenolic resins, cellulose derivatives, polymaleic acid, polyolefin, and polyester. The resin component (C) used herein is not particularly limited as long as the component has a film formation property, but is typically supplied in a water-soluble or water-dispersion state. These may be used singly, or two or more thereof may be combined.

**[0027]** In the water-based lubricating coating agent, the solid content mass ratio (C)/{(A) + (B)} of the resin component (C) to the silicate (A) and the inorganic salt (B) is preferably 0.01 to 3, and more preferably 0.1 to 1.5. The ratio of less than 0.01 may fail to provide binder action, improve the adhesion between the base material and the coating film, provide the leveling property by thickening action, stabilize the dispersing component, improve the barrier property, or the like as expected for the resin component (C), whereas in the case of the ratio in excess of 3, the amount of the silicate and inorganic salt may be relatively reduced, thereby making it impossible to sufficiently exhibit high corrosion resistance and workability.

**[0028]** Next, the lubricant (D) will be described. The lubricant (D) itself has lubricity and causes slippage, and has the function of reducing a frictional force between a die for processing and a material to be processed. In general, the

increased frictional force during plastic working increases the working energy, generates heat, causes seizure, or the like, but when the water-based lubricating coating agent according to the present invention includes the lubricant (D), the increase in frictional force will be suppressed. Examples of the lubricant (D) which has such functions and properties include waxes, polytetrafluoroethylene, fatty acid soaps, fatty acid metal soaps, fatty acid amides, molybdenum disulfide, tungsten disulfide, graphite, melamine cyanurate, amino acid compounds of layered structure, and layered clay minerals. Among these lubricants, the waxes, polytetrafluoroethylene, fatty acid soaps, fatty acid metal soaps, fatty acid amides, melamine cyanurate, amino acid compounds of layered structure, and layered clay minerals are preferably blended from the perspective of corrosion resistance and liquid stability. These may be used singly, or two or more thereof may be combined. In this regard, specific examples of the waxes include a polyethylene wax, a paraffin wax, a microcrystalline wax, a polypropylene wax, and a carnauba wax. In addition, specific examples of the fatty acid soaps include, sodium myristate, potassium myristate, sodium palmitate, potassium palmitate, sodium stearate, and potassium stearate. In addition, specific examples of the fatty acid metal soaps include calcium stearate, zinc stearate, barium stearate, magnesium stearate, and lithium stearate. In addition, the fatty acid amides refer to amide compound having two fatty acids, and specific examples thereof include ethylenebislauric acid amide, ethylenebisstearic acid amide, ethylenebisbehenic acid amide, N-N'-distearyl adipic acid amide, ethylenebisoleic acid amide, ethylenebiserucic acid amide, hexamethylenedisoleic acid amide, and N-N'-dioleyl adipic acid amide. In addition, the amino acid compounds of layered structure refer to amino acids including a hydrocarbon group having 11 or more carbon atoms in a molecular structure, or derivatives thereof. Specific examples thereof include N-lauroyl-L-lysine [ $C_{11}H_{23}CONH(CH_2)_4CH(NH_2)COOH$ ]. The layered clay minerals include natural products or synthetic products of a smectite group, a vermiculite group, a mica group, a brittle mica group, a pyrophyllite group, and a kaolinite group. More specific examples thereof include montmorillonite, beidellite, nontronite, saponite, iron saponite, hectorite, saucanite, and stevensite as the smectite group, divermiculite and trivermiculite as the vermiculite group, muscovite, palagonite, illite, phlogopite, biotite, and lepidolite, as the mica group, margarite and clintonite as the brittle mica group, pyrophyllite and talc as the pyrophyllite group, and kaolinite, dickite, nacrite, halloysite, chrysotile, lizardite, and antigorite as the kaolinite group. In addition, these layered clay minerals may be subjected to an organic treatment, thereby introducing an organic denaturant between layers. The organic treatment is carried out in accordance with a method of introducing the organic denaturant with the interlayer distance increased by causing the layered clay minerals to swell with water. The organic denaturant is an alkylamine or an alkyl quaternary ammonium salt which adsorbs in between layers to form a strong bond, and specific examples thereof include stearyltrimethylamine, distearylamine, distearyldimethylamine, stearyltrimethylammoniumchloride, and distearyldimethylammoniumchloride.

**[0029]** The blend ratio of the lubricant (D) will be described for the water-based lubricating coating agent according to the present invention. In the case of blending the lubricant (D), the solid content mass ratio  $(D)/\{(A) + (B)\}$  of the lubricant (D) to the silicate (A) and the inorganic salt (B) preferably falls within the range of 0.01 to 6, and more preferably within the range of 0.1 to 2. In this regard, the ratio  $(D)/\{(A) + (B)\}$  of less than 0.01 results in failure to sufficiently exert the friction-reducing effect expected for the lubricant (D), whereas in the case of the ratio in excess of 6, the relatively decreased amount of the silicate (A) and inorganic salt (B) may make it impossible to sufficiently exhibit high corrosion resistance and workability.

**[0030]** For the water-based lubricating coating agent according to the present invention, besides the silicate (A), the inorganic salt (B), the resin component (C), and the lubricant (D), a viscosity modifier can be blended for the purpose of providing leveling property and thixotropy in order to ensure an evenly applied state when the lubricant is applied to the base material. It is to be noted that the blending amount is preferably 0.1 to 50 mass% with respect to the total solid content mass. Specific examples of such a viscosity modifier include smectite clay minerals such as montmorillonite, sauconite, beidellite, hectorite, nontronite, saponite, iron saponite, and stevensite, and inorganic thickeners such as finely divided silica, bentonite, and kaolin.

**[0031]** The water-based lubricating coating agent according to the present invention can provide high corrosion resistance before and after processing, and for the purpose of further improving the corrosion resistance, other water-soluble rust inhibitors and inhibitors may be blended. As a specific example, known inhibitors can be used, such as various types of organic acids, e.g., oleic acid, dimer acid, tartaric acid, citric acid, various types of chelating agents, e.g., EDTA, NTA, HEDTA, DTPA, mixed components of alkanolamines such as triethanolamine, amine salts and the like of p-t-butyl benzoic acid, amine salts of carboxylic acids, diacid amine bases, and combination uses of alkenyl succinic acid and water-soluble salts thereof with aminotetrazole and water-soluble salts thereof. Further, these may be used singly, or two or more thereof may be combined. The blending amount is preferably 0.1 to 30 mass% with respect to the total solid content mass.

