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Method of Producing a Metal Material Comprising a Film

Abstract

A method of producing a metal material comprising a film using a metal surface treatment agent containing: a prescribed copolymer (A) obtained by polymerizing a compound (a) [Formula (1)] with a compound (b) [Formula (2) or (3)] and a water-soluble or water-dispersible resin (B), wherein R.sup.1 and R.sup.2 each independently represent a hydrogen atom or an alkyl group having 1 to 4 carbon atoms, R.sup.3 and R.sup.4 each independently represent an alkyl group having 1 to 5 carbon atoms, X— represents an ion of a halogen atom, or an acid anion, R.sup.5 represents a hydrogen atom or a methyl group, R.sup.6 and R.sup.7 each independently represent a hydrogen atom, an alkyl group having 1 to 4 carbon atoms, a benzyl group, or a hydroxyalkyl group having 2 or 3 carbon atoms; and R.sup.8 represents a hydrogen atom or a methyl group. ##STR00001##

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Background/Summary

CROSS-REFERENCE TO RELATED APPLICATIONS [0001] This application is a divisional of U.S. application Ser. No. 17/424,197 filed Jul. 20, 2021, which is the U.S. national stage of PCT/JP2020/002236 filed Jan. 23, 2020, which claims the priority benefit of Japan Application No. 2019-010529 filed Jan. 24, 2019, the respective disclosures of which are hereby incorporated by reference in their entirety for all purposes herein.

TECHNICAL FIELD
[0002] The present invention relates to: a metal surface treatment agent; a method of producing a metal material having a film using the metal surface treatment agent; and a metal material having a film, which is obtained by the method.
BACKGROUND ART
[0003] Technologies relating to a film having antimicrobial performance have been developed. For example, Patent Document 1 discloses a hydrophilic film formed by using a hydrophilization treatment agent for a heat exchanger, which contains a water-dispersible silica, an aqueous polyurethane resin, and an aqueous blocked urethane prepolymer. Patent Document 2 discloses a film that is formed by a hydrophilization treatment agent containing a chitosan derivative in which some or all of primary amino groups of chitosan are added by a compound having an unsaturated group between carbon atoms at the α-position of its electron-withdrawing group.
RELATED ART DOCUMENTS
Patent Documents
[0004] [Patent Document 1] Japanese Unexamined Patent Application Publication No. H8-60031
[0005] [Patent Document 2] Japanese Unexamined Patent Application Publication No. 2010-185024
SUMMARY OF THE INVENTION
Problems to be Solved by the Invention
[0006] An object of the present invention is to provide: a novel metal surface treatment agent which can form a film capable of maintaining antimicrobial performance on or over a surface of a metal material; a method of producing a metal material having a film using the metal surface treatment agent; and a metal material having a film, which is obtained by the method.
Means for Solving the Problems
[0007] The present inventors intensively studied to solve the above-described problems and consequently discovered that a film capable of maintaining antimicrobial performance can be formed on or over a surface of a metal material by combining specific resins, thereby completing the present invention.
[0008] That is, the present invention encompasses the following. [0009] [1] A metal surface

treatment agent, containing: [0010] a copolymer (A) obtained by polymerizing a compound (a) represented by the following Formula (1) with a compound (b) represented by the following Formula (2) or (3); and [0011] a water-soluble or water-dispersible resin (B), [0012] wherein [0013] a polymerization ratio [a.sub.M:b.sub.M] between the molar amount (a.sub.M) of the compound (a) and the molar amount (b.sub.M) of the compound (b) is in a range of 90:10 to 20:80, and [0014] the copolymer (A) has a weight-average molecular weight of 50,000 or higher: ##STR00002## [0015] [in Formula (1), R.sup.1 and R.sup.2 each independently represent a hydrogen atom or an alkyl group having 1 to 4 carbon atoms, R.sup.3 and R.sup.4 each independently represent an alkyl group having 1 to 5 carbon atoms, and X-represents an ion of a halogen atom, or an acid anion; [0016] in Formula (2), R.sup.5 represents a hydrogen atom or a methyl group, R.sup.6 and R.sup.7 each independently represent a hydrogen atom, an alkyl group having 1 to 4 carbon atoms, a benzyl group, or a hydroxyalkyl group having 2 or 3 carbon atoms; and [0017] in Formula (3), R.sup.8 represents a hydrogen atom or a methyl group]. [0018] [2] The metal surface treatment agent according to [1], wherein the resin (B) is one or more selected from urethane resins, polyvinyl alcohol resins, polyamide resins, epoxy resins, phenolic resins, and polyvinylpyrrolidone resins. [0019] [3] The metal surface treatment agent according to [1] or [2], wherein a ratio [A.sub.W/B.sub.W] between the mass (A.sub.W) of the copolymer (A) and the mass (B.sub.W) of the resin (B) is in a range of 0.05 to 1.0. [0020] [4] The metal surface treatment agent according to any one of [1] to [3], further containing a crosslinking component (C). [0021] [5] The metal surface treatment agent according to [4], wherein the crosslinking component (C) is a carboxyl group-containing compound (excluding the copolymer (A)) and/or a water-soluble metal compound. [0022] [6] The metal surface treatment agent according to [4] or [5], wherein a ratio [C.sub.W/(A.sub.W+B.sub.W)] between the mass (C.sub.W) of the crosslinking component (C) and a total of the mass (A.sub.W) and the mass (B.sub.W) is in a range of 0.03 to 0.43. [0023] [7] A method of producing a metal material having a film, the method including the steps of: [0024] contacting the metal surface treatment agent according to any one of [1] to [6] on or over a surface of a metal material; and [0025] drying the metal surface treatment agent thus contacted. [0026] [8] A metal material having a film, which is obtained by the method according to [7].
Effects of the Invention
[0027] According to the present invention, the followings can be provided: a novel metal surface treatment agent which can form a film capable of maintaining antimicrobial performance on or over a surface of a metal material; a method of producing a metal material having a film using the metal surface treatment agent; and a metal material having a film, which is obtained by the method.

