

SPECIFICATION

LUBRICATING AQUEOUS POLYURETHANE RESIN COMPOSITION,
METHOD FOR SURFACE-LUBRICATING ZINCIFEROUS METAL-PLATED
5 STEEL STRIP BY USING THE COMPOSITION AND
 SURFACE-TREATED STEEL STRIP PRODUCED BY THE METHOD
TECHNICAL FIELD

 The present invention relates to a lubricating
aqueous polyurethane resin composition for surface-
10 lubricated steel strip, which composition is used during
press working for home appliances, building materials and
the like, and also relates to a surface-treating method
using the composition and a product obtained by the
method.

15 BACKGROUND ART

 Conventionally, zinc- or zinc alloy-plated steel
strips are widely used for home appliances, building
materials and the like. These steel strips per se are
insufficient in corrosion resistance or coatability and
20 therefore, surface-treated steel strips obtained by
applying an undercoat treatment such as chromate chemical
conversion treatment and phosphate chemical conversion
treatment, and then coating a resin on the surface
thereof, are usually used. These surface-treated steel
25 strips include lubricating steel strips which can be
worked without using press oil during press working, and
such steel strips are widely used for home appliances and
the like.

 Conventional techniques regarding lubricating steel
30 strips are disclosed in, for example, Japanese unexamined
Patent Publication (Kokai) No. 2001-214182 (Patent
Reference 1), No. 08-267002 (Patent Reference 2) and No.
06-145559 (Patent Reference 3).

 Japanese Unexamined Patent Publication No. 2001-
35 214182 (Patent Reference 1) discloses a method of forming
a coating layer comprising a mixed resin (A) comprising
an acryl-styrene-based resin (a) having an acid value of

less than 10 in an amount of 30 to 95 mass% in terms of the solid content and a polyurethane-based resin (b) in an amount of 5 to 70 mass% in terms of the solid content, and a mixture (B) comprising a chromium compound (c) and wax particles or thermoplastic resin particles (d) having an average particle size of 1 to 5 μm and a melting point higher than the glass transition point of those two resins constituting the mixed resin (A), in an amount of 1 to 7 mass% based on the total mass of the mixed resin (A), and having a thickness of 0.5 to 4 μm on at least one surface of a zinciferous metal plated steel strip, the coat layer. Also, Japanese Unexamined Patent Publication No. 08-267002 (Patent Reference 2) discloses a method in which a chromate coating is formed in an amount of 10 to 200 mg/m^2 in terms of metal chromium per one surface, on both surfaces of a zinc- or zinciferous metal-plated steel strip and, thereon, a resin composition layer comprising a mixed resin which will be explained hereinafter, 5 to 40 parts by mass of a curing agent, 1 to 40 parts by mass of a lubricant having a melting point of 80 to 130°C and 5 to 80 parts by mass of an organic silicon compound is formed in a coating amount of 0.1 to 1.0 g/m^2 . The mixed resin contains two or more resins having a plurality of hydroxyl groups and a glass transition temperature of -30 to 90°C, namely, a component comprising at least one resin having a glass transition temperature of -30°C or more but less than 30°C and a component comprising at least one resin having a glass transition temperature of 30 to 90°C, each in a content of 10% by mass or more based on the total mass of the resins.

These techniques all are characterized by using a blend of several types of resins, but when a coating is formed from the blend, these resins can be uniformly distributed in the resultant coating only on rare occasions and the properties of the resultant coating are

scattered and thus it is difficult to say that the properties of individual resins are sufficiently utilized. Therefore, the coating prepared by the above-described conventional method cannot fully satisfy the
5 required performances such as lubricity, solvent resistance and corrosion resistance, as pursued by the present inventors.

Japanese Unexamined Patent Publication No. 06-145559 (Patent Reference 3) discloses a technique concerning a
10 lubricating, aqueous coating material composition comprising (a) a water-dispersible ether-ester-type polyurethane resin having a bisphenol-type skeleton, an ester skeleton and a carboxyl group and having an average molecular weight of 3,000 or more, (b) a water-soluble or
15 water-dispersible epoxy resin, (c) a polyolefin wax having a melting point of 70 to 160°C and an average particle size of 0.1 to 7.0 μm , and (d) a silica having an average particle size of 3 to 30 μm , wherein a solid content ratio of the total amount of (a) and (b) to the
20 total solid content ($e=a+b+c+d$) is from 0.50:1 to 0.85:1, the solid content ratio of (c) to (e) is from 0.03:1 to 0.30:1, and the solid content ratio of (d) to (e) is from 0.10:1 to 0.40:1.

According to Patent Reference 3, a crosslinking
25 agent is added to a specific polyurethane resin, to obtain thereby the objective performances of the resin. However, Patent Reference 3 is absolutely silent as to the technique for obtaining performances equal to or greater than those obtained when using a crosslinking
30 agent using a polyurethane resin composition not containing a crosslinking agent.

Patent Reference 1: Japanese Unexamined Patent Publication No. 2001-214182, claim 1

Patent Reference 2: Japanese Unexamined Patent
35 Publication No. 08-267002, claim 1

Patent Reference 3: Japanese Unexamined Patent

Publication No. 06-145559, claim 1

DISCLOSURE OF THE INVENTION

5 An object of the present invention is to solve the problem of the prior art, that is, a reduction in the performance due to unevenness of the coating, and to provide an aqueous polyurethane resin composition having excellent lubricity, solvent resistance and corrosion resistance, a method of applying a lubricating treatment to a surface of a zinciferous metal-plated steel strip by
10 using the composition, and a surface-treated steel strip obtained by the method.

