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(54) ARTICLE HAVING METALLIC SURFACE, TONE-TREATMENT METHOD THEREFOR, AND GAS PHASE OXIDATION DEVICE

(57) The present invention improves the rubbing fastness of an article including a base metal with at least the surface composed of copper-zinc alloy after being subjected to tone treatment. In addition, the present invention provides a device for tone treatment capable of reducing the amount of water used as compared with wet processes. Provided is article including: a base material 11 with at least the surface composed of a zinc-containing copper alloy; and an oxide layer 12 adjacent to the surface of the base material 11, wherein the ratio of the mean zinc concentration to the mean copper concentration in the depth range of 10 nm to 20 nm with reference to the surface of the oxide layer 12, A, is higher than the ratio of the mean zinc concentration to the mean copper concentration in the surface of the base material 11, B. Provided is a gas phase oxidation device for performing a tone-treatment method, the gas phase oxidation device including: a gas phase reaction chamber 115 including an inlet and an outlet for performing gas phase oxidation; and a conveyor 122 that allows an elongated member at least partly including a portion with at least the surface consisting of a metal to enter the inlet, pass through the gas phase reaction chamber, and continuously exit from the outlet.

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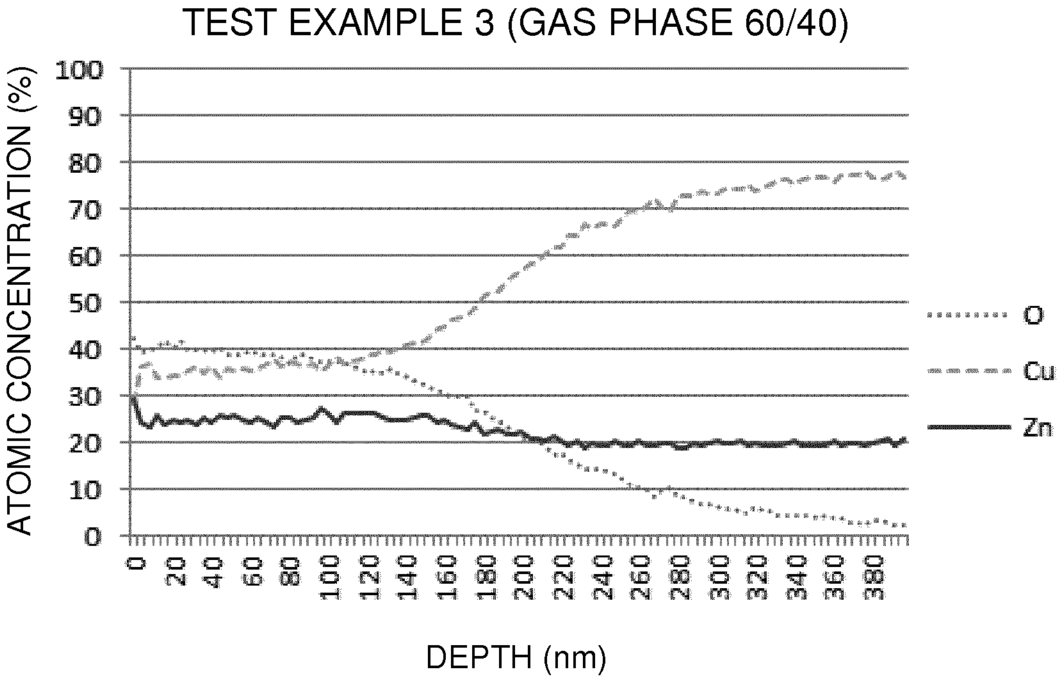
(Cont. next page)

Figure 3


TEST EXAMPLE 3 (GAS PHASE 60/40)
ATOMIC CONCENTRATION (%)
100
90
80
70
60
50
40
30
20
10
0
0
20
40
60
80
100
120
140
160
180
200
220
240
260
280
300
320
340
360
380
DEPTH (nm)
O
Cu
Zn

Description

TECHNICAL FIELD

[0001] The present invention relates to an article having a metallic surface, particular to a metal fastener member. In addition, the present invention relates to a tone-treatment method for articles having a metallic surface, particular to a tone-treatment method for metal fastener members. Further, the present invention relates to a gas phase oxidation device for performing a tone-treatment method for elongated articles having a metallic surface.

BACKGROUND ART

[0002] Fastener products include products called metallic fasteners, in which elements (engaging elements) are composed of a metal such as red brass, brass, nickel silver, and aluminum, and especially metal fasteners using copper-zinc alloy, represented by red brass, brass, and nickel silver, are frequently used because they can achieve cost performance, strength, hardness, and processability in combination in a well-balanced manner. In the field of fashion, which deals with clothes and accessories, not only superior functionality but also designability to suit with designs of articles is demanded for fasteners. Accordingly, for metallic fasteners, too, it is required to provide metal fastener members having numerous color tones to fit various designs of articles.

[0003] Conventional tone-treatment methods for metallic surfaces include methods of surface-coating with an organic coating material or the like, methods of changing tones by changing composition or plating a surface with metal having different composition, and methods of coloring a metallic surface a specific color by subjecting the surface to some chemical conversion treatment, and any of these tone treatment methods commonly uses a wet process.

[0004] For example, Japanese Patent Laid-Open No. 2014-205871 (Patent Literature 1) describes a treatment method for coloring surface appearance to give a blue tone through soaking in a chlorite chemical conversion solution. Specifically, the literature describes a blue coloration method for copper-based metallic surfaces, wherein a copper-based metal is soaked in a chlorite chemical conversion solution containing 0.5 to 250 g/L of a chlorite and 1 to 625 g/L of a hydroxide of an alkali metal. The literature discloses in Examples that a member of a button top part made of brass was copper-plated and then subjected to chemical conversion treatment.

CITATION LIST

Patent Literature

[0005] Patent Literature 1: Japanese Patent Laid-Open No. 2014-205871

SUMMARY OF INVENTION

Technical Problem

[0006] If the chemical conversion treatment as described in Patent Literature 1 is performed, the surface of copper-zinc alloy can be colored blue. However, the present inventors have found as a result of examination that if the chemical conversion treatment is performed for an article made of copper-zinc alloy, the rubbing fastness is deteriorated. Capability of adjusting to impart various color tones to articles made of copper-zinc alloy, without sacrificing rubbing fastness, is desired for providing a wide lineup of articles made of copper-zinc alloy.

[0007] In view of this, an object of the present invention is to improve the rubbing fastness of an article including a base material with at least a surface composed of a copper-zinc alloy after tone treatment is performed for the article.

[0008] In addition, the tone treatment through a wet process causes various problems such as increase in loads of wastewater treatment due to a huge amount of chemicals used, difficulty of performing in regions with poor water resources, and frequent corrosion of parts of a tone-treatment device by chemical agents..

[0009] In view of this, another object of the present is to provide a device for tone treatment, the device being capable of reducing wastewater loads as compared with wet processes.

Solution to Problem

[0010] The present inventors performed the tone treatment by the chemical conversion treatment in accordance with the method described in Patent Literature 1 on the surface of copper-zinc alloy, and then observed the cross-section in the vicinity of the surface of the copper-zinc alloy through an electron microscope to find that the cross-section had a porous structure with sporadic visible voids. The porous structure is inferred to be a result of dezincification accompanied by the chemical reaction: $Zn + 2OH^- + 2H_2O \rightarrow [Zn(OH)_4]^{2-}$ caused in the vicinity of the surface by the chemical conversion treatment.