**[0032]** The liquid medium (solvent, dispersion medium) in the water-based lubricating coating agent according to the present invention is water. Further, an alcohol that is lower in boiling point than water may be blended for reducing the time period of drying the lubricant in a drying step.

**[0033]** The water-based lubricating coating agent according to the present invention may contain a water-soluble strongly alkaline component for enhancing the liquid stability. Specific examples include lithium hydroxide, sodium

hydroxide, and potassium hydroxide. These may be used singly, or two or more thereof may be combined. The blending amount is preferably 0.01 to 10 mass% with respect to the total solid content mass.

**[0034]** For dispersing non-water-soluble substances, the use of a surfactant is also allowed. However, the additive amounts of components other than the components (A), (B), (C), and (D) preferably do not exceed 50 mass% of the solid content in the water-based lubricating coating agent, to the extent that required performance is not degraded. Conversely, the total of the additive amounts of the components (A), (B), (C), and (D) is preferably 50 mass% or more, more preferably 70 mass% or more, and further preferably 85 mass% or more on the basis of the solid content of the water-based lubricating coating agent.

<<Method for Manufacturing Water-based Lubricating Coating Agent>>

**[0035]** The water-based lubricating coating agent according to the present invention is manufactured by, for example, adding and mixing the silicate (A) and the inorganic salt (B), further the resin component (C) and the lubricant (D), etc., to and with water as a liquid medium. The mixing is carried out by a general method such as propeller stirring or a homogenizer.

«Application of Water-based Lubricating Coating Agent»

**[0036]** The water-based lubricating coating agent according to the present invention is preferably intended for plastic working in a cold working range, such as forging, wire drawing, tube drawing, roll forming, and pressing.

#### • Metal Material to be Used

**[0037]** The water-based lubricating coating agent according to the present invention is applied to metal materials such as iron or steel, stainless steel, copper or a copper alloy, aluminum or an aluminum alloy, and titanium or a titanium alloy. The shape of the metal material is not particularly limited, but the agent is applied to not only materials such as rod materials and block materials, but also forging products (e.g., gears and shafts).

#### • Use as Base Coating Film

**[0038]** The water-based lubricating coating agent according to the present invention can be also used as a base coating agent for other wet lubricants or dry lubricants. The use thereof as a base coating film can raise the level of workability and corrosion resistance of other wet lubricants and dry lubricants. The types of lubricants combined are not particularly limited, but for example, common water-based lubricating coating agents as typified by Patent Literatures 1 to 4 mentioned above, lime soaps, and forging oils can be used as the wet lubricants. In addition, for example, such typical lubricating powders and wire drawing powders that contain, as their main constituents, a higher fatty acid soap, borax, lime, molybdenum disulfide, or the like can be used as the dry lubricants.

«Method for Using Water-based Lubricating Coating Agent»

**[0039]** Next, a method for using the water-based lubricating coating agent according to the present invention will be described. The present method for the use includes a step of cleaning a metal material, a step of applying a water-based lubricating coating agent, and a drying step. The metal material to be used and the respective steps will be described below.

#### • Cleaning Step (Pretreatment Step)

**[0040]** At least one cleaning treatment selected from the group consisting of shot blasting, sand blasting, wet blasting, peeling, alkali degreasing, and acid cleaning is preferably carried out before forming a water-based lubricating coating film on a metal material. The cleaning herein is intended to remove oxidized scale grown by annealing or the like and various types of contamination (such as oils).

#### • Application Step

**[0041]** The step of applying the water-based lubricating coating agent according to the present invention to a metal material is not to be considered particularly limited, but a dipping method, a flow coating method, a spray method, and the like can be used. The time period for the application is not particularly limited as long as the metal surface is sufficiently covered with the water-based lubricating coating agent according to the present invention by the application. In order to enhance drying performance, the metal material may be warmed to 60 to 80°C, and brought into contact with the

water-based lubricating coating agent for plastic working of metal materials, or may be brought into contact with the water-based lubricating coating agent for plastic working of metal materials, which is warmed to 40 to 70°C. Thus, the drying performance may be significantly improved to make drying possible at ordinary temperature, and the loss of thermal energy can be also reduced.

**[0042]** The coating weight of the water-based lubricating coating film formed on the metal surface is appropriately controlled depending on the degree of processing to be done subsequently, but the coating weight preferably falls within the range of 0.5 to 40 g/m<sup>2</sup>, more preferably 2 to 20 g/m<sup>2</sup>. When the coating weight is less than 0.5 g/m<sup>2</sup>, the lubricity is insufficient. In addition, the coating weight in excess of 40 g/m<sup>2</sup> is not preferred because mold clogging with residues or the like is caused although there is no problem with lubricity. The coating weight can be calculated from the mass difference of the metal material between before and after processing and the surface area. In order to control the coating weight, the solid content mass (concentration) of the water-based lubricating coating agent is appropriately adjusted. The intended coating weight is obtained by creating a high concentration of water-based lubricating coating agent, and diluting the agent with water. The water for the adjustment by dilution is not particularly limited, but preferably deionized water or distilled water.

#### • Drying Step

**[0043]** The step is not to be considered particularly limited, but preferably carried out for approximately 1 to 30 minutes at 60 to 150°C.

#### • Optional Step 1 (Base Coating Step)

**[0044]** The water-based lubricating coating agent according to the present invention can prevent seizure between a mold and a material to be processed in the case of processing, and provide high corrosion resistance before and after the processing, and a base coating treatment may be carried out for the purpose of further improving workability and corrosion resistance. The base coating treatment may be intended for a reactive-type coating film or a non-reactive-type coating film. Specific examples of the reactive-type coating film include phosphates, iron oxide, zirconium oxide, zirconium hydroxide, molybdates, oxalates, and tannic acid. Specific examples of the non-reactive-type coating film include silicates, borates, zirconium compounds, vanadium compounds, colloidal silica, and resin coating films.

#### • Optional Step 2 (Film Removal Step)

**[0045]** The lubricating coating film formed from the water-based lubricating coating agent according to the present invention is able to be removed by dipping the film in a water-based alkaline cleaner or spray cleaning. The alkaline cleaner is a liquid of a typical alkaline component such as sodium hydroxide or potassium hydroxide dissolved in water, and when the water-based lubricating coating film is brought into with the cleaner, the water-based lubricating coating film is dissolved in the cleaner, thus making it possible to remove the coating film easily. Therefore, defective plating and defective peeling of oxidized scale can be prevented without contamination in the subsequent steps due to defective film removal in the alkali cleaning.