Description

MODE FOR CARRYING OUT THE INVENTION
[0028] The metal surface treatment agent according to the present embodiment, a method of producing a metal material having a film using the metal surface treatment agent, and a metal material having a film, which is obtained by the method, will now be described.
(Metal Surface Treatment Agent)
[0029] The metal surface treatment agent according to the present embodiment contains a specific copolymer (A) and a water-soluble or water-dispersible resin (B). By using this metal surface treatment agent, a film capable of maintaining antimicrobial performance can be formed on or over a surface of a metal material.
<Copolymer (A)>
[0030] The copolymer (A) is not particularly restricted as long as it is obtained by polymerizing a compound (a) represented by the above-described Formula (1) (hereinafter, simply referred to as “compound (a)”) with a compound (b) represented by the above-described Formula (2) or (3)

(hereinafter, simply referred to as “compound (b)”), and the copolymer (A) may be any of an alternating copolymer, a random copolymer, a block copolymer, and a graft copolymer. These copolymers can be produced by a known polymerization method. In the production of the copolymer (A), the ratio between the molar amount (a.sub.M) of the compound (a) and the molar amount (b.sub.M) of the compound (b) may be in a range of 90:10 to 20:80, and it is preferably in a range of 80:20 to 40:60, more preferably in a range of 70:30 to 60:40.
[0031] The weight-average molecular weight of the copolymer (A) is not particularly restricted as long as it is 50,000 or higher; however, it is preferably 100,000 or higher, more preferably 500,000 or higher. An upper limit value is preferably 2,000,000 or less. The weight-average molecular weight can be determined by a gel-permeation chromatography (GPC) analysis. In the gel-permeation chromatography analysis, polyethylene glycol is used as a standard polymer.
[0032] R.sup.1 to R.sup.4 and X— in Formula (1), R.sup.5 to R.sup.7 in Formula (2), and R.sup.8 in Formula (3) are as follows. R.sup.1 and R.sup.2 each independently represent a hydrogen atom or an alkyl group having 1 to 4 carbon atoms. R.sup.3 and R.sup.4 each independently represent an alkyl group having 1 to 5 carbon atoms. X— represents an ion of a halogen atom, or an acid anion. R.sup.5 represents a hydrogen atom or a methyl group. R.sup.6 and R.sup.7 each independently represent a hydrogen atom, an alkyl group having 1 to 4 carbon atoms, a benzyl group, or a hydroxyalkyl group having 2 or 3 carbon atoms. R.sup.8 represents a hydrogen atom or a methyl group. It is noted here that the above-described alkyl groups may be linear or branched. The halogen atom is, for example, a fluorine atom, a chlorine atom, a bromine atom, or an iodine atom. The acid anion is, for example, a carboxylate anion such as CH.sub.3COO—. Examples of the hydroxyalkyl group include a 1-hydroxyethyl group, a 2-hydroxyethyl group, a 1-hydroxypropyl group, a 2-hydroxypropyl group, a 3-hydroxypropyl group, and a 2-hydroxy-1-methylethyl group.
<Water-Soluble or Water-Dispersible Resin (B)>
[0033] The water-soluble or water-dispersible resin (B) (hereinafter, simply referred to as “resin (B)”) is not particularly restricted; however, from the standpoint of attaining an excellent effect of the present invention, it is preferred to use, for example, a urethane resin, a polyvinyl alcohol resin, a polyamide resin, an epoxy resin, a phenolic resin, or a polyvinylpyrrolidone resin. The resin (B) may be a homopolymer of a urethane resin, a polyvinyl alcohol resin, a polyamide resin, an epoxy resin, a phenolic resin, a polyvinylpyrrolidone resin or the like; a modification product obtained by modifying a side chain of the homopolymer with other compound; or a copolymer of a combination of two or more of the above-described resins and modification product. These resins may be used singly, or in combination of two or more thereof.
[0034] In the metal surface treatment agent according to the present embodiment, the content ratio of the copolymer (A) and the resin (B) is not particularly restricted; however, a ratio [A.sub.W/B.sub.W] between the mass (A.sub.W) of the copolymer (A) and the mass (B.sub.W) of the resin (B) is preferably in a range of 0.05 to 1.00, more preferably in a range of 0.10 to 0.90, particularly preferably in a range of 0.20 to 0.80.
<Other Components>
[0035] The metal surface treatment agent according to the present embodiment may consist of only the copolymer (A) and the resin (B) in addition to an aqueous medium, or may further contain other component(s). Examples of the other components include a crosslinking component (C) and a surfactant.
[0036] The crosslinking component (C) is not particularly restricted as long as it is different from the copolymer (A) and the resin (B) and links the resin (B), and the crosslinking component (C) may be, for example, a carboxyl group-containing compound or a water-soluble metal compound. Examples of the carboxyl group-containing compound include citric acid, 1,2,3,4-butanetetracarboxylic acid, tartaric acid, and malic acid. The term “water-soluble” used for the water-soluble metal compound means that 1 g of the metal compound can be dissolved in 1 L of water at 25° C. The water-soluble metal compound is not particularly restricted as long as it is