[0011] Based on the inference, the present inventors diligently examined on a surface structure to improve the rubbing fastness of an article made of copper-zinc alloy with an altered tone, finding that it is effective for solution of the problems to impart a function of tone alteration to a dense oxide layer in which zinc is concentrated in the outermost surface.

[0012] The present invention, which has been completed based on the above findings, is, in one aspect, a base material with at least a surface composed of a zinc-containing copper alloy; and an oxide layer adjacent to the surface of the base material, wherein a ratio A of a mean zinc concentration to a mean copper concentration in a depth range of 10 nm to 20 nm with reference to a surface of the oxide layer is higher than a ratio B of a mean zinc concentration to a mean copper concentration at the surface of the base material.

[0013] In one embodiment of the article according to the present invention, the mean zinc concentration at the surface of the base material is 5 to 50 at.%.

[0014] In another embodiment of the article according to the present invention, a ratio A/B of the ratio A to the ratio B is 2.0 or higher.

[0015] In yet another embodiment of the article according to the present invention, the whole of the base material is composed of a zinc-containing copper alloy.

[0016] In yet another embodiment of the article according to the present invention, the mean zinc concentration in the depth range of 10 nm to 20 nm with reference to the surface of the oxide layer is 5 to 80 at.%.

[0017] In yet another embodiment of the article according to the present invention, the article is a slide fastener member.

[0018] The present invention is, in another aspect, a slide fastener comprising the slide fastener member according to the present invention.

[0019] The present invention is, in yet another aspect, a tone-treatment method for an article, comprising subjecting an article comprising a base material with at least a surface composed of a zinc-containing copper alloy to gas phase oxidation at least in a presence of oxygen.

[0020] In one embodiment of the tone-treatment method according to the present invention, the tone-treatment method comprises forming an oxide layer adjacent to the surface of the base material through gas phase oxidation, wherein a ratio A of a mean zinc concentration to a mean copper concentration in a depth range of 10 nm to 20 nm with reference to a surface of the oxide layer is higher than a ratio B of a mean zinc concentration to a mean copper concentration at the surface of the base material.

[0021] In another embodiment of the tone-treatment method according to the present invention, the gas phase oxidation is performed in a presence of ammonia.

[0022] In yet another embodiment of the tone-treatment method according to the present invention, tone control through the gas phase oxidation is performed by changing one or more selected from a group consisting of ammonia concentration, oxygen concentration, another reactive gas concentration, humidity in a reaction system, temperature in a reaction system, treatment time, and article temperature.

[0023] In yet another embodiment of the tone-treatment method according to the present invention, the article is a fastener member.

[0024] In yet another embodiment of the tone-treatment method according to the present invention, the gas phase oxidation is performed at an atmosphere temperature of 20 to 80°C.

[0025] In yet another embodiment of the tone-treatment method according to the present invention, the gas phase oxidation is performed under negative pressure.

[0026] In yet another embodiment of the tone-treatment method according to the present invention, the tone-treatment method comprises performing activation treatment followed by water washing of the surface of the base material before performing the gas phase oxidation.

[0027] In yet another embodiment of the tone-treatment method according to the present invention, the tone-treatment method comprises degreasing followed by water washing of the surface of the base material before performing the gas phase oxidation.

[0028] In yet another embodiment of the tone-treatment method according to the present invention, the tone-treatment method comprises performing at least one or more surface treatments selected from a group consisting of clear coating, antirust treatment, and waxing, on the surface of the oxide layer formed through the gas phase oxidation.

[0029] The present invention is, in yet another aspect, a gas phase oxidation device for performing a tone-treatment method, the gas phase oxidation device comprising: a gas phase reaction chamber for performing gas phase oxidation including an inlet and an outlet; a conveyor that allows an elongated member at least partly including a portion with at least a surface composed of a metal to enter the inlet, pass through the gas phase reaction chamber, and continuously exit from the outlet; a discharge port for feeding a gas phase oxidation gas into the gas phase reaction chamber; and a suction port for discharging a gas in the gas phase reaction chamber out of the chamber.

[0030] In one embodiment of the gas phase oxidation device according to the present invention, a water seal unit for blocking the gas in the gas phase reaction chamber is provided on either one or both of an outlet side and an inlet side of the gas phase reaction chamber.

[0031] In another embodiment of the gas phase oxidation device according to the present invention, the water seal unit for blocking the gas in the gas phase reaction chamber from an outside is provided only on the outlet side of the gas phase reaction chamber.

[0032] In yet another embodiment of the gas phase oxidation device according to the present invention, the gas phase oxidation device comprises a gas flow controller for controlling the gas phase oxidation gas fed into the gas phase reaction chamber to flow from the inlet side to the outlet side.

[0033] In yet another embodiment of the gas phase oxidation device according to the present invention, the gas flow controller includes: one or more discharge ports for feeding the gas phase oxidation gas placed in the gas phase reaction chamber; and one or more suction ports for discharging the gas in the chamber out of the chamber, wherein all of the one or more suction ports are disposed closer to the outlet side than all of the one or more discharge ports.

[0034] In yet another embodiment of the gas phase oxidation device according to the present invention, the conveyor is configured to allow the article to pass through the gas phase reaction chamber in a direction including one or both of a generally vertically upward direction and a generally vertically downward direction.

[0035] In yet another embodiment of the gas phase oxidation device according to the present invention, the gas phase reaction chamber includes: a first chamber placed on the inlet side; a second chamber placed on the outlet side; and a third chamber placed between the first chamber and the second chamber, and the conveyor is configured to allow the article to sequentially pass through the first chamber, the third chamber, and the second chamber, and configured to allow the article to pass through the third chamber in a direction including either one or both of the substantially vertically upward direction and the substantially vertically downward direction.

[0036] In yet another embodiment of the gas phase oxidation device according to the present invention, the third chamber includes: a third chamber upper portion located at the same height as the first chamber and the second chamber; and a third chamber lower portion located below the third chamber upper portion, and the conveyor is configured to allow the article to pass through the first chamber, the third chamber upper portion, the third chamber lower portion, and the second chamber.

[0037] In yet another embodiment of the gas phase oxidation device according to the present invention, the gas phase oxidation device comprises: the gas phase oxidation device comprises: at least one of the discharge ports in the third chamber lower portion; and at least one of the suction ports in the second chamber.

[0038] In yet another embodiment of the gas phase oxidation device according to the present invention, the conveyor is configured to allow the article to pass through the third chamber in a direction including both of the substantially vertically upward direction and the substantially vertically downward direction.

Advantageous Effects of Invention

[0039] The present invention enables improvement of the rubbing fastness of an article the surface of which is made of copper-zinc alloy with an altered tone. Rubbing fastness is an important property particularly when application to metal fastener members is intended, and capability of imparting altered tones to fastener members made of copper-zinc alloy without sacrificing rubbing fastness is of great significance in a commercial sense. The present invention enables alteration of color tones of articles with copper-zinc alloy in the surface into various color tones with ease by modifying the type and proportion of oxide constituting the oxide layer. Zn remains in the vicinity of the surface of the article according to the present invention, and hence this Zn can be advantageously utilized for color tone alteration. Specifically, while Cu and O are primary elements involved in color tone alteration in the conventional chemical conversion treatments because dezincification is caused in the vicinity of the surface, zinc remains in the surface in the present invention, and hence Zn can be involved in color tone alteration in addition to Cu and O, which enables formation of colorful tones. For this reason, the present invention is advantageous also in that it enables launch of a wide variety of products. In addition, it should be noted that the gas phase oxidation device according to the present invention does not basically need to use water in the reaction chamber.