As a result of intensive investigations on aqueous chemicals satisfying all of the required lubricity, solvent resistance and corrosion resistance and surface-
15 treated steel strips produced by using the chemicals, the present inventors have found that the above-described problem can be overcome mainly by using a specified urethane resin. The present invention has been completed based on this finding.

20 The lubricating aqueous polyurethane resin composition of the present invention is characterized by comprising the following components (a), (b) and (c):

(a) a polyurethane resin comprising a polyester skeleton moiety and a polyether skeleton moiety and
25 having a tensile strength at break of 3.92 kN/cm^2 (400 kgf/cm^2) or more and a tensile elongation at break of 50% or less, determined in accordance with to JIS K 7113, and a glass transition temperature (T_g) of 80 to 150°C , determined in accordance with to JIS K 7121,

30 (b) fine particles of a polyolefin resin having a melting point of 70 to 160°C and a particle size of 0.5 to $5 \mu\text{m}$, and

(c) a colloidal silica having a particle size of 5 to 50 nm,
35 wherein, based on the total solid content mass (a+b+c) of said components (a), (b) and (c),

the solid content $((a)/(a+b+c))$ of the component (a) is from 50 to 93% by mass,

the solid content $((b)/(a+b+c))$ of the component (b) is from 2 to 20% by mass, and

5 the solid content $((c)/(a+b+c))$ of the component (c) is from 5 to 40% by mass.

In the lubricating aqueous polyurethane resin composition of the present invention, the ratio in mass of the polyester skeleton moiety to the polyether
10 skeleton moiety in the polyurethane resin (a) is preferably in the range of from 1/9 to 5/5.

The method of the present invention for lubricating a zinciferous metal-plated steel strip comprises coating a treating liquid containing the lubricating aqueous
15 polyurethane resin composition as claimed in claim 1 or 2 on a surface of a zinciferous metal-plated metal strip, and drying the coated liquid to form a lubricant layer having a dry solid mass of 0.1 to 5 g/m².

The surface-lubricated zinciferous metal-plated
20 steel strip of the present invention is one produced by the method for lubricating a zinciferous metal-plated steel strip as mentioned above.

By coating the lubricating aqueous polyurethane resin composition of the present invention on a surface
25 of a zinciferous metal-plated steel sheet, a coating having excellent corrosion resistance, alkali resistance, paint adhesion and lubricity can be formed.

The term "aqueous polyurethane resin composition" used in the present invention refers to --a polyurethane
30 resin composition soluble, dispersible or emulsible in a medium containing water--.

BEST MODE FOR CARRYING OUT THE INVENTION

The polyurethane resin (a) contained in the resin composition of the present invention has a tensile
35 strength at break of 3.92 kN/cm² (400 kgf/cm²) or more, preferably from 4.9 to 9.8 N/cm², a tensile elongation at break of 50% or less, preferably from 1 to 40%, and a

glass transition temperature (Tg) of 80 to 150°C (determined in accordance with JIS K 7121). In the shaping work typically press working, the resin coating is generally exposed to a strong shear force. In the case where this shear force surpasses the tensile strength at break of the coating, the coating itself is damaged. In other words, when the tensile strength at break of the coating is high, this coating is less damaged. The inventors of the present invention have made intensive studies and found that when the resin coating itself has a tensile strength at break of 3.92 kN/cm² (400 Kgf/cm²) or more, a tensile elongation at break of 50% or less and Tg of 80 to 150°C, the resultant coating can exhibit the target lubricity. Incidentally, the tensile strength at break and elongation at break of the polyurethane resin were measured by the procedure such that the resin was coated on a polyester sheet and dried at room temperature for 24 hours to form a coating having a dry thickness of 50 μm, and baked at 150°C for 30 minutes to produce a film, and then this film was gently peeled off from the polyester sheet and subjected to a tensile test. The tensile test was performed according to JIS K 6732. The glass transition temperature of the polyurethane resin was measured by using a commercially available dynamic viscoelastometer (Rheograph Solid S-1, manufactured by Toyo Seiki Seisaku-Sho, Ltd.). At this time, a specimen having a film thickness of 100 μm, a width of 8 mm and a length of 30 mm was used after drying at 100°C for 30 minutes, the frequency for measurement was 100 Hz, and the glass transition temperature was determined from the inflection point of loss factor in elastic modulus.

The solid content of the component (a) is from 50 to 93%, preferably from 55 to 90%, more preferably from 50 to 85%, based on the total solid content by mass (a+b+c) of the components (a), (b) and (c). If the solid content

of the component (a) is less than 50% based on the total solid content by mass (a+b+c) of the components (a), (b) and (c), the resultant polyurethane resin composition exhibits a low film continuity and thus the resultant polyurethane resin has unsatisfactory workability and adhesion. Also, if the solid content of the component (a) exceeds 93% based on the total solid content by mass (a+b+c) of the components (a), (b) and (c), the effect obtainable by the addition of the components (b) and (c) is poor and therefore, the resultant coating formed from the polyurethane resin composition exhibits insufficient corrosion resistance and workability.

The polyurethane resin for the component (a) usable for the present invention has a polyester skeleton and a polyether skeleton. The polyester skeleton is formed from a polyester polyol compound and the polyether skeleton is formed from a polyether polyol.

The polyester polyol compound for the formation of the polyester skeleton is a compound produced for example, by the reaction of low molecular weight polyols for example, ethylene glycol, diethylene glycol, triethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol, neopentyl glycol, 1,2-butylene glycol, 1,3-butylene glycol, 1,4-butylene glycol, 3-methylpentanediol, hexamethylene glycol, hydrogenated bisphenol A, trimethylolpropane and glycerin, with polybasic acids, for example, succinic acid, glutaric acid, adipic acid, sebacic acid, phthalic acid, isophthalic acid, terephthalic acid, trimellitic acid, tetrahydrophthalic acid, endomethylenetetrahydrophthalic acid and hexahydrophthalic acid, and having an ester structure and terminal hydroxyl groups.