[Examples]

**[0046]** Advantageous effects of the present invention will be specifically described with reference to examples of the present invention along with comparative examples. It is to be noted that the present invention is not to be considered limited by these examples.

«Example A»

#### (1-1) Manufacture of Water-based Lubricating Coating Agent

**[0047]** Water-based lubricating coating agents according to Examples 1 to 16 and Comparative Examples 1 to 8 were prepared by adopting the respective components listed below in combinations and proportions as shown in Tables 1 to 2. It is to be noted that Comparative Example 9 corresponds to a phosphate/soap treatment.

<Silicate>

**[0048]**

- (A-1) Sodium Silicate ( $\text{Na}_2\text{O} \cdot n\text{SiO}_2$ ,  $n = 3$ )  
 (A-2) Lithium Silicate ( $\text{Li}_2\text{O} \cdot n\text{SiO}_2$ ,  $n = 3.5$ )  
 (A-3) Potassium Silicate ( $\text{K}_2\text{O} \cdot n\text{SiO}_2$ ,  $n = 2.3$ )

5 <Inorganic Salt>

**[0049]**

- (B-1) Sodium Tungstate  
 10 (B-2) Sodium Tripolyphosphate  
 (B-3) Potassium Metaborate

<Resin Component>

15 **[0050]**

- (C-1) Sodium Neutralization Salt of Isobutylene-Maleic Anhydride Copolymer (Molecular Weight: approximately 165,000)

20 <Lubricating Component>

**[0051]**

- (D-1) Anionic Polyethylene Wax (Average Particle Size: 5  $\mu\text{m}$ )  
 25 (D-2) Non-Swelling Synthetic Mica (Average Particle Size: 5.0  $\mu\text{m}$ )

(1-2) Method for Using Water-based Lubricating Coating Agent

<Standard Steps>

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**[0052]**

- (a) Degreasing: commercial degreasing agent (FINECLEANER E6400 from Nihon Parkerizing Co., Ltd.) concentration: 20 g/L, temperature: 60°C, immersion: 10 min  
 35 (b) Water rinsing: tap water, ordinary temperature, immersion: 20 sec  
 (c) Acid cleaning: 17.5% hydrochloric acid, ordinary temperature, immersion: 20 min  
 (d) Water rinsing: tap water, ordinary temperature, immersion: 20 sec  
 (e1) to (e3) Lubricating Treatment: described for each of examples and comparative examples  
 (f) Drying: 100°C, 10 min

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<Lubrication Treatment in Examples 1 to 15 and Comparative Examples 1 to 8>

**[0053]**

- 45 (e1) Lubricating Coating Treatment: water-based lubricating coating agent manufactured in the section (1-1), temperature: 60°C, immersion: 1 min

<Pretreatment and Coating Treatment in Example 16>

50 **[0054]**

- (e1) Base Treatment: commercially available zirconium chemical conversion agent (PALLUCID 1500 from Nihon Parkerizing Co., Ltd.) concentration: 50 g/L, temperature: 45°C, pH 4.0, immersion: 2 min  
 (e2) Water Rinsing: tap water, ordinary temperature, immersion: 20 sec  
 55 (e3) Lubricating Coating Treatment: water-based lubricating coating agent manufactured in the section (1-1), temperature: 60°C, immersion: 1 min



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<Pretreatment and Coating Treatment in Comparative Example 9 (Phosphate/Soap Treatment)>

### [0055]

(e1) Chemical Conversion Treatment: commercially available zinc phosphate chemical conversion agent (PALBOND 181X from Nihon Parkerizing Co., Ltd.) concentration: 75 g/L, temperature: 80°C, immersion: 7 min  
(e2) Water Rinsing: tap water, ordinary temperature, immersion: 30 sec  
(e3) Soap Treatment: commercially available reactive-type soap lubricant (PALUBE 235 from Nihon Parkerizing Co., Ltd.) concentration: 70 g/L, temperature: 85°C, immersion: 3 min  
\*Dried Coating Weight: 10 g/m<sup>2</sup>

(1-3) Evaluation Test

(1-3-1) Spike Test

**[0056]** Examples 1 to 16 and Comparative Examples 1 to 9 were evaluated for workability by a spike test. The spike test was carried out according to the method described in JP H5-7969 A. The lubricity was evaluated with the spike height after the test and the forming load. The lubricity is better as the spike height is larger, and as the forming load is lower. Further, according to the publication, the area enlargement ratio in the spike test is supposed to be approximately 10 times. The lubricity of the coating film was evaluated by measuring the load at working and the spike height.

Test Specimen for Evaluation: S45C spheroidizing annealed material 25 mmφ × 30 mm

Evaluation Criteria:

### [0057]

$$\text{Spike Performance} = \text{Spike Height (mm)} / \text{Working Load (kNf)} \times 100$$

**[0058]** The lubricity is more favorable as the value is larger.

- ⊙: 0.96 or more
- : 0.94 or more and less than 0.96
- △: 0.92 or more and less than 0.94
- ▲: 0.90 or more and less than 0.92
- ×: less than 0.90

(1-3-2) Upsetting-ball Ironing Tribo-Test (Seizure Resistance Evaluation)

**[0059]** Examples 1 to 16 and Comparative Examples 1 to 9 were evaluated for workability by an upsetting-ball ironing tribo-test. The upsetting-ball ironing tribo-test was carried out according to the method described in JP 2013-215773 A. The area enlargement ratio in the upsetting-ball ironing tribo-test is supposed to be 150 times or more at a maximum, and the test has a higher area enlargement ratio and reproduces stronger working as compared with the spike test mentioned above. The seizure resistance of the coating film in strong working was evaluated by evaluating the amount of seizure generated at the ironing surface.

Test Specimen for Evaluation: S10C spheroidizing annealed material 14 mmφ × 32 mm

Bearing Ball: 10 mmφ SUJ2

Evaluation Criteria:

**[0060]** The entire area of the ironing surface was evaluated for how much the area had seizure. Fig. 1 shows indications of the evaluation.