BRIEF DESCRIPTION OF DRAWINGS

[0040]

[Figure 1] Figure 1 shows a drawing schematically illustrating an example of the cross-sectional structure of the article according to the present invention.

[Figure 2] Figure 2 shows a drawing schematically illustrating another example of the cross-sectional structure of the article according to the present invention.

[Figure 3] Figure 3 shows a graph of depth profiles of atomic concentrations of O, Cu, and Zn when AES analysis was performed for an element surface of Test Example 3.

[Figure 4] Figure 4 shows a graph of depth profiles of atomic concentrations of O, Cu, and Zn when AES analysis was performed for an element surface of Test Example 6.

[Figure 5] Figure 5 shows a schematic elevation view illustrating a first embodiment of the gas phase oxidation device according to the present invention.

[Figure 6] Figure 6 shows a schematic elevation view illustrating a second embodiment of the gas phase oxidation device according to the present invention.

[Figure 7] Figure 7 shows a schematic elevation view illustrating a third embodiment of the gas phase oxidation device according to the present invention.

[Figure 8] Figure 8 shows a schematic elevation view illustrating an example of the device configuration of the color tone-treatment system according to the present invention.

DESCRIPTION OF EMBODIMENTS

<1. Article>

[0041] The article according to the present invention includes, in one embodiment, a base material with at least the surface composed of a zinc-containing copper alloy. Copper-zinc alloy such as brass, red brass, and nickel silver and copper-zinc-nickel alloy are superior in terms of strength, cost, and processability, and can be suitably used as the zinc-containing copper alloy. The zinc-containing copper alloy contains, for example, 1 to 40% by mass of Zn, preferably contains 4 to 40% by mass of Zn, and contains 0 to 10% by mass of one or more selected from Ni, Be, Mo, Al, Sn, Pb, Mn, Fe, P, and S, and the balance being copper and inevitable impurities. The base material is only required to be such that at least the surface is composed of the zinc-containing copper alloy, and may have a laminated structure in which the inside is composed of resin, ceramic, or the like. Needless to say, the whole of the base material, including not only the surface but also the inside, may be composed of the zinc-containing copper alloy.

[0042] The article according to the present invention is not limited with respect to applications and the type, and can be used as a metal fastener member in a typical embodiment. Examples of the metal fastener include slide fasteners and snap fasteners. Examples of fields other than metallic fasteners include ball chains. Examples of members for slide fasteners include, but not limited to, elements (engaging elements), sliders, pull-tabs, top stops, bottom stops, and slider inserts. Examples of members for snap fasteners include male elements and female elements. The metal fastener member may be in a final shape of a part to be attached to fastener products as above, or, for example, in the form of a wire, a sheet, a tube, or a bar before shaping.

[0043] Figure 1 schematically illustrates the cross-sectional structure of one embodiment of the article according to the present invention. The article 10 includes a base material 11 and an oxide layer 12 adjacent to the surface of the base material 11. In the present embodiment, the ratio A of the mean zinc concentration to the mean copper concentration in the oxide layer 12 is higher than the ratio B of the mean zinc concentration to the mean copper concentration in the surface of the base material 11. That is, zinc is concentrated in the oxide layer 12. This indicates no occurrence of dezincification in the oxide layer 12, and the oxide layer 12 can be thereby prevented from exhibiting a porous structure. When elemental composition analysis with AES (Auger electron spectroscopy) is performed from the surface of the oxide layer in the depth direction through Ar ion etching, the mean zinc concentration and mean copper concentration of the oxide layer 12 are respectively expressed as the mean atomic concentration of Zn and mean atomic concentration of Cu in the depth range of 10 nm to 20 nm with reference to the surface of the oxide layer, as the total number of Cu, Zn, and O atoms is assumed as 100%. In the present invention, depths when composition analysis with AES is performed in the depth direction refer to depths converted from sputtering time with an etching speed of 8.0 nm/min for SiO_2 standard material (the same applies hereinafter). If a finishing layer 13 described later is not present on the oxide layer 12, the oxide layer 12 serves as the outermost layer.

[0044] In a preferred embodiment of the article according to the present invention, the ratio A/B of the ratio A in the oxide layer 12 to the ratio B in the surface of the base material 11 is higher than 1.0, and the ratio A/B can be 1.5 or higher, 2.0 or higher, or, for example, 1.2 to 3.0.

[0045] The mean zinc concentration in the depth range of 10 nm to 20 nm with reference to the surface of the oxide layer 12 is 5 at.% or more in one embodiment of the article according to the present invention, and 10 at.% or more in a more typical embodiment. The mean zinc concentration in the depth range of 10 nm to 20 nm with reference to the surface of the oxide layer 12 is 80 at.% or less in one embodiment of the article according to the present invention, 60 at.% or less in a more typical embodiment, 40 at.% or less in an even more typical embodiment, and 30 at.% or less in a further more typical embodiment. The mean zinc concentration of the oxide layer 12 is expressed as the mean atomic concentration of Zn, as the total number of Cu, Zn, and O atoms is assumed as 100%, when composition analysis with AES (Auger electron spectroscopy) is performed from the surface of the oxide layer in the depth direction.

[0046] The mean oxygen concentration in the depth range of 10 nm to 20 nm with reference to the surface of the oxide layer 12 is 20 at.% or more in one embodiment of the article according to the present invention, 20 to 60 at.% in a typical embodiment, and 30 to 50 at.% in a more typical embodiment. The mean oxygen concentration of the oxide layer 12 is expressed as the mean atomic concentration of O, as the total number of Cu, Zn, and O atoms is assumed as 100%, when composition analysis with AES (Auger electron spectroscopy) is performed from the surface of the oxide layer toward the base material in the depth direction.

[0047] In the present invention, the boundary between the oxide layer and the base material refers to a point of depth at which the atomic concentration of O first reaches 5 at.% or less as the total number of Cu, Zn, and O atoms is assumed as 100% when composition analysis with AES (Auger electron spectroscopy) is performed from the surface of the oxide layer toward the base material in the depth direction. An additional layer (finishing layer) may be further formed on the oxide layer, and definition of the surface of the oxide layer in this case (the boundary between the additional layer and the oxide layer) will be described later.

[0048] The mean zinc concentration at the surface of the base material is preferably 5 at.% or more, and more preferably 10 at.% or more, for the purpose of enhancing the strength. The mean zinc concentration at the surface of the base material is preferably 50 at.% or less, and more preferably 40 at.% or less, for the purpose of enhancing the processability. The mean zinc concentration and mean copper concentration in the surface of the base material are respectively expressed as the mean atomic concentration of Zn and mean atomic concentration of Cu in the range from the surface of the base material to a depth of 20 nm, as the total number of Cu, Zn, and O atoms is assumed as 100%, when composition analysis with AES (Auger electron spectroscopy) is performed in the depth direction from the surface of the base material to the depth.