The polyether polyol usable for the formation of the polyether skeleton is preferably a compound produced by an addition reaction of bisphenol skeleton-containing glycols, for example, methylene bisphenol, ethylidene bisphenol, butylidene bisphenol and isopropylidene

bisphenol with alkylene oxides having 2 to 4 carbon atoms (for example, ethylene oxide, propylene oxide and butylene oxide). The molar number of the addition reacted alkylene oxides is preferably from 1 to 10.

5 The ratio in mass of the polyester skeleton to the polyether skeleton in the polyurethane resin for the component (a) is preferably in the range of from 1/9 to 5/5 (polyester skeleton/polyether skeleton). If the mass
10 ratio of the polyester skeleton to the polyether skeleton is less than 1/9 (polyester skeleton/polyether skeleton), the content of the relatively rigid polyether skeleton becomes high and, thus, the elongatability of the coating decreases and, as a result, the resultant coating may be fragile and may exhibit an insufficient tensile strength
15 at break. Also, if the mass ratio of the polyester skeleton to the polyether skeleton is more than 5/5 (polyester skeleton/polyether skeleton), the content of the relatively soft polyester skeleton becomes high and thus the resultant coating may have a high elongatability
20 and an insufficient tensile strength at break.

 The fine particles (b) of the polyolefin resin contained in the polyurethane resin composition of the present invention has a melting point of 70 to 160°C and a particle size of 0.5 to 5 μm . Generally, the temperature
25 of the shaped article sometimes reaches 80°C during the press shaping procedure. Therefore, if the melting point of the polyolefin resin fine particles is less than 70°C, the polyolefin resin fine particles contained in the coating formed from the polyurethane resin composition
30 all are all melted during the shaping procedure and a coating having lubricity sufficiently high for the shaping work cannot be obtained. Also, if the melting point of the polyolefin resin fine particles is higher than 160°C, the polyolefin resin fine particles are hardly
35 melted by the sliding frictional heat and thus the resultant coating exhibits an insufficient lubricity at

the sliding. Also, if the particle size of the polyolefin resin fine particles is less than 0.5 μm , the resultant resin coating has insufficient lubricity, whereas if the particle size is more than 5.0 μm , the polyolefin resin fine particles readily comes off from the resultant resin coating. The polyolefin resin fine particles preferably have a true spherical shape so as to obtain a polyurethane resin composition having high-level workability.

10 The solid content of the component (b) is from 2 to 20%, preferably from 3 to 20%, more preferably from 3 to 18%, based on the total solid content in mass (a+b+c) of the components (a), (b) and (c). If the solid content of the component (b) is less than 2% based on the total
15 solid content in mass (a+b+c) of the components (a), (b) and (c), the resultant polyurethane resin composition has an insufficient lubricity, and if the solid content of the component (b) is more than 20% based on the total solid content in mass (a+b+c) of the components (a), (b)
20 and (c), a coating formed from the resultant polyurethane resin composition exhibits an insufficient adhesion to an overcoat material applied thereon.

 The particle size of the colloidal silica particles for the component (c) is from 5 to 50 nm, preferably from
25 5 to 40 nm, more preferably from 5 to 30 nm. If the particle size of the colloidal silica particles for the component (c) is more than 50 nm, the coating formed from the resultant polyurethane resin composition has an insufficient uniformity and thus the coating exhibits
30 unsatisfactory corrosion resistance, adhesive properties, etc. Also, if the particle size of the colloidal silica particles for the component (c) is less than 5 nm, the particles per se are difficult to industrially produce, and thus an economical disadvantage occurs. The solid
35 content of the component (c) is from 5 to 40%, preferably from 5 to 35%, more preferably from 5 to 30%, based on the total solid content in mass (a+b+c) of the components

(a), (b) and (c). If the solid content of the component (c) is less than 5% based on the total solid content in mass (a+b+c) of the components (a), (b) and (c), the effect of the resultant polyurethane resin on enhancing the corrosion resistance is insufficient. Also, if the solid content of the component (c) is more than 40% based on the total solid content in mass (a+b+c) of the components (a), (b) and (c), the coating formed from the resultant polyurethane resin composition is fragile and exhibits insufficient corrosion resistance, adhesive property and workability.

The aqueous polyurethane resin composition for metal surface treatment of the present invention may contain one or more members selected from a surfactant which is referred to as a wettability-enhancing agent for forming a uniform coating on the surface of a metal material, a thickening agent for adjusting the viscosity, an electrically conducting substance for enhancing the weldability, a colored pigment for enhancing the design property, a rust-preventive additive having inhibitor effect, a metal compound, etc.

There is no limitation to the type of the metal materials for the surface-treating with the lubricating aqueous polyurethane resin composition of the present invention. Usually, the composition of the present invention it is most advantageously applied to a zinciferous metal-plated steel strips. The amount of the coating for covering the surface of a zinciferous metal-plated steel strip is from 0.1 to 5.0 g/m², preferably from 0.2 to 4.0 g/m², more preferably from 0.3 to 4 g/m², in terms of the dry mass. If the dry mass of the coating formed on the surface of a zinciferous metal-plated steel strip is less than 0.1 g/m², the effect on enhancement of the lubricity of the polyurethane resin composition is insufficient. Also, if the dry mass of the coating formed on the surface of the zinciferous metal-plated steel strip is more than 5.0 g/m², the effect on the

enhancement of the lubricity is saturated and an economical disadvantage occurs. The method for coating with the treating solution containing the polyurethane resin composition of the present invention includes a
5 roll coater method, a dipping method and an electrostatic coating method but, in the present invention, there is no limitation to the coating method. Also, there is no limitation to the treatment temperature for the treating solution layer coated or the dry coating thereof.
10 Preferably the peak temperature of the steel strip is controlled in the range of from 100 to 200°C.