soluble in water, and examples thereof include: organic titanium compounds, such as diisopropoxy titanium bis(triethanolaminate) titanium; chromium-containing compounds, such as chromium (III) sulfate and chromium (III) nitrate; inorganic zirconium-containing compounds, such as hexafluorozirconic acid; and inorganic titanium-containing compounds, such as hexafluorotitanic acid. The term "organic titanium compound" used herein means a titanium-containing compound having an organic group.
[0037] When the metal surface treatment agent according to the present embodiment further contains the crosslinking component (C), the content ratio of the copolymer (A), the resin (B), and the crosslinking component (C) is not particularly restricted; however, a ratio [C.sub.W/(A.sub.W+B.sub.W)] between the mass (C.sub.W) of the crosslinking component (C) and a total of the mass (A.sub.W) of the copolymer (A) and the mass (B.sub.W) of the resin (B) is preferably in a range of 0.03 to 0.43, more preferably in a range of 0.1 to 0.3.
[0038] As the surfactant, a cationic, anionic, amphoteric, or nonionic surfactant can be used, and examples thereof include: cationic surfactants, such as alkylamine salts and alkyltrimethyl ammonium halides; anionic surfactants, such as alkyl sulfonates, polyoxyethylene alkylphenyl ether sulfates, sodium dodecyldiphenyl ether disulfonate, and sodium dodecyl sulfate; amphoteric surfactants, such as alkyl aminopropionates and alkyldimethyl betaines; and nonionic surfactants, such as polyoxyethylene alkylphenyl ethers, polyoxyalkylene fatty acid esters, fatty acid glycerin esters, sorbitan fatty acid esters, polyoxyethylene glycerin fatty acids, and polyoxyethylene propylene glycol fatty acid esters. These surfactants may be used singly, or in combination of two or more thereof.
<Aqueous Medium>
[0039] The aqueous medium is not particularly restricted as long as it contains water in an amount of not less than 50% by mass, and the aqueous medium may consist of only water, or may be a mixture containing water and a water-miscible organic solvent. The water-miscible organic solvent is not particularly restricted as long as it is miscible with water, and examples thereof include: ketone-based solvents, such as acetone and methyl ethyl ketone; amide-based solvents, such as N,N-dimethylformamide and dimethylacetamide; alcohol-based solvents, such as methanol, ethanol, and isopropanol; ether-based solvents, such as ethylene glycol monobutyl ether and ethylene glycol monohexyl ether; and pyrrolidone-based solvents, such as 1-methyl-2-pyrrolidone and 1-ethyl-2-pyrrolidone.
[0040] These water-miscible organic solvents may be mixed with water singly, or two or more thereof may be mixed with water.
(Method of Producing Metal Surface Treatment Agent)
[0041] The metal surface treatment agent according to the present embodiment can be produced by, for example, mixing prescribed amounts of the copolymer (A), the resin (B) and, as required, other component(s) in an aqueous medium.
(Metal Material Having Film and Production Method Thereof)
[0042] The method of producing a metal material having a film according to the present embodiment (hereinafter, simply referred to as "the production method according to the present embodiment") includes: the contact step of contacting the above-described metal surface treatment agent on or over a surface of a metal material; and the drying step of drying the metal surface treatment agent thus contacted. By this production method, a metal material which has a film capable of maintaining antimicrobial performance on or over the surface can be obtained. In the production method according to the present embodiment, the degreasing step and/or the chemical conversion treatment step may be performed before the contact step.
<Metal Material>
[0043] The shape, the structure and the like of the metal material on which a film is to be formed are not particularly restricted, and the metal material may be in the form of, for example, a plate or a foil. The type of the metal material is also not particularly restricted, and examples thereof