[0049] Also when the whole of the base material is composed of a zinc-containing copper alloy, the mean zinc concentration of the whole of the base material is preferably 5 at.% or more, and more preferably 10 at.% or more, for the purpose of enhancing the strength. The mean zinc concentration of the whole of the base material is preferably 50 at.% or less, and more preferably 40 at.% or less, for the purpose of enhancing the workability. The mean zinc concentration of the whole of the base material is expressed as the atomic concentration of Zn as the total number of Cu, Zn, and O atoms is assumed as 100%, and can be analyzed by using an X-ray fluorescence analyzer.

[0050] Figure 2 schematically illustrates the cross-sectional structure of another embodiment of the article according to the present invention. The article 20 includes a base material 11, an oxide layer 12 adjacent to the surface of the base material 11, and a finishing layer 13 adjacent to the surface of the oxide layer 12. The difference between the present embodiment and the embodiment of Figure 1 is that the finishing layer 13 is formed on the oxide layer 12. Examples of the finishing layer 13 include at least one or more surface treatment layers formed with one or two or more surface treatment agents such as a clear lacquer, an antirust agent, and a wax. One surface treatment agent may be used singly, and two or more surface treatment agents may be used as a mixture. One finishing layer or a plurality of finishing layers may be formed.

[0051] Examples of chemical agents for clear lacquer coating include, but are not limited to, a chemical agent prepared by dissolving or dispersing, in an organic solvent or water, one or two or more resin components selected from acrylic resin, polyester resin, alkyd resin, urethane resin, epoxy resin, and so forth; one or two or more crosslinking agents selected from blocked polyisocyanate, melamine resin, urea resin, and so forth; and other additives. Examples of chemical agents for antirust treatment include, but are not limited to, benzotriazole-based chemical agents, phosphate-based chemical agents, and imidazole-based chemical agents. Examples of chemical agents typically used for waxes include, but are not limited to, chemical agents containing paraffin as a primary component, and conventional wax components may be added thereto, as necessary.

[0052] When the finishing layer is present, the mean copper concentration and mean zinc concentration of the oxide layer 12 and the mean copper concentration and mean zinc concentration in the surface of the base material 11 can be measured through AES analysis while etching is performed in the depth direction from the finishing layer to the surface of the base material. If the finishing layer is thick, they can be measured through AES analysis similarly in the depth direction after the finishing layer is removed to a depth just before the oxide layer.

[0053] The finishing layer can be removed with a release agent in some cases. For example, the finishing layer can be released by soaking the article in the release agent "S-BACK H-300", a product name (produced by SASAKI CHEMICAL CO., LTD.), at normal temperature nearly overnight. The time of soaking in a release agent can be changed depending on the thickness of the finishing layer. However, if such removal extends to the oxide layer over the finishing layer, the boundary between the finishing layer and the oxide layer is lost, and hence it is desired to remove the finishing layer to an extent that the finishing layer is partially left unremoved.

[0054] The boundary between the finishing layer and the oxide layer is identifiable by change in Cu concentration and Zn concentration. While Cu and Zn are hardly detected in the finishing layer, large amounts of Cu and Zn are detected in the oxide layer. In view of this, a point of depth at which the total of atomic concentrations of Cu and Zn first reaches 1% or more when AES analysis is performed in the depth direction is herein defined as the boundary between the finishing layer and the oxide layer. Atomic concentrations of Cu and Zn are expressed as the ratio of the number of Cu atoms to the total number of Cu, Zn, and O atoms and that of Zn atoms, respectively.

<2. Method for producing article>

[0055] The article according to the present invention can be produced, for example, by subjecting the surface of the base material to gas phase oxidation. Gas phase oxidation significantly reduces problems relating to environmental loads caused by harmful substances and cost of wastewater treatment, in addition allows oxidation reaction conditions to be modified with ease, and hence is advantageous in that multiple coloring is achieved with a single facility. Hereinafter, a specific mode of gas phase oxidation will be described in detail. Gas phase oxidation can be performed for the base material as a single member, or for the base material bonded to another part. When the base material is elements of a slide fastener, for example, gas phase oxidation can be performed for a fastener stringer in which an array of elements of a slide fastener is attached to a piece of fastener tape, or for a fastener chain in which an array of elements of one fastener stringer and that of another fastener stringer are engaged together.

(2-1 Pretreatment)

[0056] It is preferred to perform pretreatment before the surface of the base metal is subjected to gas phase oxidation. This is because advantageous effects according to the type of pretreatment, such as enhancement of the reactivity and homogeneity of gas phase oxidation, are obtained. Examples of specific pretreatment methods include metal activation treatment. Metal activation treatment can enhance the reaction efficiency of gas phase oxidation.

[0057] There are wet processes and dry processes for metal activation treatment.

[0058] Examples of wet processes include a method of treating by contacting an acidic or alkaline aqueous solution with the surface of the base material. Examples of acidic aqueous solution include aqueous solutions of inorganic acid such as hydrochloric acid, sulfuric acid, nitric acid, chromic acid, and phosphoric acid, and aqueous solutions of organic acid such as acetic acid and dibasic acids (e.g., oxalic acid, malonic acid, succinic acid, aspartic acid). Examples of alkaline solution include aqueous ammonia, NaOH aqueous solution, sodium carbonate, and sodium silicate. Preferred among these is hydrochloric acid for acidic aqueous solution, and NaOH aqueous solution for alkaline aqueous solution, with respect to removability of oxide films or the like after treatment. Examples of methods of contacting an acidic or alkaline aqueous solution with the surface of the base material include, but are not limited to, soaking of the base material in the aqueous solution, spraying, dropping, and applying the aqueous solution onto the base material, roll coating of the base material with the aqueous solution, and flowing the aqueous solution onto the base material.

[0059] Examples of dry processes include plasma treatment (e.g., O_2 plasma treatment), UV ozone methods, the Malcomizing method, and halogen-based gas treatment.

[0060] It is desirable in any of wet processes and dry processes to perform water washing to remove residual components after metal activation treatment.

[0061] It is preferred to further perform degreasing and water-washing treatment for the base material before the above-described pretreatment, in order to enhance the effect of the pretreatment. Any known degreasing method can be employed, and examples thereof include a method of contacting a degreasing agent with the surface of the base material, for example, through soaking, wiping, brushing, or spraying. In soaking, rocking or ultrasonication may be applied to enhance the degreasing effect. Before degreasing and water-washing treatment, a conventional surface treatment may be performed, such as chemical polishing treatment, metal plating treatment, physical polishing treatment, and preliminary degreasing treatment.

(2-2 Gas phase oxidation)

[0062] Any gas phase oxidation method capable of forming a specific oxide layer on the surface of the base material may be used without limitation. Various gas phase oxidation methods are contemplated. For example, when copper and zinc are to be oxidized in the presence of oxygen, chemical reactions as shown below can progress to convert copper and zinc to copper oxide and zinc oxide. Modification of conditions for gas phase oxidation changes the oxidation states of Cu and Zn in the surface of the base material, enabling adjustment of various tones.