Also, with respect to the surface-treated steel strip of the present invention, there is no limitation to the kind and conditions of the pretreatment applied to
15 the zinciferous metal-plated steel strip prior to the lubricating treatment procedure in accordance with the method of the present invention when, for example, a degreasing treatment for keeping the plating layer surface clean, a chromate or phosphate treatment for
20 enhancing the corrosion resistance, or a non-chromate treatment using a treating solution having an excellent rust preventive effect and not containing a chromium-containing compound is applied, the resultant coating film formed from the lubricating polyurethane resin
25 composition can exhibit excellent lubricity and adhesive property.

EXAMPLES

The present invention will be further explained by the following examples. The aqueous polyurethane resin
30 compositions used in the examples and comparative examples were produced in the following manner.

Production Example 1

Production of Aqueous Polyurethane Resin al for Examples

40 Parts of a polyester polyol prepared from an
35 adipic acid having terminal hydroxyl groups and having an average molecular weight of 1,000, and 1,6-hexanediol, 160 parts of an adduct of a bisphenol A with 3 moles of

propylene oxide per mole of the bisphenol A and having an average molecular weight of 660, and 10 parts of 2,2-bis(hydroxymethyl)propionic acid were mixed into 100 parts of N-methyl-2-pyrrolidone and the mixture was dissolved under heat at 80°C. Then, to the resultant solution, 120 parts of dicyclohexylmethane diisocyanate were added and this mixture was reacted under heat at 110°C for 2 hours. The reaction product was neutralized with 10 parts of triethylamine. The resultant solution was added dropwise with vigorous stirring to an aqueous solution prepared by mixing 5 parts of ethylenediamine and 570 parts of deionized water, to produce an aqueous polyurethane resin. This resin had a tensile strength at break of 7.35 kN/cm² (750 Kgf/cm²), a tensile elongation at break of 10% and a Tg of 105°C. Also, the ratio in mass of polyester skeleton to polyether skeleton (polyester skeleton/polyether skeleton) in the polyurethane was 2:8.

Production Example 2

20 Production of Aqueous Polyurethane Resin a2 for Examples

20 Parts of a polyester polyol prepared from an adipic acid having terminal hydroxyl groups and 1,6-hexanediol and, having an average molecular weight of 1,000, 180 parts of an adduct of bisphenol A with 3 moles of propylene oxide per mole of bisphenol A and having an average molecular weight of 660, and 12 parts of 2,2-bis(hydroxymethyl)propionic acid were mixed into 100 parts of N-methyl-2-pyrrolidone, and the resultant mixture was dissolved under heat at 80°C. Then, to the resultant solution, 110 parts of dicyclohexylmethane diisocyanate was mixed and the resultant mixture was subjected to a reaction under heat at 110°C for 2 hours. The resultant reaction product was neutralized with 11 parts of triethylamine and the resultant solution was added dropwise with vigorous stirring to an aqueous solution prepared by mixing 5 parts of ethylenediamine

with 570 parts of deionized water, while the aqueous solution was vigorously stirred to produce an aqueous polyurethane resin. This resin had a tensile strength at break of 7.84 kN/cm² (800 Kgf/cm²), a tensile elongation at break of 5% and a Tg of 125°C. Also, the ratio in mass of polyester skeleton to polyether skeleton (polyester skeleton/polyether skeleton) in the polyurethane was 1:9.

Production Example 3

Production of Aqueous Polyurethane Resin a3 for Examples

80 Parts of a polyester polyol produced from an adipic acid having terminal hydroxyl groups and 1,6-hexanediol, and having an average molecular weight of 1,000, 120 parts of an adduct of bisphenol A with 3 moles of propylene oxide per mole of bisphenol A and having an average molecular weight of 660, and 12 parts of 2,2-bis(hydroxymethyl)propionic acid were mixed into 100 parts of N-methyl-2-pyrrolidone, and the resultant mixture was dissolved under heat at 80°C. Then, to the resultant solution, 100 parts of dicyclohexylmethane diisocyanate were mixed and the resultant mixture was subjected to a reaction under heat at 110°C for 2 hours. The reaction product was neutralized by adding 11 parts of triethylamine and the resultant solution was added dropwise with vigorous stirring to an aqueous solution prepared by mixing 5 parts of ethylenediamine with 570 parts of deionized water, to produce an aqueous polyurethane resin. This resin had a tensile strength at break of 6.37 kN/cm² (650 Kgf/cm²), a tensile elongation at break of 25% and a Tg of 85°C. Also, the ratio in mass of polyester skeleton to polyether skeleton (polyester skeleton/polyether skeleton), in the polyurethane was 4:6.