include: steel materials (e.g., cold-rolled steel sheets, hot-rolled steel sheets, mill scale materials, pickled steel sheets, high tensile steel sheets, tool steels, alloy tool steels, spheroidal graphite cast irons, and gray cast irons); plated materials, such as zinc-plated materials (e.g., electrogalvanized materials, hot-dip galvanized materials, aluminum-containing galvanized materials, electrogalvanized materials, zinc-nickel plated materials, zinc-cobalt plated materials, and zinc vapor-deposited materials), zinc alloy-plated materials (e.g., alloyed molten zinc-plated materials, Zn—Al alloy-plated materials, Zn—Al—Mg alloy-plated materials, and zinc alloy-electroplated materials), aluminum-plated materials, nickel-plated materials, tin-plated materials, chromium-plated materials, and chromium alloy-plated materials (e.g., Cr—Ni alloy-plated materials); aluminum materials and aluminum alloy materials (e.g., 1,000 series, 2,000 series, 3,000 series, 4,000 series, 5,000 series, 6,000 series, aluminum casts, aluminum alloy casts, and die-cast materials); copper materials and copper alloy materials; titanium materials and titanium alloy materials; and magnesium materials and magnesium alloy materials.

<Contact Step>

[0044] Examples of a contact method include, but not limited to: a spray method, an immersion method, a roll coating method, a bar coating method, a curtain coating method, a spin coating method, and a combination of these methods. The contact temperature and the contact time are set as appropriate in accordance with the formulation and the concentration of the metal surface treatment agent; however, usually, the contact temperature is in a range of 0° C. to 50° C., and the contact time is in a range of 1 second to 300 seconds.

<Drying Step>

[0045] A drying method is not particularly restricted, and examples thereof include drying methods using a known drying equipment, such as a batch-type drying furnace, a continuous hot air circulation-type drying furnace, a conveyer-type hot-air drying furnace, and an electromagnetic induction heating furnace using an IH heater. The drying temperature and the drying time are set as appropriate in accordance with the type of the metal material and the formulation or the amount of the metal surface treatment agent brought into contact with the metal material; however, usually, the drying temperature is in a range of 120° C. to 200° C., and the drying time is in a range of 2 seconds to 1,800 seconds.

<Degreasing Step>

[0046] As a degreasing method, any method may be employed as long as oils/fats and dirt can be removed, and examples thereof include solvent degreasing and known methods using an alkali-based or acid-based degreasing agent or the like. In cases where the contact step or the chemical conversion treatment step is performed after the degreasing step, the water washing step may or may not be performed on or over the surface of the metal material after the degreasing step but before the contact step or the chemical conversion treatment step. When the water washing step is performed, drying may or may not be subsequently performed on or over the surface of the metal material.

<Chemical Conversion Treatment Step>

[0047] The chemical conversion treatment step is not particularly restricted as long as it is a treatment of forming a chemical conversion coating, and examples thereof include the zirconium chemical conversion treatment step, the titanium chemical conversion treatment step, the hafnium chemical conversion treatment step, the phosphate chemical conversion treatment step, and the chromate chemical conversion treatment step. The water washing step may or may not be performed on or over the surface of the metal material after the chemical conversion treatment step but before the contact step. When the water washing step is performed, drying may or may not be subsequently performed on or over the surface of the metal material. In cases where the phosphate chemical conversion treatment step using zinc phosphate is performed as the chemical conversion treatment step, the surface-adjusting treatment step may be performed on the metal material between the degreasing step and the phosphate chemical conversion treatment step for the purpose