- $Cu + 1/2O_2 \rightarrow Cu_2O$ (monovalent) $\rightarrow CuO$ (divalent)

- $Zn + 1/2O_2 \rightarrow ZnO$ (divalent)

[0063] However, because the rate of oxidation reaction is low under low-temperature conditions, it is preferred to accelerate oxidation. Heating temperature may be raised to accelerate oxidation; however, if the base material is combined with another material of low thermal resistance, for example, if the base material is elements of a slide fastener and subjected to gas phase oxidation in the form of a fastener chain, there is restriction, for example, that it is needed to perform gas phase oxidation at a temperature equal to or lower than the heatproof temperature of fastener tape or the like made of a synthetic fiber. For this reason, it is preferred to add ammonia (NH_3) as an oxidation accelerator in order to accelerate oxidation reaction even under low-temperature conditions.

[0064] Accordingly, in a preferred embodiment of the tone-treatment method for a base material according to the present invention, the gas phase oxidation is performed in the presence of oxygen and ammonia. Examples of methods for feeding oxygen include, but are not limited to, a method of feeding oxygen in the form of air, oxygen gas, or a mixed gas of oxygen gas and an inert gas (e.g., nitrogen, noble gases), and a method of feeding oxygen in the form of air is preferred for cost.

[0065] Ammonia is a versatile gas which is inexpensive and available all over the world and can be converted to nitrogen (N_2) and hydrogen (H_2) through pyrolysis ($NH_3 \rightarrow 1/2N_2 + 3/2H_2$), and hydrogen can be further converted to water ($H_2 \rightarrow H_2O$). Therefore, clean exhaust gas can be discharged. Ammonia-containing water which can be generated through washing the article with water after the gas phase oxidation can be converted to ammonium sulfate (a raw material for fertilizers) through neutralization. Thus, ammonia is an economical material with low environmental loads.

[0066] The gas phase oxidation can be performed, for example, at 0 to 100°C, even at room temperature. Thus, the gas phase oxidation can be performed without spending any cooling cost or heating cost; however, it is preferred to heat to some extent for acceleration of the reaction. For this reason, the gas phase reaction is performed preferably at an atmosphere temperature of 20°C or higher, more preferably at an atmosphere temperature of 30°C or higher.

[0067] The gas phase oxidation can be performed under the atmospheric pressure, and need not to be performed under reduced pressure or increased pressure. However, for safety, it is preferred to set the pressure in the reaction chamber to negative pressure to prevent inner gases including ammonia from leaking. For this reason, the gas phase oxidation is preferably performed under reduced pressure (a negative pressure slightly lower than the atmospheric pressure).

[0068] Although it is not intended to limit the present invention by any theory, it is expected that if an appropriate amount of moisture (H_2 O) is present on the surface of the base material (wet condition), NH_3 is ionized into $NH_4{}^+$ and $NH_4{}^+$ bonds to metal (e.g., Cu and Zn) on the surface of a fastener member to accelerate the oxidation reaction. Taking oxidation of Cu as an example, reactions shown below are inferred to quickly progress to accelerate the oxidation. The color tone changes through generation of oxides or hydroxides of the metal. For example, Cu_2O appears reddish brown, CuO appears black, and $Cu(OH)_2$ appears blue.

- $NH_3 + H_2O \rightarrow NH_4^+ + OH^-$
- $Cu + 1/2O_2 + 4NH3 + H_2O \rightarrow [CU(NH_3)_4]^{2+} + 2OH^-$
- $Cu^{2\,+} + 2OH^- \rightarrow Cu(OH)_2$
- $Cu(OH)_2 + O_2 \rightarrow Cu_2O \rightarrow CuO + H_2O$

[0069] Further, the following reaction proceeds under ammonia-rich conditions, giving blueish color.

- $Cu(OH)_2 + 4NH_3 \rightarrow [Cu(NH_3)_4](OH)_2$

[0070] Furthermore, if hydrogen peroxide, a strong peroxide agent, is present, the following oxidation reaction quickly proceeds, thereby stabilizing the color tone.

- $Cu + H_2O_2 + 4NH_3 \rightarrow [Cu(NH_3)_4]^{2+} + 2OH^-$

[0071] In these reactions, oxide of Zn, which has higher affinity with oxygen than Cu has (standard free energy of formation ΔG: CuO (-14) > Cu_2O (-35) > ZnO (-76)), is expected to form on the outermost layer. For this reason, when the gas phase oxidation is performed for the base material the surface of which is formed of copper-zinc alloy, the zinc ratio (Zn/Cu) in the outermost layer tends to be higher than that in the composition of the copper-zinc alloy as a parent material. Although it is not intended to limit the invention by any theory, a dense oxide layer is formed by concentration of Zn in the oxide layer through this reaction mechanism.

[0072] In the above reactions, the color tone can be controlled by changing one or more selected from the group consisting of ammonia concentration, oxygen concentration, another reactive gas concentration, humidity in the reaction system, temperature in the reaction system, treatment time, and article temperature. By merely changing any of these parameters, multiple coloring can be achieved with ease by using one facility.

[0073] In the tone treatment for the surface of Cu-Zn alloy, for example, in coloring with a conventional chemical conversion treatment using an alkali, dezincification reaction ($Zn + 2OH^- + 2H_2\ O \rightarrow [Zn(OH)_4]^{2-} + H_2$), through which Zn is eluted, and oxidation reactions of Cu and Zn simultaneously occur, which generates an oxide film with a porous structure due to the dezincification reaction (ionization tendency: Cu < Zn), causing large unevenness of tones that possibly leads to deterioration of performance in terms of rubbing fastness. If the gas phase oxidation is used, in contrast, zinc is merely oxidized ($Zn + 1/2O_2 \rightarrow ZnO$) without dezincification in the gas phase reaction, and hence macrovoids are not observed and a denser film structure than in using chemical conversion treatment is obtained, and thus the rubbing fastness can be enhanced.

[0074] For further multiple coloring, one or more compounds including carbonates, sulfides, and sulfates of a metal may be generated, in addition to oxides and/or hydroxides, in the surface of a fastener member. In the case of copper, the carbonate gives yellow/green/blue color, the sulfide gives black color, and the sulfate gives blue color. Wider color tone variation is achieved through modification of the composition ratios of these metal compounds and the depth to which the surface reaction propagates. Examples of methods for generating metal compounds in the surface of a fastener member include a method of adding a reactive substance to generate desired metal compounds during the pretreatment or gas phase oxidation process.

[0075] For example, a gas used for bubbling of water or an aqueous solution in which a desired compound capable of coloring to an intended color is dissolved can be used as a gas to feed for the gas phase oxidation for color tone alteration because the gas has become moist. Alternatively, for example, a halogen gas (e.g., Cl_2, Br_2), carbon dioxide (CO_2), or hydrogen peroxide can be added. The color tone can be adjusted through use of an aqueous solution of a desired compound capable of coloring to an intended color in the metal activation treatment. Examples of such aqueous solution include aqueous solutions of inorganic acid such as hydrochloric acid, sulfuric acid, peroxodisulfuric acid, nitric acid, chromic acid, and phosphoric acid; aqueous solutions of organic acid such as acetic acid and dibasic acids (e.g., oxalic acid, malonic acid, succinic acid, aspartic acid); aqueous solutions of a salt such as a carbonate, a sulfate, a peroxodisulfate, and sulfide; and aqueous hydrogen peroxide.