- ⊙: significantly superior to phosphate/soap coating film

- : superior to phosphate/soap coating film
- △: comparable to phosphate/soap coating film
- ▲: inferior to phosphate/soap coating film
- ×: significantly inferior to phosphate/soap coating film

#### (1-3-3) Film Removability Test

**[0061]** Examples 1 to 16 and Comparative Examples 1 to 8 were subjected to a film removability test. It is to be noted that Comparative Example 9 was excluded from the test standard, because of the difference in typical film removal method. In the film removability test, a columnar test specimen was subjected to upsetting at a compressibility of 50% with the use of both upper and lower planar molds, and then immersed in an alkaline cleaner to remove the coating film. After the (d) water rinsing in the step (1-2), the (f) drying was carried out, and the mass of the test specimen was measured after cooling. Thereafter, after the (e) lubricating treatment, the (f) drying was carried out, and the mass of the test specimen was measured after cooling. The mass of a coating film was obtained by the conversion from the mass difference between before and after the test. After the alkali cleaning, the (f) drying was carried out, and the mass of the test specimen was measured after cooling. The mass of coating film after the degreasing treatment was obtained by the conversion from the mass after the alkali cleaning and the mass after acid cleaning.

Test Specimen for Evaluation: S45C spheroidizing annealed material 25 mmφ × 30 mm

Alkaline Cleaner: 2% NaOH aqueous solution

Film Removal Condition: liquid temperature 60°C, immersion time 2 min

$$\text{Film Residual Ratio (\%)} = \left( \frac{\text{Mass of a coating film after Film Removal Treatment}}{\text{Mass of a coating film before Film Removal Treatment}} \right) \times 100$$

Evaluation Criteria:

**[0062]** The film removal is more preferable as the film residual ratio is lower.

- ◎: film residual ratio of 0%
- : film residual ratio of more than 0% and less than 8%
- △: film residual ratio of 8% or more and less than 16%
- ▲: film residual ratio of 16% or more and less than 25%
- ×: film residual ratio of 25% or more

#### (1-3-4) Corrosion Resistance Test

**[0063]** Examples 1 to 16 and Comparative Examples 1 to 9 were subjected to a corrosion resistance test. Five test specimens were simultaneously subjected to a lubricating treatment with the use of a barrel, and the test specimens were exposed to indoors for 3 months in an open atmosphere in summer, thereby observing the degree of rust. It has been determined that the corrosion resistance is more inferior as the rusted area is larger. All of the five test specimens were evaluated.

Test Specimen for Evaluation: S45C spheroidizing annealed material 25 mmφ × 30 mm

Evaluation Criteria:

**[0064]**

- ◎: rusted area that accounts for 3% or less (significantly superior to phosphate/soap coating film)
- : rusted area that accounts for more than 3% and 10% or less (superior to phosphate/soap coating film)
- △: rusted area that accounts for more than 10% and 20% or less (comparable to phosphate/soap coating film)
- ▲: rusted area that accounts for more than 20% and 30% or less (inferior to phosphate/soap coating film)
- ×: rusted area that accounts for more than 30% (significantly inferior to phosphate/soap coating film)

## (1-3-5) Evaluation for Total Score

[0065] The four evaluation results were scored on the basis as shown in Table 3, and the total scores were listed.

[0066] The test results are shown in Tables 4 and 5. It is to be noted that Table 5 shows details of the corrosion resistance test. As is clear from the tables, the examples have achieved favorable workability (spike test, ball ironing test), film removal, and corrosion resistance (indoor exposure). In addition, in regard to corrosion resistance, the blend with the sodium tungstate tends to have a favorable level, and also varies less in performance. Comparative Examples 1 to 8 where the ratios of the silicate (A) and the inorganic salt (B) fall outside the scope of the claims, tend to create inferior results in the ball ironing test and the corrosion resistance test. The phosphate coating film according to Comparative Example 9, subjected to the reactive soap treatment, demonstrates relatively great performance, but inferior performance as compared with the examples.

[0067] The present invention will be further specifically described below along with advantageous effects thereof by providing examples of the present invention along with comparative examples, for the case of using the present invention as base coating films for dry lubricants and wet lubricants. It is to be noted that the present invention is not to be considered limited by these examples.

«Example B»

## (2-1) Manufacture of Water-based Lubricating Coating Agent

[0068] Water-based lubricating coating agents according to Examples 17 to 42 and Comparative Examples 11 to 18 and 20 to 27 were prepared by adopting the respective components mentioned above in combinations and proportions as shown in Tables 6 and 7. For Comparative Example 10, only wire drawing powder was used without any lubricating coating film according to the present invention. For Comparative Example 19, a lime soap was used without any lubricating coating film according to the present invention. Comparative Example 28 corresponds to a phosphate/soap treatment. It is to be noted that there is no wire drawing powder used for Examples 30 to 42 and Comparative Examples 19 to 28.

## (2-2) Lubricating Treatment

<Lubricating Treatment in Examples 17 to 28 and Comparative Examples 11 to 18>

[0069] The treatment was carried out in accordance with the standard steps listed in the section (1-2).

(e) Lubricating Coating Treatment: water-based lubricating coating agent manufactured in the section (2-1), temperature: 60°C, immersion: 1 min

<Pretreatment and Coating Treatment in Examples 30 to 41 and Comparative Examples 20 to 27>

[0070] The treatment was carried out in accordance with the standard steps listed in the section (1-2).

(e1) Lubricating Coating Treatment: water-based lubricating coating agent manufactured in the section (2-1), temperature: 60°C, immersion: 1 min

[0071] Thereafter, as an upper layer coating film, the treatment of immersion for 1 min was carried out at 60°C with 250 g/L of a commercially available lime soap (LUB-CA02 from Nihon Parkerizing Co., Ltd.), and the same drying as the (f) drying was carried out to obtain a lime soap coating amount of 5 g/m<sup>2</sup>.

<Pretreatment and Coating Treatment in Example 29>

[0072]

(e1) Base Treatment: commercially available zirconium chemical conversion agent (PALLUCID 1500 from Nihon Parkerizing Co., Ltd.) concentration: 50 g/L, temperature: 45°C, pH 4.0, immersion: 2 min

(e2) Water Rinsing: tap water, ordinary temperature, immersion: 20 sec

(e3) Lubricating Coating Treatment: water-based lubricating coating agent manufactured in the section (2-1), temperature: 60°C, immersion: 1 min

<Pretreatment and Coating Treatment in Example 42>

[0073]

- 5 (e1) Base Treatment: commercially available zirconium chemical conversion agent (PALLUCID 1500 from Nihon Parkerizing Co., Ltd.) concentration: 50 g/L, temperature: 45°C, pH 4.0, immersion: 2 min  
 (e2) Water Rinsing: tap water, ordinary temperature, immersion: 20 sec  
 (e3) Lubricating Coating Treatment: water-based lubricating coating agent manufactured in the section (2-1), temperature: 60°C, immersion: 1 min

10 [0074] Thereafter, as an upper layer coating film, the treatment of immersion for 1 min was carried out at 60°C with 250 g/L of a commercially available lime soap (LUB-CAO2 from Nihon Parkerizing Co., Ltd.), and the same drying as the (f) drying was carried out to obtain a lime soap coating amount of 5 g/m<sup>2</sup>.