Production Example 4

Production of Aqueous Urethane Resin a4 for Comparative Examples

230 Parts of a polyester polyol prepared from an

adipic acid having terminal hydroxyl groups and 1,6-hexanediol, and having an average molecular weight of 1,000, and 15 parts of 2,2-bis(hydroxymethyl)-propionic acid were mixed in 100 parts of N-methyl-2-pyrrolidone, and the resultant mixture was dissolved under heat at 80°C. To the resultant solution, 100 parts of dicyclohexylmethane diisocyanate were mixed and the resultant mixture was subjected to a reaction under heat at 110°C for 2 hours. The resultant reaction product was neutralized with 11 parts of triethylamine. The resultant solution was added dropwise with vigorous stirring to an aqueous solution prepared by mixing 5 parts of ethylenediamine with 570 parts of deionized water, to produce an aqueous urethane resin. This resin had a tensile strength at break of 3.92 kN/cm² (400 Kgf/cm²), a tensile elongation at break of 400% and a Tg of 30°C. Also, the ratio in of polyester skeleton to polyether skeleton (polyester skeleton/polyether skeleton) in this polyurethane resin was 10:0.

Production Example 5

Production of Aqueous Polyurethane Resin a5 for Comparative Examples

200 Parts of an adduct of bisphenol A with 3 moles of propylene oxide per mole of bisphenol A and having an average molecular weight 660, and 15 parts of 2,2-bis(hydroxymethyl)propionic acid were mixed in 100 parts of N-methyl-2-pyrrolidone, and the resultant mixture was dissolved under heat at 80°C. To the resultant solution, 120 parts of dicyclohexylmethane diisocyanate were mixed and the resultant mixture was subjected to a reaction under heat at 110°C for 2 hours. The reaction product was neutralized with 15 parts of triethylamine and the resultant solution was added dropwise with vigorous stirring to an aqueous solution prepared by mixing 5 parts of ethylenediamine and 570 parts of deionized water, to produce an aqueous urethane resin. The

resultant resin had a tensile strength at break of 6.37 kN/cm² (650 Kgf/cm²), a tensile elongation at break of 5% and a Tg of 140°C. Also, the ratio in mass of polyester skeleton to polyether skeleton (polyester skeleton/polyether skeleton) in this polyurethane resin was 0:10.

The metal materials used in the following examples and comparative Examples were prepared as follows.

Raw Material

- 10 (1) Zn-electroplated steel strip (symbol: EG)
sheet thickness of strip = 0.8 mm (basis mass (front/back) = 20/20 (g/m²))
(2) Hot-dip Zn-plated steel strip (symbol: GI)
thickness of strip = 0.8 mm (basis mass of plated Z
15 (front/back) = 60/60 (g/m²))
(3) Hot-dip 55% Al-Zn alloy-plated steel strip (symbol: GL)
thickness of strip = 0.8 mm (basis mass of plated alloy (front/back) = 90/90 (g/m²))
20 (4) Steel strip electroplated with a Zn-Ni alloy having an Ni content of 12% by mass (symbol: ZL)
thickness of strip = 0.8 mm (basis mass of plated alloy (front/back) = 20/20 (g/m²))
(5) Hot-dip 11% Al, 3% Mg, and 0.2% Si containing Zn
25 alloy-plated steel strip (symbol: SD)
thickness of strip = 0.8 mm (basis mass of plated alloy (front/back) = 60/60 (g/m²))

Degreasing Treatment

A degreasing agent (trademark: Fine Cleaner 4336, produced by Nihon Parkerizing Co., Ltd., effective ingredient concentration = 20 g/liter), was sprayed toward the raw material at a temperature of 60°C for 2 minutes and immediately after this degreasing treatment, the degreased steel strip was washed with water and then
35 subjected to the undercoat chromate treatment, undercoat zinc phosphate treatment or non-chromate treatment, as mentioned below.

Undercoat Treatment

(1) Chromate treatment

A chromate treating agent (trademark: Zinchrome 357, produced by Nihon Parkerizing Co., Ltd.), was sprayed toward the degreased steel strip (bath temperature = 50°C, treatment time = 5 seconds), and the resultant undercoat layer was washed with water and then dried at an atmospheric temperature (peak metal temperature of steel strip = 100°C) of 220°C for 10 seconds. The coverage of chromium by this treatment was 10 mg/m².

(2) Zinc phosphate treatment

The degreased steel strip was dip-treated (at 45°C for 2 minutes) with a zinc phosphate treating agent, (trademark: Palbond L3020, produced by Nihon Parkerizing Co., Ltd.), then washed with water and air-dried. The amount in mass of the chemical conversion coating formed on the strip was 2.0 g/m².

(3) Non-chromate treatment

A non-chromate treating agent (trademark: Palcoat 3841, produced by Nihon Parkerizing Co., Ltd.) containing a silane compound) was coated on the degreased steel sheet by using a roll coater to treat the steel strip, and the treatment layer was immediately dried for 10 seconds at an atmosphere temperature of 220°C (peak temperature of steel sheet = 100°C). In this case, the mass of dry coating was 0.2 g/m².

Aqueous Dispersion of Polyolefin Resin for Component (b)

The trademarks, solid contents and particle sizes of aqueous dispersion of polyolefin resins used in the examples and the comparative examples are shown in Table 1. These aqueous dispersions are all produced by Mitsui Chemicals, Inc.

Table 1

Polyolefin Resin Aqueous Dispersions for component (b)
for examples and comparative examples

No.	Trademark	Solid Content	Melting Point	Particle Size	Remarks
b1	Chemipearl WF640	40%	113°C	1.0 μm	for Examples
b2	Chemipearl WP250	40%	148°C	0.8 μm	for Examples
b3	Chemipearl W400	40%	113°C	4.0 μm	for Examples
b4	Chemipearl W200	40%	113°C	6.0 μm	for Comparative Examples

5 Colloidal Silica for Component (c)

The trademarks, solid contents and particle sizes of colloidal silicas used in the examples and the comparative examples are shown in Table 2. These colloidal silicas are all produced by Nissan Chemical Industries, Ltd.