of improving the reactivity. Any known method can be employed as a surface-adjusting treatment method of this step.
<Chemical Conversion Agent>
[0048] The chemical conversion treatment step is performed by bringing a chemical conversion agent into contact with or over the surface of the metal material. Examples of the chemical conversion agent include, but not limited to: zirconium chemical conversion agents, titanium chemical conversion agents, hafnium chemical conversion agents, phosphate chemical conversion agents, and chromate chemical conversion agents. Examples of a method of bringing the chemical conversion agent into contact include, but not limited to: known contact methods such as an immersion treatment method, a spray treatment method, a pouring method, and a combination of these methods. In the above-described various chemical conversion treatment steps, the temperature and the contact time of the chemical conversion agent can be set as appropriate in accordance with the type of the chemical conversion treatment step and the concentration and the like of the chemical conversion agent.
<Film>
[0049] The thickness of the film formed by the metal surface treatment agent on or over the surface of the metal material is not particularly restricted as long as the performance of the present invention can be exerted, and the thickness of the film is, for example, preferably in a range of 0.1 μm to 2.0 μm, more preferably in a range of 0.3 μm to 1.5 μm.
EXAMPLES
[0050] The present invention will now be described in more detail by way of Examples and Comparative Examples. It is noted here, however, that the present invention is not restricted to the below-described Examples.
(Preparation of Metal Surface Treatment Agents)
[0051] The formulations of the metal surface treatment agents of Examples 01 to 07 and Comparative Examples 01 to 05 are shown in Table 1. The details of the symbols shown in Table 1 under the columns of “Polymer”, “Resin (B)” and “Crosslinking component (C)” are provided in Tables 2 to 4. The metal surface treatment agents were each prepared by mixing the respective components in water. The solid content in each metal surface treatment agent was adjusted to be 4%. The production method of each polymer will be described below.
TABLE-US-00001 TABLE 1 Formulations of Metal Surface Treatment Agents of Examples and Comparative Examples Component Example/ Crosslinking Mass of Cw/(Mass of Comparative Poly- component polymer/ polymer + Exampke mer Resin(B) (C) Bw Bw) Example 01 A1 B1 — 0.4 — Example 02 A3 B1 — 0.03 — Example 03 A4 B3 — 1.2 — Example 04 A1 B2 C3 0.5 0.1 Example 05 A2 B1 C2 0.5 0.2 Example 06 A5 B2 C1 0.4 0.02 Example 07 A6 B3 C1 0.6 0.5 Comparative A3 — — — — Example 01 Comparative — B1 — — — Example 02 Comparative D1 B3 — 0.6 — Example 03 Comparative D2 B2 — 0.4 — Example 04 Comparative D3 B3 — 0.8 — Example 05
TABLE-US-00002 TABLE 2 Type of polymer Compound (a) Compound (b) Molar ratio Weight-average R.sup.1 R.sup.2 R.sup.3 R.sup.4 X R.sup.5 R.sup.6 R.sup.7 R.sup.8 Compound(a):Compound(b) molecular weight A1 H H CH.sub.3 CH.sub.3 Cl H H H — 50:50 500,000 A2 H H CH.sub.3 CH.sub.3 Cl — — — H 20:80 250,000 A3 CH.sub.3 H H H Cl H CH.sub.3 H — 60:40 50,000 A4 CH.sub.3 CH.sub.3 H H Cl CH.sub.3 CH.sub.3 H — 90:10 200,000 A5 CH.sub.3 H CH.sub.3 CH.sub.3 Cl — — — CH.sub.3 70:30 200,000 A6 CH.sub.3 CH.sub.3 CH.sub.3 CH.sub.3 OH H H H — 60:40 150,000 D1 H H CH.sub.3 CH.sub.3 Cl — — — — 100:0 500,000 D2 H H CH.sub.3 CH.sub.3 Cl H H H — 10:90 500,000 D3 H H CH.sub.3 CH.sub.3 Cl H H H — 80:20 22,000
TABLE-US-00003 TABLE 3 Type of water-soluble or water-dispersible resin (B) No. Type Manufacturer Product name B1 Urethane resin DSK Co., Ltd. SUPERFLEX E-2000 B2 Polyvinyl alcohol Kuraray Co., Ltd. KURARAY POVAL PVA-103 B3 Modified polyamide Toray Industries,