15 <Pretreatment and Coating Treatment in Comparative Example 10>

[0075]

- 20 (e) Pure Water rinsing: deionized water, ordinary temperature, immersion: 30°C

<Pretreatment and Coating Treatment in Comparative Example 19>

[0076]

- 25 (e) Lubrication: commercially available lime soap (LUB-CAO2 from Nihon Parkerizing Co., Ltd.) 250 g/L, temperature 60°C, immersion 1 min  
 (f) Drying: 100°C, 10 min  
 \* Lime Soap Coating Weight: 5 g/m<sup>2</sup>

30 <Pretreatment and Coating Treatment in Comparative Example 28 (Phosphate/Soap Treatment)>

[0077]

- 35 (e1) Chemical Conversion Treatment: commercially available zinc phosphate chemical conversion agent (PALBOND 421 WD from Nihon Parkerizing Co., Ltd.) concentration: 75 g/L, temperature: 80°C, immersion: 10 min  
 (e2) Water Rinsing: tap water, ordinary temperature, immersion: 30 sec  
 (e3) Soap Treatment: commercially available reactive soap lubricant (PALUBE 235 from Nihon Parkerizing Co., Ltd.) concentration: 70 g/L, temperature: 85°C, immersion: 3 min  
 \*Dried Coating Weight: 10 g/m<sup>2</sup>

40 (2-3) Evaluation Test

(2-3-1) Wire Drawing Test (Lubricity Evaluation)

45 [0078] Examples 17 to 42 and Comparative Examples 10 to 28 were evaluated for workability by a wire drawing test. Wire drawing was carried out by drawing a steel wire of φ3.2 mm through a die of φ2.76. In Examples 17 to 29 and Comparative Examples 10 to 18, Missile C40 from Matsuura Industry Co., Ltd. was used as a dry lubricant. The dry lubricant was put in a die box immediately before drawing the material so as to naturally adhere to the material. The evaluation was made from seizure of the test material and the residual amount of the lubrication film after the wire drawing. It is to be noted that the coating amount after the wire drawing was obtained from the mass difference between before and after removal by removing the coating film with the use of the following film remover.

Test Specimen for Evaluation: SWCH45K material, φ3.2 mm × 20 m  
 Die Diameter: φ2.76

55 Film Remover: commercially available alkaline remover (FC-E6463 from Nihon Parkerizing Co., Ltd.), 20 g/L  
 Film Removal Condition: liquid temperature 60°C, immersion time 2 min

Evaluation Criteria:

**[0079]**

$$\text{Film Residual Ratio (\%)} = (\text{Coating Amount before Working} / \text{Coating Amount after Working}) \times 100$$

**[0080]** \*The coating amount before working includes no lubricating powder. The coating amount after working includes the lubricating powder.

- ⊙: film residual ratio of 85% or more
- : film residual ratio of 75% or more and less than 85%
- △: film residual ratio of 65% or more and less than 75%
- ▲: film residual ratio of 50% or more and less than 65%
- ×: film residual ratio of less than 50%, or seizure generated

(2-3-2) Corrosion Resistance Test

**[0081]** Examples 17 to 42 and Comparative Examples 10 to 28 were evaluated for corrosion resistance. The wire rod subjected to the wire drawing test mentioned above was exposed to indoors for 3 months in an open atmosphere in summer, thereby observing the degree of rust. It has been determined that the corrosion resistance is more inferior as the rusted area is larger.

Evaluation Criteria:

**[0082]**

- ⊙: significantly superior to phosphate/soap coating film (rusted area that accounts for 3% or less)
- : superior to phosphate/soap coating film (rusted area that accounts for 3% or more and less than 10%)
- △: comparable to phosphate/soap coating film (rusted area that accounts for 10% or more and less than 20%)
- ▲: inferior to phosphate/soap coating film (rusted area that accounts for 20% or more and less than 30%)
- x: significantly inferior to phosphate/soap coating film (rusted area that accounts for 30% or more)

**[0083]** The test results are shown in Table 8. The examples all with the coating films mostly left resulted in favorable workability and corrosion resistance. Also from the high corrosion resistance after the wire drawing, it is determined that the lubricating coating film according to the invention is mostly left after the working. Comparative Examples 10 and 19, which have the standard without the use of the lubricant according to the present invention, are significantly inferior in wire drawability and corrosion resistance. Comparative Examples 11 to 18 and 20 to 27 with the ratios of the silicate (A) and the inorganic salt (B) inappropriately set are inferior in coating residual amount and corrosion resistance after the wire drawing. The phosphate coating film subjected to the reactive soap treatment according to Comparative Example 28 demonstrates great performance, but requires wastewater treatment or liquid management, thus fails to be used in simple processing steps or systems, and produces waste with reaction, thereby resulting in an increased environmental burden.

**[0084]** As is clear from the foregoing description, the use of the water-based lubricant according to the present invention can achieve a balance between high workability and corrosion resistance. Furthermore, the lubricating coating film after the processing with the cleaner is also favorably removed. Accordingly, the present invention has an extremely great deal of potential in industry.

[Table 1]

[Table 1]

	(A)Component			(B)Component			(C)Component	(D)Component	Base Coating Film	Coating Weight (g/m)	(B) / (A)	(C) / {(A) + (B)}	(D) / {(A) + (B)}
	(A-1)	(A-2)	(A-3)	(B-1)	(B-2)	(B-3)	(C-1)	(D-1)					
Example 1	22	0	0	43	0	0	15	20	No	10.1	1.95	0.23	0.31
Example 2	31	0	0	34	0	0	15	20	No	9.9	1.10	0.23	0.31
Example 3	17	0	0	48	0	0	15	20	No	10.5	2.82	0.23	0.31
Example 4	34	0	0	31	0	0	15	20	No	9.5	0.91	0.23	0.31
Example 5	6	0	0	59	0	0	15	20	No	10.0	9.83	0.23	0.31
Example 6	38	0	0	27	0	0	15	20	No	9.5	0.71	0.23	0.31
Example 7	3	0	0	62	0	0	15	20	No	9.8	20.67	0.23	0.31
Example 8	0	22	0	43	0	0	15	20	No	10.0	1.95	0.35	0.47
Example 9	0	0	22	43	0	0	15	20	No	9.9	1.95	0.35	0.47
Example 10	22	0	0	0	43	0	15	20	No	10.5	1.95	0.23	0.31
Example 11	22	0	0	0	0	43	15	20	No	9.9	1.95	0.23	0.31
Example 12	10	0	0	20	0	0	50	20	No	10.0	2.00	1.67	0.67
Example 13	10	0	0	20	0	0	15	55	No	10.3	2.00	0.50	1.83
Example 14	22	0	0	43	0	0	15	20	No	0.8	1.95	0.23	0.31