Table 2

Colloidal Silica for examples and comparative Examples

No.	Trademark	Solid Content	Particle Size	Remarks
c1	Snowtex-C	20%	20 nm	for Examples
c2	Snowtex-XS	15%	5 nm	for Examples
c3	MP-2040	40%	200 nm	for Comparative Examples

Composition of Lubricating Aqueous Resin Compositions

15 Compositions of Lubricating Aqueous Polyurethane Resin Compositions d1 to d9 used in the examples are shown in Table 3. Also, compositions of Resin Compositions d10 to d15 used in the comparative examples are shown in Table 4. In Tables 3 and 4, the numerical value in the parentheses indicates the ratios (%) in mass, of the solid contents of individual components to the entire solid content of the aqueous polyurethane resin composition.

Table 3
Compositions of Polyurethane Resin Compositions for
Examples

No.	(a) Urethane Resin	(b) Polyolefin Resin	(c) Colloidal Silica
d1	a1 (70)	b1 (10)	c1 (20)
d2	a2 (75)	b1 (10)	c1 (15)
d3	a3 (65)	b1 (10)	c1 (25)
d4	a3 (60)	b1 (2)	c1 (38)
d5	a1 (60)	b1 (20)	c1 (20)
d6	a1 (80)	b1 (15)	c1 (5)
d7	a1 (70)	b2 (10)	c1 (20)
d8	a1 (70)	b3 (10)	c1 (20)
d9	a1 (70)	b1 (10)	c2 (20)

5

Table 4
Compositions of Aqueous Resin Compositions for
Comparative Examples

No.	(a) Polyurethane Resin	(b) Polyolefin Resin	(c) Colloidal Silica	Remarks
d10	a4 (70)	b1 (10)	c1 (20)	component (a) falls outside of the present invention
d11	a5 (75)	b1 (10)	c1 (15)	component (a) falls outside of the present invention
d12	a1 (65)	b4 (10)	c1 (25)	component (b) falls outside of the present invention
d13	a1 (70)	b1 (10)	c3 (20)	component (c) falls outside of the present invention
d14	a1 (80)	none	c1 (20)	no component (b)
d15	a1 (85)	b1 (15)	none	no component (c)

Lubricating Treatment

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The coating solutions containing the lubricating aqueous resins compositions shown in Tables 3 and 4 were coated on the steel material surfaces by a bar coater, and the resultant coating solution layers were dried at

an atmospheric temperature of 320°C for 12 seconds. In these cases, the peak temperature of the steel material was 100 to 200°C (preferably 120°C), and the amounts of the resultant coatings were 1.0 g/m².

- 5 When the peak temperature of the steel material was other than 120°C, the heating atmosphere temperature and the heating time were as follows.

100°C: 320°C × 9 seconds
150°C: 320°C × 16 seconds
180°C: 320°C × 22 seconds
200°C: 320°C × 27 seconds

Performance Test for Coated Steel Strips

(1) Corrosion resistance

- 10 A salt spray test was applied to the coated steel strips for 200 hours and the white rust generation on the coated steel strips was observed, in accordance with JIS Z 2731.

<Evaluation Criteria>

- 4 The rust generated area was less than 3% of the entire area.
3 The rust generated area was 3% or more but less than 10% of the entire area.
2 The rust generated area was 10% or more but less than 30% of the entire area.
1 The rust generated area was 30% or more of the entire area.

- 15 (2) Alkali resistance

The coated steel strips were dipped in an alkali degreasing agent (trademark: Palclean N364S, produced by Nihon Parkerizing Co., Ltd., concentration = 20 g/liter, temperature = 60°C) and then subjected to the above-

20 described corrosion resistance evaluation test.

<Evaluation Criteria>

- 4 The rust generated area was less than 3% of the entire area.

- 3 The rust generated area was from 3% or more but less than 10% of the entire area.
- 2 The rust generated area was 10% or more and no deterioration in performance was found.
- 1 The rust generated area was 10% or more and no deterioration in performance was found.

(3) Paint adhesion

A melamine-based paint (trademark: Amilac #1000, produced by Kansai Paint Co., Ltd.) was coated on the steel material and dried and baked at 125°C for 20 minutes to form a coating having a thickness of 25 μm . Then, after 24 hours, the baked material was dipped in boiling water for 2 hours. After another 24 hours, the evaluation test was performed on the resultant product. As for the evaluation method, the adhesion and blistering were evaluated in accordance with the crosscut Erichsen test of JIS K 5400 and the paint adhesion was generally evaluated on the basis of the results of the above-mentioned tests.

<Evaluation Criteria>

- 4 No separation of coating layer occurs and no blister is found.
- 3 No separation of coating layer occurs but very slight blistering is found.
- 2 From 1 to 10% of coating layer is separated.
- 1 More than 10% of coating layer is separated.

(4) Lubricity

By using a blank (control) sheet with a diameter of 115 mm, a high-speed cylinder deep-drawing test was performed under the conditions such that the punch diameter was 50 mm, the unwrinkling pressure was 1 ton, and the deep drawing rate was 30 m/min. In the test, 2 g/m² of a press oil (#640, produced by Nihon Kohsaku Co., Ltd.) was optionally applied to the test pieces. In this test, the draw ratio was 2.30.

<Evaluation Criteria>

- 4 Successfully drawn up to a draw ratio of 2.40 without oil application.
- 3 Successfully drawn up to a draw ratio of 2.30 without oil application.
- 2 Successfully drawn up to a draw ratio of 2.30 with oil application.
- 1 Cannot be successfully drawn at a draw ratio of 2.30 with oil application.