AQ NYLON T-70 resin Inc.
TABLE-US-00004 TABLE 4 Type of crosslinking component (C) No. Type Manufacturer Product name C1 Organic titanium Matsumoto Fine ORGATIX TC-400 Chemical Co., Ltd. C2 1,2,3,4-butanetetra- New Japan Chemical RIKACID BT-W carboxylic acid Co., Ltd. C3 Chromium (III) Nippon Chemical 35% chromium sulfate Industrial sulfate Co., Ltd. Organic titanium: diisopropoxy titanium bis(triethanolaminate) titanium
(Production of Polymers)
Production of Polymer A1
[0052] First, 201 g of an aqueous solution of the compound (a) (60%), 53 g of the compound (b) and 580 g of water were mixed and heated to 70° C. in nitrogen gas. Next, 15 g of an aqueous ammonium persulfate solution (20%) was added and allowed to react at 70° C. for 15 hours, after which the reaction was quenched by cooling, whereby a polymer A1 was produced.
Production of Polymer A2
[0053] After mixing 81 g of an aqueous solution of the compound (a) (60%) with 30 g of water and stirring the resulting mixture to uniformly dissolve the compound (a), the mixture was heated to 70° C., and 6 g of an aqueous ammonium persulfate solution (20%) was added thereto with stirring. After the start of heat generation, an aqueous solution obtained by mixing 108 g of an aqueous solution of the compound (b) (80%) with 108 g of water was added dropwise to the mixture while maintaining the temperature at 70 to 80° C. After the completion of the dropwise addition, the resultant was allowed to react for 2 hours. Subsequently, 70 g of water was added, and the resultant was stirred and then cooled to quench the reaction. Thereafter, an aqueous sodium hydroxide solution (20%) was added to adjust the pH to 4.8, whereby a polymer A2 was produced.
Production of Polymer A3
[0054] First, 221 g of an aqueous solution of the compound (a) (60%), 51 g of the compound (b) and 322 g of water were mixed and heated to 70° C. in nitrogen gas. Next, 15 g of an aqueous ammonium persulfate solution (20%) was added and allowed to react at 70° C. for 7 hours, after which the reaction was quenched by cooling, whereby a polymer A3 was produced.
Production of Polymer A4
[0055] First, 362 g of an aqueous solution of the compound (a) (60%), 15 g of the compound (b) and 774 g of water were mixed and heated to 70° C. in nitrogen gas. Next, 15 g of an aqueous ammonium persulfate solution (20%) was added and allowed to react at 70° C. for 10 hours, after which the reaction was quenched by cooling, whereby a polymer A4 was produced.
Production of Polymer A5
[0056] After mixing 306 g of an aqueous solution of the compound (a) (60%) with 300 g of water and stirring the resulting mixture to uniformly dissolve the compound (a), the mixture was heated to 70° C., and 6 g of an aqueous ammonium persulfate solution (20%) was added thereto with stirring. After the start of heat generation, an aqueous solution obtained by mixing 48 g of an aqueous solution of the compound (b) (80%) with 150 g of water was added dropwise to the mixture while maintaining the temperature at 70 to 80° C. After the completion of the dropwise addition, the resultant was allowed to react for 2 hours. Subsequently, 150 g of water was added, and the resultant was stirred and then cooled to quench the reaction. Thereafter, an aqueous sodium hydroxide solution (20%) was added to adjust the pH to 4.8, whereby a polymer A5 was produced.
Production of Polymer A6
[0057] First, 308 g of an aqueous solution of the compound (a) (60%), 51 g of the compound (b) and 786 g of water were mixed and heated to 70° C. in nitrogen gas. Next, 15 g of an aqueous ammonium persulfate solution (20%) was added and allowed to react at 70° C. for 10 hours, after which the reaction was quenched by cooling, whereby a polymer A6 was produced.
Production of Polymer D2
[0058] First, 161 g of an aqueous solution of the compound (a) (60%), 383 g of the compound (b) and 960 g of water were mixed and heated to 70° C. in nitrogen gas. Next, 15 g of an aqueous