[0076] In terms of removal of residual components, It is preferred to wash out unreacted components (e.g., ammonia) adhering to the surface of the base material with water after the gas phase oxidation. In addition, one or two or more surface treatments such as antirust treatment, clear lacquer coating, and waxing can be performed, as necessary, after the gas phase oxidation. Examples of applicable methods for the surface treatment include, but are not limited to, soaking in a surface treatment solution, spraying, dropping, and applying a surface treatment solution, roll coating with a surface treatment solution, and flowing a surface treatment solution.

[0077] As described above, the present invention provides a tone-treatment method for an article, including subjecting an article including a base material with at least the surface composed of a zinc-containing copper alloy to gas phase oxidation in the presence of oxygen to form an oxide layer adjacent to the surface of the base material, wherein the ratio A of the mean zinc concentration to the mean copper concentration in the oxide layer is higher than the ratio B of the mean zinc concentration to the mean copper concentration in the surface of the base material. Further, the present invention provides a method for producing a fastener, the method including using this tone-treatment method. Slider fasteners and snap fasteners can be fabricated by using a fastener member subjected to the tone treatment according to the present invention through any conventional approach. When the fastener member is elements for slide fasteners, for example, a fastener chain is assembled, and the assembled fastener chain is subjected to the tone treatment according to the present invention, to which parts including a slider, a pull-tab, a top stop, a bottom stop, and a slider insert are appropriately attached to complete a slider fastener.

(2-3 Gas phase oxidation device)

[0078] Next will be described an example of the configuration of a gas phase oxidation device suitable for continuous tone treatment of, as a target to be treated, an elongated member at least partly including a portion with at least the surface composed of a metal.

[0079] Examples of such elongated members at least partly including metal include a slide fastener part (a fastener chain) including a fastener stringer in which an array of elements are attached to one side edge of an elongated strip of fastener tape; a ball chain including metal balls linked together; a wire-shaped metal fastener member; and a metal wire member. Further, a slide fastener assemblage including a fastener chain to which parts including a slider, a top stop, and a bottom stop have been attached is another example. The device enables performing of a tone-treatment method on an elongated member at least partly including a portion with at least the surface composed of a metal, the tone-treatment method including: conveying a metal fastener member continuously in the longitudinal direction to introduce it into a reaction chamber kept at the atmospheric pressure or negative pressure; subjecting the surface of the member to gas phase oxidation in the reaction chamber; and discharging the member from an outlet of the reaction chamber.

<2-3-1 First embodiment>

[0080] An example of the configuration of a gas phase oxidation device applicable to the tone treatment according to the present invention will be described. In description of a specific example relating to the device, a slide fastener chain is used as an exemplary target to be treated, the slide fastener chain obtained from a pair of fastener stringers each including an array of elements attached to one side edge of an elongated strip of fastener tape by engaging together the arrays of elements facing each other.

[0081] Figure 5 schematically illustrates an elevation view of a gas phase oxidation device 110 according to the first embodiment. The gas phase oxidation device 110 includes: a water seal unit 116 on the upstream side; a gas phase reaction chamber 115 including an inlet 115in and an outlet 115out; a gas phase oxidation gas-feeding system 114; a water seal unit 116 on the downstream side; a conveyor 122; a gas aspirator 113; and an ammonia gas decomposer 112, and operations of these components are controllable by a controller 118. Use of stainless steel, in particular, use of austenitic stainless steel for portions to be in contact with a gas phase oxidation gas can ensure corrosion resistance.

[0082] By the conveyor 122, a fastener chain 120 is allowed to continuously pass through the gas phase reaction chamber 115 placed inside the gas phase oxidation device 110 in the direction of an arrow. The conveyor 122 includes a plurality of guide rollers 122a, and the fastener chain 120 passes through the gas phase reaction chamber 115 while being guided by the guide rollers 122a. One or more of the plurality guide rollers 122a may be each linked to a driver such as a motor to serve in itself as a driver for the fastener chain 120. A driver 122b may be provided outside on the downstream side of the gas phase oxidation device 110 to convey the fastener chain 120 from the outside in a traction mode.

[0083] The gas phase oxidation gas-feeding system 114 in the first embodiment includes a gas storage unit 114a, gas piping 114b, and a gas discharge port 114c. The gas phase oxidation gas stored in the gas storage unit 114a goes through the gas piping 114b, and fed from the gas discharge port 114c into the gas phase reaction chamber 115. If a plurality of gas phase reaction gases is present, a plurality of gas storage units may be provided. In the first embodiment, a gas storage unit 114d is provided in addition to the gas storage unit 114a, and the gas phase oxidation gas from the gas storage unit 114d is mixed in advance with the gas phase oxidation gas from the gas storage unit 114a during passing through the gas piping 114b. In an example, the gas storage unit 114a and the gas storage unit 114d can store ammonia and air, respectively. Instead of air from the gas storage unit, compressed air from a compressor can be used.

[0084] Although one gas discharge port 114c may be provided, a plurality of gas discharge ports 114c can be provided to enhance reaction efficiency. For higher homogeneity of tones between the face and back of the fastener chain 120, it is preferable that a gas discharge port 114c be disposed on each side of the fastener chain 120. Needless to say, a gas discharge port 114c can be disposed only on one side of the fastener chain 120 when it is intended to impart color tone variation between the face and back of the fastener chain 120. In the first embodiment, a plurality of gas discharge ports 114c is alternately disposed in arrays on the upper side and lower side of the fastener chain 120 along the conveyance direction of the fastener chain 120 in the gas phase reaction chamber 115.

[0085] The fastener chain 120 is subjected to tone treatment based on oxidation reaction in the presence of a gas phase oxidation gas during passing through the gas phase reaction chamber 115. The gas in the gas phase reaction chamber 115 is sucked by the gas aspirator 113 such as a blower from a suction port 121 disposed near the outlet, and goes through piping 123 to be discharged out of the gas phase reaction chamber 115, and unreacted ammonia is decomposed into H_2 O and N_2 in the ammonia gas decomposer 112, and then the gas is discharged out of the device 110. There is no limitation to the decomposition mode for ammonia gas, and examples thereof include catalytic decomposition, combustion, gas decomposition, and wet scrubber modes. It is preferred to provide the ammonia gas decomposer as necessary; however, the ammonia gas decomposer is not necessarily essential in the present invention.

[0086] The pressure in the gas phase reaction chamber 115 can be kept under negative pressure by setting the suction power of the gas aspirator 113 so that the suction of gas from the suction port 121 is more than the discharge of gas from the discharge port 114c. This can prevent the gas in the gas phase reaction chamber 115 from leaking out. However, it is preferred for stable gas phase treatment under an atmosphere with the concentration more reliably kept constant to provide at least one water seal unit 116 on the inlet 115in side (upstream side) and/or outlet 115out side (downstream side) of the gas phase reaction chamber 115. A water seal unit 116 may be disposed only on one of the inlet 115in side and the outlet 115out side, but, in view of airtightness in the gas phase treatment chamber, it is preferable that a water seal unit 116 be disposed at least on the outlet side, and it is more preferable that a water seal unit 116 be disposed on each side. However, if the water seal unit 116 is disposed on the inlet 115in side, the fastener chain 120 gets wet, which often causes color unevenness in tone treatment through gas phase oxidation. Thus, it is preferable for prevention of color unevenness that no water seal unit 116 be disposed on the inlet 115in side. In this case, air will enter the gas phase reaction chamber 115 in the situation that the pressure in the gas phase reaction chamber 115 is kept under negative pressure. For this reason, air can be fed without use of the gas piping 114b, and can also be fed in combination with the air from the gas piping 114b.