Examples 1 to 74 and Comparative Examples 1 to 10

5 In each of Examples 1 to 74 and Comparative Examples 1 to 10, the zinciferous metal-plated steel strips as shown in Tables 5 to 7 and 8 were used as the raw material, and were subjected to the undercoat treatment and then to the treatment for coating the steel strips with lubricating resin compositions. The performances of the resultant lubricating resin composition coating are shown in Tables 5 to 7 and 8.

Performance Evaluation Results of Aqueous Polyurethane Resin Composition of the Present Invention

Example No.	Raw Material	Undercoat Treatment		Treatment with Lubricating Resin Composition			Film Performance			
		Type	Coverage *1	Type	Coverage (g/m ²) *1	Temperature (°C) *2	Corrosion Resistance	Alkali Resistance	Adhesion	Lubricity
1	EG	chromate	0.02	d1	1.0	120	4	4	4	4
2	EG	chromate	0.02	d2	1.0	120	4	4	4	4
3	EG	chromate	0.02	d3	1.0	120	4	4	4	4
4	EG	chromate	0.02	d4	1.0	120	4	4	4	4
5	EG	chromate	0.02	d5	1.0	120	4	4	4	4
6	EG	chromate	0.02	d6	1.0	120	4	4	4	4
7	EG	chromate	0.02	d7	1.0	120	4	4	4	4
8	EG	chromate	0.02	d8	1.0	120	4	4	4	4
9	EG	chromate	0.02	d9	1.0	120	4	4	4	4
10	GI	chromate	0.02	d1	1.0	120	4	4	4	4
11	GI	chromate	0.02	d2	1.0	120	4	4	4	4
12	GI	chromate	0.02	d3	1.0	120	4	4	4	4
13	GI	chromate	0.02	d7	1.0	120	4	4	4	4
14	GI	chromate	0.02	d8	1.0	120	4	4	4	4
15	GL	chromate	0.02	d1	1.0	120	4	4	4	4
16	GL	chromate	0.02	d2	1.0	120	4	4	4	4
17	GL	chromate	0.02	d3	1.0	120	4	4	4	4
18	GL	chromate	0.02	d7	1.0	120	4	4	4	4
19	GL	chromate	0.02	d8	1.0	120	4	4	4	4
20	ZL	chromate	0.02	d1	1.0	120	4	4	4	4
21	ZL	chromate	0.02	d2	1.0	120	4	4	4	4
22	ZL	chromate	0.02	d3	1.0	120	4	4	4	4
24	ZL	chromate	0.02	d7	1.0	120	4	4	4	4
25	ZL	chromate	0.02	d8	1.0	120	4	4	4	4

[Note] *1: Unit of coverage is g/m²; in the case of chromate treatment, in terms of metal chromium.

*2: Peak temperature of metal sheet

Performance Evaluation Results of Aqueous Polyurethane Resin Composition
of the Present Invention (continued)

Example No.	Raw Material	Undercoat Treatment		Treatment with Lubricating Resin Composition			Film Performance			
		Kind	Coverage *1	Kind	Coverage (g/m ²) *1	Temperature (°C) *2	Corrosion Resistance	Alkali Resistance	Adhesion	Lubricity
26	SD	chromate	0.02	d1	1.0	120	4	4	4	4
27	SD	chromate	0.02	d2	1.0	120	4	4	4	4
28	SD	chromate	0.02	d3	1.0	120	4	4	4	4
29	SD	chromate	0.02	d7	1.0	120	4	4	4	4
30	SD	chromate	0.02	d8	1.0	120	4	4	4	4
31	EG	chromate	0.02	d1	0.5	120	4	3	4	4
32	EG	chromate	0.02	d1	3.0	120	4	4	4	4
33	GI	chromate	0.02	d1	3.0	120	4	4	4	4
34	GL	chromate	0.02	d1	3.0	120	4	4	4	4
35	ZL	chromate	0.02	d1	3.0	120	4	4	4	4
36	SD	chromate	0.02	d1	3.0	120	4	4	4	4
37	EG	chromate	0.02	d1	5.0	120	4	4	4	4
38	EG	chromate	0.001	d1	1.0	120	3	4	3	4
39	EG	chromate	0.1	d1	1.0	120	4	4	4	4
40	EG	chromate	0.02	d1	1.0	100	4	4	4	4
41	EG	chromate	0.02	d1	1.0	150	4	4	4	4
42	EG	chromate	0.02	d1	1.0	180	4	4	4	4
43	GI	chromate	0.02	d1	1.0	180	4	4	4	4
44	GL	chromate	0.02	d1	1.0	180	4	4	4	4
45	ZL	chromate	0.02	d1	1.0	180	4	4	4	4
46	SD	chromate	0.02	d1	1.0	180	4	4	4	4
47	EG	chromate	0.02	d1	1.0	200	4	4	4	4
48	EG	phosphate	2.0	d1	1.0	120	4	4	4	4
49	EG	phosphate	2.0	d2	1.0	120	4	4	4	4
50	EG	phosphate	2.0	d3	1.0	120	4	4	4	4
51	EG	phosphate	2.0	d4	1.0	120	4	4	4	4
52	EG	phosphate	2.0	d5	1.0	120	4	4	4	4
53	EG	phosphate	2.0	d6	1.0	120	4	4	4	4

Table 7

Performance Evaluation Results of Aqueous Polyurethane Resin Composition
of the Present Invention (continued)