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(continued)

	(A)Component			(B)Component			(C) Component	(D) Component	Base Coating Film	Coating Weight (g/m)	(B) / (A)	(C) / {(A) + (B)}	(D) / {(A) + (B)}
	(A-1)	(A-2)	(A-3)	(B-1)	(B-2)	(B-3)	(C-1)	(D-1)					
Example 15	22	0	0	43	0	0	15	20	No	39.5	1.95	0.23	0.31
Example 16	22	0	0	43	0	0	15	20	Yes	10.0	1.95	0.23	0.31

[Table 2]

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[Table 2]

	(A)Component (A-1)	(B)Component			(C)Component (C-1)	(D)Component (D-1)	Coating Weight (g/m)	(B) / (A)	(C)/ {(A) + (B)}	(D)/ {(A) + (B)}
		(B-1)	(B-2)	(B-3)						
Comparative Example 1.	65	0	0	0	15	20	10.2	0.00	0.23	0.31
Comparative Example 2	0	65	0	0	15	20	10.5	-	0.23	0.31
Comparative Example 3	50	15	0	0	15	20	10.1	0.30	0.23	0.31
Comparative Example 4	1	64	0	0	15	20	10.1	64.00	0.23	0.31
Comparative Example 5	50	0	15	0	15	20	10.3	0.30	0.23	0.31
Comparative Example 6	1	0	64	0	15	20	9.7	64.00	0.23	0.31
Comparative Example 7	50	0	0	15	15	20	10.2	0.30	0.23	0.31
Comparative Example 8	1	0	0	64	15	20	9.9	64.00	0.23	0.31
Comparative Example 9	Phosphate/Soap Treatment									

[Table 3]

[Table 3]

	Spike	Ball Ironing	Film Removability	Corrosion Resistance
⊙	5	10	5	10
○	4	8	4	8
△	3	6	3	6
▲	2	4	2	4
×	1	2	1	2

[Table 4]

[Table 4]

	Spike	Ball Ironing	Film Removability	Corrosion Resistance	Total Score
Example 1	⊙	⊙	⊙	⊙	30
Example 2	⊙	⊙	⊙	⊙	30
Example 3	⊙	⊙	⊙	⊙	30
Example 4	⊙	○	○	⊙	27
Example 5	⊙	⊙	⊙	○	28
Example 6	⊙	○	○	○	25
Example 7	○	○	⊙	○	25
Example 8	⊙	⊙	⊙	⊙	30
Example 9	⊙	⊙	⊙	⊙	30
Example 10	⊙	⊙	⊙	○	28
Example 11	⊙	⊙	⊙	○	28
Example 12	⊙	⊙	⊙	⊙	30
Example 13	⊙	⊙	⊙	⊙	30
Example 14	⊙	⊙	⊙	⊙	30
Example 15	⊙	⊙	⊙	⊙	30
Example 16	⊙	⊙	⊙	⊙	30
Comparative Example 1	○	▲	×	▲	13
Comparative Example 2	○	▲	⊙	▲	17
Comparative Example 3	○	△	▲	▲	19
Comparative Example 4	○	▲	⊙	▲	17
Comparative Example 5	○	▲	▲	▲	14
Comparative Example 6	○	▲	⊙	×	15
Comparative Example 7	○	▲	⊙	▲	17
Comparative Examples 8	○	▲	⊙	×	15
Comparative Example 9	△	△	⊗	△	20
⊗ Comparative Example 9 not evaluated because of the different film removal method. The total score of Comparative Example 9 calculated as the film removability being ⊙.					

[Table 5]

[Table 5]

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	N=1	N=2	N=3	N=4	N=5	Comprehensive Evaluation
Example 1	⊙	⊙	⊙	⊙	⊙	
Example 2	⊙	⊙	⊙	⊙	⊙	⊙
Example 3	⊙	⊙	⊙		⊙	⊙
Example 4	⊙	⊙	⊙	⊙	○	⊙
Example 5	⊙	⊙	○	○	○	○
Example 6	⊙	○	○	○	○	○
Example 7	○	○	○	○	○	○
Example 8	⊙	⊙	⊙	⊙	⊙	⊙
Example 9	⊙	⊙	⊙	⊙	○	⊙
Example 10	⊙	○	○	△	△	○
Example 11	⊙	○	○	○	△	○
Example 12	⊙	⊙	⊙	⊙	⊙	⊙
Example 13	⊙	⊙	⊙	⊙	⊙	⊙
Example 14	⊙	⊙	⊙	⊙	○	⊙
Example 15	⊙	⊙	⊙	⊙	⊙	⊙
Example 16	⊙	⊙	⊙	⊙	⊙	⊙
Comparative Example 1	△	▲	▲	▲	×	▲
Comparative Example 2	▲	▲	▲	▲	×	×
Comparative Example 3	△	△	▲	▲	▲	▲
Comparative Example 4	▲	▲	▲	▲	▲	▲
Comparative Example 5	▲	▲	▲	×	×	▲
Comparative Example 6	▲	×	×	×	×	×
Comparative Example 7	▲	▲	▲	▲	×	▲
Comparative Example 8	▲	▲	×	×	×	×
Comparative Example 9	△	△	△	△	△	△

[Table 6]

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[Table 6]