ammonium persulfate solution (20%) was added and allowed to react at 70° C. for 6 hours, after which the reaction was quenched by cooling, whereby a polymer D2 was produced.
Production of Polymer D3
[0059] First, 56 g of an aqueous solution of the compound (a) (60%), 4 g of the compound (b) and 124 g of water were mixed and heated to 70° C. in nitrogen gas. Next, 15 g of an aqueous ammonium persulfate solution (20%) was added and allowed to react at 70° C. for 5 hours, after which the reaction was quenched by cooling, whereby a polymer D3 was produced.
Measurement of Weight-Average Molecular Weight of Polymers
[0060] For each of the thus obtained polymers A1 to A6, D2 and D3, the weight-average molecular weight was determined by gel-permeation chromatography (GPC) analysis. The results thereof are shown in Table 2.
(Preparation of Evaluation Samples)
[0061] As test materials, an aluminum sheet (A1050P manufactured by Paltec Co., Ltd., size: 40 mm×40 mm, thickness: 0.8 mm) (M1) and a hot-dip galvanized steel sheet [amount of adhered zinc per side: 50 g/m.sup.2 (galvanized on both sides), size: 40 mm×40 mm, thickness: 0.6 mm] (M2) were used.
[0062] The test materials were each immersed in an alkali-based degreasing agent [FINE CLEANER 315E (manufactured by Nihon Parkerizing Co., Ltd.) dissolved in water at a mass concentration of 2%] at 60° C. for 2 minutes to perform a degreasing treatment. Subsequently, the surface of each test material was washed with water.
[0063] The test materials, which had been thus degreased and washed with water, were each immersed in a zirconium-based chemical conversion agent [PALCOAT 3790M (manufactured by Nihon Parkerizing Co., Ltd.) dissolved in water at a mass concentration of 20% and adjusted to have a pH of 3.7] at 60° C. for 2 minutes to perform a chemical conversion treatment. After the chemical conversion treatment, the surface of each test material was washed with water.
[0064] The test materials, on which a chemical conversion film had been formed by the chemical conversion treatment, were immersed in the respective metal surface treatment agents at 20° C. for 15 seconds and subsequently heat-dried at 150° C. for 6 minutes using a blow dryer, whereby test materials having a film (evaluation samples No. 1 to 12) were produced.
(Method of Evaluating Antimicrobial Performance)
[0065] For the thus obtained evaluation samples No. 1 to 12, the antimicrobial performance (initial) was evaluated in accordance with the evaluation method prescribed in ISO 22196:2011 (film adhesion method). As bacteria, *Staphylococcus aureus* and *Escherichia coli* were used. The antimicrobial performance was evaluated based on the following antimicrobial performance evaluation criteria in terms of the reduction rate of subject bacteria (%) that was calculated using an equation [Reduction rate of subject bacteria (%)=100−Y/Z×100]. In this equation, Y means the number of colonies formed by culturing the bacteria along with an evaluation sample, and Z means the number of colonies formed by culturing the bacteria without an evaluation sample.
[0066] Further, for the evaluation samples No. 1 to 12 which had been immersed in deionized water for 96 hours and then dried naturally, the antimicrobial performance (persistence) was evaluated in the same manner. The results thereof are shown in Table 5.
<Antimicrobial Performance Evaluation Criteria>
[0067] ◎ (with antimicrobial performance): reduction rate of subject bacteria=99.9% or higher
[0068] ∘ (with antimicrobial performance): reduction rate of subject bacteria=99.0% or higher but lower than 99.9% [0069] x (insufficient antimicrobial performance): reduction rate of subject bacteria=lower than 99.0%
(Method of Evaluating Fungus Resistance)
[0070] For the evaluation samples No. 1 to 12, the fungus resistance (initial) was evaluated in accordance with the evaluation method prescribed in ISO 846:1997 Method A. As fungi, a mixed spore suspension (a mixture of five species of fungi: *Aspergillus niger*, *Penicillium pinophilum*,

Chaetomium globosum, *Trichoderma*, and *Paecilomyces variotii*) was used. The fungus resistance was evaluated based on the following fungus resistance evaluation criteria using the hyphal growth state as an index.
[0071] Further, for the evaluation samples No. 1 to 12 which had been immersed in deionized water for 96 hours and then dried naturally, the fungus resistance (persistence) was evaluated in the same manner. The results thereof are shown in Table 5.
<Fungus Resistance Evaluation Criteria>
[0072] ⊚ (with fungus resistance): Fungal growth was not observed with the naked eye or under a microscope. [0073] ∘ (with fungus resistance): Fungal growth was not observed with the naked eye; however, it was clearly confirmed under a microscope. [0074] x (insufficient fungus resistance): Fungal growth was observed with the naked eye.
TABLE-US-00005 TABLE 5 Evaluation results Antimicrobial Fungus Evaluation Metal surface performance resistance sample Material treatment agent Initial Persistence Initial Persistence No. 1 M1 Example 01 ⊚ ◯ ⊚ ◯ No. 2 M1 Example 02 ◯ ◯ ◯ ◯ No. 3 M1 Example 03 ⊚ ◯ ◯ ◯ No. 4 M1 Example 04 ⊚ ⊚ ⊚ ⊚ No. 5 M2 Example 05 ⊚ ⊚ ⊚ ⊚ No. 6 M1 Example 06 ⊚ ◯ ⊚ ◯ No. 7 M1 Example 07 ⊚ ◯ ⊚ ◯ No. 8 M1 Comparative X X X X Example 01 No. 9 M1 Comparative X X X X Example 02 No. 10 M1 Comparative ⊚ X ⊚ X Example 03 No. 11 M1 Comparative X X X X Example 04 No. 12 M1 Comparative ◯ X ◯ X Example 05