Example No.	Raw Material	Undercoat Treatment		Treatment with Lubricating Resin Composition			Film Performance			
		Kind	Coverage *1	Kind	Coverage (g/m ²) *1	Temperature (°C) *2	Corrosion Resistance	Alkali Resistance	Adhesion	Lubricity
54	EG	phosphate	2.0	d7	1.0	120	4	4	4	4
55	EG	phosphate	2.0	d8	1.0	120	4	4	4	4
56	EG	phosphate	2.0	d9	1.0	120	4	4	4	4
57	GI	phosphate	2.0	d1	1.0	120	4	4	4	4
58	GL	phosphate	2.0	d1	1.0	120	4	4	4	4
59	ZL	phosphate	2.0	d1	1.0	120	4	4	4	4
60	SD	phosphate	2.0	d1	1.0	120	4	4	4	4
61	EG	non-chro	0.2	d1	1.0	120	4	4	4	4
62	EG	non-chro	0.2	d2	1.0	120	4	4	4	4
63	EG	non-chro	0.2	d3	1.0	120	4	4	4	4
64	EG	non-chro	0.2	d4	1.0	120	4	4	4	4
65	EG	non-chro	0.2	d5	1.0	120	4	4	4	4
66	EG	non-chro	0.2	d6	1.0	120	4	4	4	4
67	EG	non-chro	0.2	d7	1.0	120	4	4	4	4
68	EG	non-chro	0.2	d8	1.0	120	4	4	4	4
69	EG	non-chro	0.2	d9	1.0	120	4	4	4	4
70	GI	non-chro	0.2	d1	1.0	120	4	4	4	4
71	GL	non-chro	0.2	d1	1.0	120	4	4	4	4
72	ZL	non-chro	0.2	d1	1.0	120	4	4	4	4
73	SD	non-chro	0.2	d1	1.0	120	4	4	4	4
74	SD	none	-	d1	2.0	120	3	3	3	4

[Note] Non-chro: non-chromate treatment

Performance Evaluation Results of Resin Composition of Comparative Example

Comparative Example No.	Con-struction Material	Undercoat Treatment		Treatment with Lubricating Resin Composition			Film Performance			
		Kind	Coverage *1	Kind	Coverage (g/m ²) *1	Temperature (°C) *2	Corrosion Resistance	Alkali Resistance	Adhesion	Lubricity
1	EG	chromate	0.02	d10	1.0	120	3	2	1	2
2	EG	chromate	0.02	d11	1.0	120	3	2	3	1
3	EG	chromate	0.02	d12	1.0	120	3	3	3	1
4	EG	chromate	0.02	d13	1.0	120	2	1	3	3
5	EG	chromate	0.02	d14	1.0	120	3	2	3	1
6	EG	chromate	0.02	d15	1.0	120	1	1	1	2
7	GI	chromate	0.02	d10	1.0	120	3	2	1	2
8	GL	chromate	0.02	d10	1.0	120	3	2	1	2
9	ZL	chromate	0.02	d10	1.0	120	3	2	1	2
10	SD	chromate	0.02	d10	1.0	120	3	2	1	2

Table 8

As is apparent from Tables 5 to 7, in Examples 1 to 73 of the present invention where a chromate or phosphate coating or non-chromate coating was formed on each of various zinciferous metal-plated steel strips and then
5 the aqueous polyurethane resin composition of the present invention was coated thereon and dried to form a coating, the resultant resin coating was excellent in all of corrosion resistance, alkali resistance, paint adhesion and lubricity. On the other hand, as seen from Table 8,
10 in Comparative Examples 1 to 10 which fall outside of the scope of the present invention, the resultant resin composition coatings were unsatisfactory in at least one of the corrosion resistance, alkali resistance, paint adhesion and lubricity.

15

Industrial Applicability

The lubricating aqueous polyurethane resin composition of the present invention can form a surface coating having excellent corrosion resistance, alkali
20 resistance, paint adhesion and lubricity, when coated on a surface of a zinciferous metal-plated steel strip, and therefore, has a high utilizability in industry.

CLAIMS

1. A lubricating aqueous polyurethane resin composition comprising the following components (a), (b) and (c):

5 (a) a polyurethane resin comprising a polyester skeleton moiety and a polyether skeleton moiety and having a tensile strength at break of 3.92 kN/cm^2 (400 kgf/cm^2) or more and a tensile elongation at break of 50% or less, determined in accordance with to JIS K 7113, and
10 a glass transition temperature (T_g) of 80 to 150°C , determined in accordance with to JIS K 7121,

(b) fine particles of a polyolefin resin having a melting point of 70 to 160°C and a particle size of 0.5 to $5 \mu\text{m}$, and

15 (c) a colloidal silica having a particle size of 5 to 50 nm ,

wherein, based on the total solid content mass ($a+b+c$) of said components (a), (b) and (c),

the solid content $((a)/(a+b+c))$ of the
20 component (a) is from 50 to 93% by mass,

the solid content $((b)/(a+b+c))$ of the component (b) is from 2 to 20% by mass, and

the solid content $((c)/(a+b+c))$ of the component (c) is from 5 to 40% by mass.

25 2. The lubricating aqueous polyurethane resin composition as claimed in claim 1, wherein the ratio in mass of the polyester skeleton moiety to the polyether skeleton moiety in the polyurethane resin (a) is in the range of from $1/9$ to $5/5$.

30 3. A method for lubricating a zinciferous metal-plated steel strip, comprising coating a treating liquid containing the lubricating aqueous polyurethane resin composition as claimed in claim 1 or 2 on a surface of a zinciferous metal-plated metal strip, and drying the
35 coated liquid to form a lubricant layer having a dry solid mass of 0.1 to 5 g/m^2 .

4. A surface-lubricated zinciferous metal-plated steel strip produced by the method for lubricating a zinciferous metal-plated steel strip as claimed in claim 3.