(A) Component	(A) Component			(B) Component			(C)Component	(D) Component		Coating Weight (g/m)	Upper Layer Coating Film	(B) / (A)	(C)/ {(A) + (B)}	(D) / {(A)+ (B)}
	(A- 1)	(A-2)	(A-3)	(B- 1)	(B-2)	(B-3)	(C-1)	(D-1)						
Example 17	37	0	0	63	0	0	0	0	No	5.0	Dry	1.70	0.00	0.00
Example 18	30	0	0	50	0	0	10	10	No	5.1	Dry	1.67	0.13	0.13
Example 19	38	0	0	42	0	0	10	10	No	5.3	Dry	1.11	0.13	0.13
Example 20	20	0	0	60	0	0	10	10	No	5.2	Dry	3.00	0.13	0.13
Example 21	42	0	0	38	0	0	10	10	No	5.0	Dry	0.90	0.13	0.13
Example 22	8	0	0	72	0	0	10	10	No	5.0	Dry	9.00	0.13	0.13
Example 23	47	0	0	33	0	0	10	10	No	5.1	Dry	0.70	0.13	0.13
Example 24	4	0	0	76	0	0	10	10	No	4.9	Dry	19.00	0.13	0.13
Example 25	10	20	0	50	0	0	10	10	No	5.0	Dry	2.50	0.17	0.17
Example 26	0	0	30	50	0	0	10	10	No	5.0	Dry	1.67	0.20	0.20
Example 27	30	0	0	0	50	0	10	10	No	5.2	Dry	1.67	0.13	0.13
Example 28	30	0	0	0	0	50	10	10	No	4.8	Dry	1.67	0.13	0.13
Example 29	30	0	0	50	0	0	10	10	Yes	5.0	Dry	1.67	0.13	0.13
Example 30	30	0	0	50	0	0	10	10	No	5.0	Wet	1.67	0.13	0.13
Example 31	40	0	0	60	0	0	0	0	No	5.0	Wet	1.50	0.00	0.00
Example 32	46	0	0	54	0	0	0	0	No	4.9	Wet	1.17	0.00	0.00
Example 33	25	0	0	75	0	0	0	0	No	4.8	Wet	3.00	0.00	0.00
Example 34	52	0	0	48	0	0	0	0	No	5.3	Wet	0.92	0.00	0.00
Example 35	10	0	0	90	0	0	0	0	No	4.7	Wet	9.00	0.00	0.00
Example 36	58	0	0	42	0	0	0	0	No	5.0	Wet	0.72	0.00	0.00
Example 37	4	0	0	96	0	0	0	0	No	5.0	Wet	24.00	0.00	0.00
Example 38	15	25	0	60	0	0	0	0	No	5.4	wet	2.40	0.00	0.00
Example 39	0	0	40	60	0	0	0	0	No	5.1	Wet	1.50	0.00	0.00

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(continued)

(A) Component	(A) Component			(B) Component			(C) Component	(D) Component	Base Coating Film	Coating Weight (g/m)	Upper Layer Coating Film	(B) / (A)	(C) / {(A) + (B)}	(D) / {(A) + (B)}
	(A- 1)	(A-2)	(A-3)	(B- 1)	(B-2)	(B-3)	(C-1)	(D-1)						
Example 40	40	0	0	0	60	0	0	0	No	5.4	Wet	1.50	0.00	0.00
Example 41	40	0	0	0	0	60	0	0	No	5.1	Wet	1.50	6.00	0.00
Example 42	40	0	0	60	0	0	0	0	Yes	5.1	Wet	1.50	0.00	0.00

[Table 7]

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[Table 7]

	(A) Component	(B) Component			(C) Component	(D) Component	Coating Weight (g/m)	Upper Layer Coating Film	(B)/(A)	(C)/{(A) + (B)}	(D)/{(A) + (B)}
	(A-1)	(B-1) 1)	(B-2) (B-2)	(B-3) (B-3)	(C-1) (C-1)	(D-1) (D-1)					
Comparative Example 10		No Coating						-	Dry	-	-
Comparative Example 11	80	0	0	0	10	10	5.0	Dry	0.00	0.13	0.13
Comparative Example 12	0	80	0	0	10	10	5.0	Dry		0.13	0.13
Comparative Example 13	60	20	0	0	10	10	5.3	Dry	0.33	0.13	0.13
Comparative Example 14	1	79	0	0	10	10	5.2	Dry	79.00	0.13	0.13
Comparative Example 15	60	0	20	0	10	10	5.3	Dry	0.33	0.13	0.13
Comparative Example 16	1	0	79	0	10	10	5.1	Dry	79.00	0.13	0.13
Comparative Example 17	60	0	0	20	10	10	4.9	Dry	0.33	0.13	0.13
Comparative Example 18	1	0	0	79	10	10	4.8	Dry	79.00	0.13	0.13
Comparative Example 19		No Coating						-	Wet	-	-
Comparative Example 20	100	0	0	0	0	0	4.9	wet	0.00	0.00	0.00
Comparative Example 21	0	100	0	0	0	0	5.0	wet	-	0.00	0.00
Comparative Example 22	75	25	0	0	0	0	4.8	wet	0.33	0.00	0.00

(continued)

	(A) Component	(B) Component			(C) Component	(D) Component	Coating Weight (g/m)	Upper Layer Coating Film	(B)/(A)	(C)/{(A) + (B)}	(D)/{(A) + (B)}
	(A-1)	(B-1)	(B-2)	(B-3)	(C-1)	(D-1)					
Comparative Example 23	1	99	0	0	0	0	4.9	wet	99.00	0.00	0.00
Comparative Example 24	75	0	25	0	0	0	5.0	wet	0.33	0.00	0.00
Comparative Example 25		0	99	0	0	0	5.1	wet	99.00	0.00	0.00
Comparative Example 26	75	0	0	25	0	0	5.0	wet	0.33	0.00	0.00
Comparative Example 27	1	0	0	99	0	0	5.3	wet	99.00	0.00	0.00
Comparative Example 28	Zink Phosphate/Soap Treatment										
									-	-	-



[Table 8]

[Table 8]

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	Drawability	Corrosion Resistance
Example 17	⊙	⊙
Example 18	⊙	⊙
Example 19	⊙	⊙
Example 20	⊙	⊙
Example 21	○	⊙
Example 22	⊙	○
Example 23	○	○
Example 24	○	○
Example 25	⊙	⊙
Example 26	⊙	⊙
Example 27	⊙	○
Example 28	⊙	○
Example 29	⊙	⊙
Example 30	⊙	⊙
Example 31	⊙	⊙
Example 32	⊙	⊙
Example 33	⊙	⊙
Example 34	○	⊙
Example 35	⊙	○
Example 36	○	○
Example 37	○	○
Example 38	⊙	⊙
Example 39	⊙	⊙
Example 40	⊙	○
Example 41	⊙	○
Example 42	⊙	⊙
Comparative Example 10	×	×
Comparative Example 11	▲	▲
Comparative Example 12	▲	×
comparative Example 13	△	▲
Comparative Example 14	▲	▲
Comparative Example 15	▲	×
Comparative Example 16	▲	×
Comparative Example 17	▲	×
Comparative Example 18	▲	×
Comparative Example 19	▲	×
Comparative Example 20	△	▲