[0087] With respect to safety management, on the other hand, it is advantageous that water sealing is successfully established in an emergency. While a water seal unit 116 is provided on each of the inlet 115in side and the outlet side in the first embodiment, for that reason only the outlet 115out side is water-sealed and the inlet 115in side is not water-sealed in normal operation.

[0088] It is preferable that the gas phase oxidation device 110 include a gas flow controller that controls the gas phase oxidation gas fed into the gas phase reaction chamber 115 to flow from the inlet 115in side to the outlet 115out side. Inclusion of such a gas flow controller is particularly effective for prevention of gas leakage in the situation that a water seal unit 116 is used for water sealing on the outlet 115out side while a water seal unit 116 is not disposed or disposed but not used for water sealing on the inlet 115in side. On the other hand, in a situation that a water seal unit 116 on the inlet 115in side is used for water sealing and a water seal unit 116 is not disposed or disposed but not used for water sealing on the outlet 115out side, the situation corresponding to a third embodiment described later, it is preferred to control the gas phase oxidation gas fed into the gas phase reaction chamber 115 to flow from the outlet 115out side to the inlet 115in side.

[0089] Whereas there is no limitation to the gas flow controller, the gas flow controller in the first embodiment includes: one or more discharge ports 114c for feeding a gas phase oxidation gas placed in the gas phase reaction chamber 115; one or more suction ports 121 for discharging a gas in the chamber 115 out of the chamber 115. The configuration in which the suction port nearest to the outlet among the one or more suction ports 121 is disposed closer to the outlet 115out side than all of the one or more discharge ports 114c allows the gas phase oxidation gas fed into the gas phase reaction chamber 115 to flow from the inlet 115in side to the outlet 115out side. In a preferred embodiment, all of the one or more suction ports 121 are disposed closer to the outlet 115out side than all of the one or more discharge ports 114c. Here, by controlling the total suction of gas from the one or more suction ports 121 to be more than the total discharge of gas from the one or more discharge ports 114c, negative pressure is established in the gas phase reaction chamber 115, and thus gas leakage can be prevented.

[0090] Discharge of the fastener chain 120 while blocking the gas in the gas phase reaction chamber 115 from the outside can be achieved with the configuration in which the fastener chain 120 passes through the water seal unit 116 (outlet) to be discharged from the gas phase reaction chamber 115. An NH_3 sensor (not shown) may be disposed on the outside air side of the gas phase oxidation device 110. If NH_3 leaks, the NH_3 sensor (not shown) detects it, and feeding of NH_3 can be stopped by a command from the controller 118.

[0091] The controller 118 is capable of controlling the flow rate of the gas phase oxidation gas fed from the gas phase oxidation gas storage units 114a and 114d through the discharge ports 114c, and thus the gas concentration in the gas phase reaction chamber 115. The gas phase oxidation device 110 can be disposed in a thermostatic humidity control box, which allows introduction of air with the temperature and humidity controlled into the gas phase oxidation device 110. The temperature in the gas phase reaction chamber 115 can be controlled by a heating unit (not shown).

[0092] While conveyed by the conveyor 122, the fastener chain 120 passes through the water seal unit (upstream) 116 (not water-sealed in normal operation, but water-sealed only in an emergency) to enter the gas phase reaction chamber 115, where the gas phase oxidation gas fed into the gas phase reaction chamber 115 reacts with a copper alloy constituting the element surface of the fastener chain 120 which has been pretreated as appropriate, and the color tone changes through the above-described reaction mechanism. Thereafter, the fastener chain 120, while conveyed by the conveyor 122, passes through the water seal unit (downstream) 116 to be discharged from the gas phase oxidation device 110. Unreacted gas attaching to the fastener chain 120 is washed out and removed through soaking in water in passing through the water seal unit (downstream) 116.

<2-3-2 Second embodiment>

[0093] Figure 6 schematically illustrate an elevation view of a gas phase oxidation device 210 according to the second embodiment. Unless otherwise specified, each reference sign in Figure 6 has the same meaning as the corresponding reference sign in the description of the first embodiment, and hence description is omitted. The gas phase oxidation device 210 according to the second embodiment is an effective when a smaller area is used for installation. It can be said that the second embodiment is an embodiment particularly advantageous when the space for installation is small in the plane direction. Although a controller is likewise present in the second embodiment, the illustration is omitted.

[0094] In the second embodiment, the gas phase reaction chamber 115 includes: a first chamber 115a placed on the inlet side; a second chamber 115b placed on the outlet side; and a third chamber 115c placed between the first chamber 115a and the second chamber 115b. The conveyor 122 is configured to allow the article to sequentially pass through the first chamber 115a, the third chamber 115c, and the second chamber 115b, and can include guide rollers 122a so as to allow the fastener chain 120 to pass through the third chamber 115c in a direction including one or both of the vertically upward direction and the vertically downward direction. The fastener chain 120 is conveyed by a driver 122b disposed outside in the downstream direction of the gas phase oxidation device 210.

[0095] Assuming that the distance of conveyance of the fastener chain 120 when the fastener chain 120 passes through the gas phase reaction chamber 115 is constant, the distance of conveyance in the horizontal direction is reduced by inclusion of the vertically upward direction and the vertically downward direction in the direction of conveyance of the fastener chain 120, which enables reduction of the area for installation of the gas phase oxidation device 210.

[0096] In the second embodiment, the third chamber 115c includes: a third chamber upper portion 115c1 placed at the same height as the first chamber 115a and the second chamber 115b; and a third chamber lower portion 115c2 placed below the third chamber upper portion, and the conveyor 122 is configured to allow the fastener chain 120 to pass through the first chamber 115a, the third chamber upper portion 115c1, the third chamber lower portion 115c2, and the second chamber 115b.

[0097] In the second embodiment, the fastener chain 120 passes through the first chamber in the horizontal direction, and then enters the third chamber 115c. The fastener chain 120 undergoes multiple up-and-down cycles with moving in the vertical direction (two up-and-down cycles in the second embodiment) in the third chamber 115c, then enters the second chamber 115b, and thereafter passes through a water seal unit 116 on the outlet side to be discharged from the gas phase oxidation device 210.

[0098] The higher the proportion of distance of conveyance in the vertical direction in the third chamber 115c, the more the area for installation of the gas phase oxidation device 210 can be reduced. In order to save the space for installation, the total distance (d1) of conveyance of the fastener chain 120 in the vertical direction in the third chamber 115c is preferably larger than the total distance (d2) of conveyance of the fastener chain 120 in the horizontal direction in the first chamber 115a and the second chamber 115b more preferably $d1/d2 \geq 2$ is satisfied, more preferably $d1/d2 \geq 3$ is satisfied, and even more preferably $d1/d2 \geq 4$ is satisfied. Although there is no upper limit of d1/d2, $d1/d2 \leq 20$ is satisfied in normal situations, and $d1/d2 \leq 10$ is satisfied in typical situations.