Claims

1. A method of producing a metal material comprising a film, the method comprising the steps of: contacting a metal surface treatment agent on or over a surface of a metal material; and drying the metal surface treatment agent thus contacted, wherein the metal surface treatment agent, comprising: a copolymer (A), a water-soluble or water-dispersible resin (B), and 1, 2, 3, 4-butanetetracarboxylic acid as a crosslinking component (C), the copolymer (A) being at least one selected from the group consisting of: a bipolymer obtained by polymerizing compounds consisting of a compound (a) represented by the following Formula (1) and a compound (b) represented by the following Formula (2) and a bipolymer obtained by polymerizing compounds consisting of a compound (a) represented by the following Formula (1) and a compound (b) represented by the following Formula (3), wherein a polymerization ratio [a.sub.M:b.sub.M] between a molar amount (a.sub.M) of the compound (a) and a molar amount (b.sub.M) of the compound (b) is in a range of 90:10 to 20:80, the copolymer (A) has a weight-average molecular weight of 50,000 to 2,000,000, and the resin (B) is one or more selected from urethane resins, polyvinyl alcohol resins, polyamide resins, epoxy resins, phenolic resins, and polyvinylpyrrolidone resins: ##STR00003## [in Formula (1), R.sup.1 and R.sup.2 each independently represent a hydrogen atom or an alkyl group having 1 to 4 carbon atoms, R.sup.3 and R.sup.4 each independently represent an alkyl group having 1 to 5 carbon atoms, and X-represents an ion of a halogen atom, or an acid anion; in Formula (2), R.sup.5 represents a hydrogen atom or a methyl group, R.sup.6 and R.sup.7 each independently represent a hydrogen atom, an alkyl group having 1 to 4 carbon atoms, a benzyl group, or a hydroxyalkyl group having 2 or 3 carbon atoms; and in Formula (3), R.sup.8 represents a hydrogen atom or a methyl group].
2. The method according to claim 1, wherein a ratio [A.sub.W/B.sub.W] between the mass (A.sub.W) of the copolymer (A) and the mass (B.sub.W) of the resin (B) is in a range of 0.05 to 1.0.
3. The method according to claim 1, wherein a ratio [C.sub.W/(A.sub.W+B.sub.W)] between the mass (C.sub.W) of the crosslinking component (C) and a total of the mass (A.sub.W) and the mass (B.sub.W) is in a range of 0.03 to 0.43.
4. The method according to claim 1, wherein the copolymer (A) has a weight-average molecular

weight of 50,000 to 500,000.

5. The method according to claim 1, further comprising at least one step selected from the group consisting of a degreasing step and a chemical conversion treatment step before the contacting step.

6. A method of producing a metal material comprising a film, the method comprising the steps of: contacting a metal surface treatment agent on or over a surface of a metal material; and drying the metal surface treatment agent thus contacted, wherein the metal surface treatment agent, comprising: a copolymer (A), a water-soluble or water-dispersible resin (B), and a water soluble metal compound as a crosslinking component (C), the copolymer (A) being a bipolymer obtained by polymerizing compounds consisting of a compound (a) represented by the following Formula (1) and a compound (b) represented by the following Formula (2) or a bipolymer obtained by polymerizing compounds consisting of a compound (a) represented by the following Formula (1) and a compound (b) represented by the following Formula (3), the water soluble metal compound being a chromium-containing compound, wherein a polymerization ratio [aM:bM] between a molar amount (aM) of the compound (a) and a molar amount (b.sub.M) of the compound (b) is in a range of 90:10 to 20:80, the copolymer (A) has a weight-average molecular weight of 50,000 to 2,000,000, and the resin (B) is one or more selected from urethane resins, polyvinyl alcohol resins, polyamide resins, epoxy resins, phenolic resins, and polyvinylpyrrolidone resins: ##STR00004## [in Formula (1), R.sup.1 and R.sup.2 each independently represent a hydrogen atom or an alkyl group having 1 to 4 carbon atoms, R.sup.3 and R.sup.4 each independently represent an alkyl group having 1 to 5 carbon atoms, and X-represents an ion of a halogen atom, or an acid anion; in Formula (2), R.sup.5 represents a hydrogen atom or a methyl group, R.sup.6 and R.sup.7 each independently represent a hydrogen atom, an alkyl group having 1 to 4 carbon atoms, a benzyl group, or a hydroxyalkyl group having 2 or 3 carbon atoms; and in Formula (3), R.sup.8 represents a hydrogen atom or a methyl group].

7. The method according to claim 6, wherein the chromium-containing compound is chromium (III) sulfate.

8. The method according to claim 6, wherein a ratio [A.sub.W/B.sub.W] between the mass (A.sub.W) of the copolymer (A) and the mass (B.sub.W) of the resin (B) is in a range of 0.05 to 1.0.

9. The method according to claim 6, wherein a ratio [C.sub.W/(A.sub.W+B.sub.W)] between the mass (C.sub.W) of the crosslinking component (C) and a total of the mass (A.sub.W) and the mass (B.sub.W) is in a range of 0.03 to 0.43.

10. The method according to claim 6, wherein the copolymer (A) has a weight-average molecular weight of 50,000 to 500,000.

11. The method according to claim 6, further comprising a step selected from the group consisting of a degreasing step and a chemical conversion treatment step before the contacting step.

12. A metal material comprising a film, which is obtained by the method according to claim 1.

13. A metal material comprising a film, which is obtained by the method according to claim 6.