(continued)

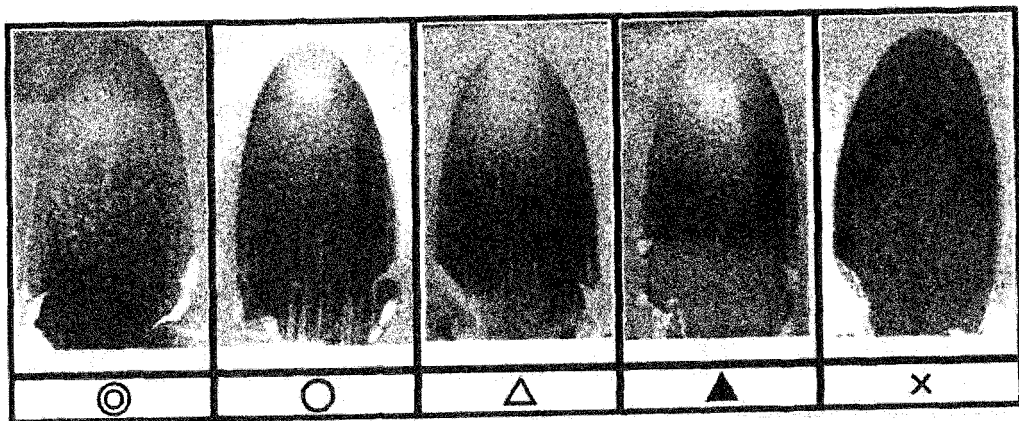
	Drawability	Corrosion Resistance
Comparative Example 21	▲	×
Comparative Example 22	Δ	Δ
Comparative Example 23	Δ	▲
Comparative Example 24	Δ	×
Comparative Example 25	Δ	×
Comparative Example 26	Δ	×
Comparative Example 27	Δ	×
Comparative Example 28	○	Δ

### Claims

1. A water-based lubricating coating agent wherein a water-soluble silicate (A) and at least one water-soluble inorganic salt (B) selected from a tungstate, a phosphate and a borate are blended such that a solid content mass ratio (B)/(A) falls within a range of 0.7 to 25.
2. The water-based lubricating coating agent according to claim 1, wherein the agent comprises a resin component (C), and a solid content mass ratio (C)/{(A) + (B)} is 0.01 to 3.
3. The water-based lubricating coating agent according to claim 2, wherein the resin component (C) is at least one selected from the group consisting of a vinyl resin, an acrylic resin, an epoxy resin, an urethane resin, a phenolic resin, a cellulose derivative, a polymaleic acid, a polyolefin, and a polyester.
4. The water-based lubricating coating agent according to any one of claims 1 to 3, wherein the agent comprises a lubricant (D), and a solid content mass ratio (D)/{(A) + (B)} is 0.01 to 6.
5. The water-based lubricating coating agent according to claim 4, wherein the lubricant (D) is at least one selected from the group consisting of a wax, polytetrafluoroethylene, a fatty acid soap, a fatty acid metal soap, a fatty acid amide, molybdenum disulfide, tungsten disulfide, graphite, melamine cyanurate, an amino acid compound of layered structure, and a layered clay mineral.
6. A metal material with a lubricating coating film of 0.5 to 40 g/m<sup>2</sup> as coating weight, formed on a metal material surface by applying and drying the water-based lubricating coating agent according to any one of claims 1 to 5.

[FIG. 1]

【Fig. 1】



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2015/058425

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)

C10M173/02, C10M103/06, C10M125/02, C10M125/10, C10M125/22, C10M125/24, C10M125/26, C10M129/28, C10M133/16, C10M133/42, C10M145/04, C10M145/14, C10M145/16, C10M145/20, C10M145/22, C10M145/40, C10M147/02, C10M149/20,

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

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

JSTPlus/JST7580/JSTChina(JDreamIII)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2012/043087 A1 (Nippon Seisen Co., Ltd.), 05 April 2012 (05.04.2012), claims 1 to 3, 10; paragraphs [0047], [0053], [0056], [0090] to [0092]; table 2, composition 6 & CN 103154216 A & KR 10-2013-0124148 A	1-6
X	JP 2010-018829 A (Sumitomo Metal Industries, Ltd.), 28 January 2010 (28.01.2010), claims 8 to 10, 12 to 13; paragraphs [0034] to [0035], [0039], [0042] to [0045], [0058], [0060], [0064], [0071] to [0077]; table 1, test no.26 (Family: none)	1-6

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

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Date of the actual completion of the international search  
17 April 2015 (17.04.15)

Date of mailing of the international search report  
28 April 2015 (28.04.15)

Name and mailing address of the ISA/  
Japan Patent Office  
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Tokyo 100-8915, Japan

Authorized officer

Telephone No.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2015/058425

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2002-363593 A (Kobe Steel, Ltd.), 18 December 2002 (18.12.2002), (Family: none)	1-6
A	JP 61-002797 A (Lonza Ltd.), 08 January 1986 (08.01.1986), & EP 164637 A1 & CN 85103499 A	1-6
A	JP 51-084786 A (Ball Brothers Research Corp.), 24 July 1976 (24.07.1976), & US 4039337 A	1-6

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

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2015/058425

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

C10M173/02(2006.01)i, C10M103/06(2006.01)n, C10M125/02(2006.01)n,  
C10M125/10(2006.01)n, C10M125/22(2006.01)n, C10M125/24(2006.01)n,  
C10M125/26(2006.01)n, C10M129/28(2006.01)n, C10M133/16(2006.01)n,  
C10M133/42(2006.01)n, C10M145/04(2006.01)n, C10M145/14(2006.01)n,  
C10M145/16(2006.01)n, C10M145/20(2006.01)n, C10M145/22(2006.01)n,  
C10M145/40(2006.01)n, C10M147/02(2006.01)n, C10M149/20(2006.01)n,  
C10M159/06(2006.01)n, C10N10/12(2006.01)n, C10N30/00(2006.01)n,  
C10N30/06(2006.01)n, C10N30/12(2006.01)n, C10N40/24(2006.01)n

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

## Continuation of B. FIELDS SEARCHED

Minimum documentation searched (International Patent Classification (IPC))

C10M159/06, C10N10/12, C10N30/00, C10N30/06, C10N30/12, C10N40/24

Minimum documentation searched (classification system followed by  
classification symbols)

**REFERENCES CITED IN THE DESCRIPTION**

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