[0099] Each of the guide rollers 122 to be disposed in the third chamber lower portion 115c2 can be a dancer roller. Through up-and-down movement, dancer rollers can be advantageously used as a means to adjust the tension applied to the fastener chain 120 conveyed. In addition, the distance for the fastener chain 120 to pass through the gas phase reaction chamber 115 can be adjusted by changing the positions to dispose dance rollers in the up-and-down direction in accordance with the type of the fastener chain 120. This allows variation of treatment time without changing the conveyance speed for the fastener chain 120, and further provides an advantage of ease in imparting color shade variation.

[0100] It is preferable that one or more discharge ports 114c for the gas phase oxidation gas be disposed in the third chamber lower portion 115c2, and it is more preferable that one or more discharge ports 114c be disposed at positions lower than the lowest point through which the fastener chain 120 passes in the third chamber lower portion 115c2. Thereby, the homogeneity of the concentration of the gas phase oxidation gas can be enhanced.

[0101] Since the gas phase oxidation gas flows into the third chamber 115c, the concentration of the gas phase oxidation gas in the third chamber 115c tends to be higher than those in the first chamber 115a and the second chamber 115b. The configuration in which the third chamber 115c is disposed between the first chamber 115a and the second chamber 115b reduces the risk of leakage of the gas phase oxidation gas to the outside of the device, enhancing the safety of the gas phase oxidation device 210.

[0102] In the second embodiment, a water seal unit 116 is disposed only on the outlet side. Hence, the gas phase oxidation device 210 preferably includes one or more suction ports 121 in the second chamber 115b on the outlet side, and more preferably includes the suction ports 121 only in the second chamber 115b. In the second embodiment, the gas phase oxidation gas which has flowed into the third chamber lower portion 115c2 moves to the third chamber upper portion 115c1, is at least partly used for oxidation reaction of the fastener chain, and passes through the second chamber 115b to be discharged from the suction ports 121.

[0103] In the case of the above-described first embodiment, if ammonia is used as the gas phase reaction gas, for example, a concentration distribution may be generated in the reaction chamber 115 because of the tendency of ammonia to move upward, since ammonia is lighter than air. Thus, the color tone homogeneity of fastener chain 120 in the up-and-down direction may be deteriorated. In the case of the second embodiment, in contrast, the fastener chain 120 is conveyed in the up-and-down direction (vertical direction) in the third chamber lower portion 115c2, and by virtue of this the influence on the color tone homogeneity of the fastener chain 120 in the up-and-down direction is reduced even when a concentration distribution of the gas phase reaction gas is generated in the up-and-down direction. Accordingly, the second embodiment is also advantageous in that the color tone homogeneity between the face and back of the fastener chain 120 can be enhanced.

<2-3-3 Third embodiment>

[0104] Figure 7 schematically illustrates an elevation view of a gas phase oxidation device 310 according to the third embodiment. Unless otherwise specified, each reference sign in Figure 7 has the same meaning as the corresponding reference sign in the description of the first embodiment, and hence description is omitted. A difference of the third embodiment from the first embodiment is that the water seal unit 116 on the outlet side is not used for water sealing and only the water seal unit 116 on the inlet side is used for water sealing in normal operation. According to the present embodiment, the fastener chain 120 gets wet immediately before being subjected to gas phase oxidation, and hence color unevenness is likely to occur in the fastener chain 120 after tone treatment; however, the present embodiment can be said to be an embodiment suitable when color unevenness is acceptable or when a design utilizing color unevenness is desired.

[0105] Because the position to dispose the water seal unit 116 is changed to the inlet 115in side of the gas phase reaction chamber 115 in the third embodiment, it is preferable that the gas phase oxidation device 310 include a gas flow controller that controls the gas phase oxidation gas fed into the gas phase reaction chamber 115 to flow from the outlet side to the inlet side. Inclusion of such a gas flow controller is effective for prevention of gas leakage in the situation that a water seal unit 116 is used for water sealing on the inlet side while a water seal unit 116 is not disposed or disposed but not used for water sealing on the outlet side. Whereas there is no limitation to the gas flow controller, the gas flow controller in the third embodiment includes: one or more discharge ports 114c for feeding the gas phase oxidation gas placed in the gas phase reaction chamber 115; and one or more suction ports 121 for discharging a gas in the chamber 115 out of the chamber 115. The configuration in which the suction port nearest to the inlet 115in among the one or more suction ports 121 is disposed closer to the inlet 115in side than all of the one or more discharge ports 114c allows the gas phase oxidation gas fed into the gas phase reaction chamber 115 to flow from the outlet 115out side to the inlet 115in side. In a preferred embodiment, all of the one or more suction ports 121 are disposed closer to the inlet 115in side than all of the one or more discharge ports 114c. Here, By controlling the total suction of gas from the one or more suction ports 121 to be more than the total discharge of gas from the one or more discharge ports 114c, negative pressure is established in the gas phase reaction chamber 115, and thus gas leakage can be prevented.

[0106] Through this configuration, the gas in the gas phase reaction chamber 115 is sucked by a gas aspirator 113 such as a blower from the suction ports 121 disposed near the inlet 115in of the gas phase reaction chamber 115 to be discharged out of the gas phase reaction chamber 115.

(2-4 Tone-treatment system)

[0107] Figure 8 illustrates an example of the configuration of a tone-treatment system 30 to successively perform the pretreatment described hereinabove, gas phase oxidation, and antirust treatment. The tone-treatment system 30 includes a degreasing device 31, a water-washing device 32, a gas phase oxidation device 34, a water-washing device 35, an antirust-treatment device 36, a dryer 37, a surface-treatment device 38, and a dryer 39 disposed in this order, and an elongated slide fastener part 41 such as a fastener chain, while conveyed in a reel-to-reel mode in the direction of an arrow, passes through these devices sequentially to undergo predetermined treatments for tone treatment. Surface treatment such as clear lacquer coating and waxing can be performed through the surface-treatment device 38.

EXAMPLES

[0108] Hereinafter, Examples of the present invention will be demonstrated; however, these are provided for better understanding of the present invention and its advantages, and are not intended to limit the present invention.

(Test Example 1)

[0109] Prepared was a metallic fastener chain of 200 to 250 mm in length after degreasing and water washing. The element array of the metallic fastener chain was made of copper-zinc alloy (Cu: 85% by mass (85.4 at.%), Zn: 15% by mass (14.6 at.%)). The composition is a value not considering inevitable impurities, and the composition of the elements can contain inevitable impurities. The same applies in the following Test Examples. The element array was a molded product obtained through pressing a Y-shaped bar annealed in a reductive atmosphere into an element shape, and fixed to a fastener tape by calking.

[0110] The fastener chain was set in a tubular furnace batch processing apparatus for gas phase reaction (ϕ75 mm quartz tube (capacity: 0.6 L)), and subjected to gas phase oxidation by using a mixed gas of air and ammonia gas under reaction conditions shown in Tables 1. After the gas phase oxidation, the fastener chain was water-washed in 2 L of water, and then soaked in benzotriazole aqueous solution for 1 minute for antirust treatment, and thereafter water-washed and naturally dried. Neither clear lacquer coating nor waxing was performed.

(Test Example 2)

[0111] Prepared was a metallic fastener chain of 200 to 250 mm in length after degreasing and water washing. The element array of the metallic fastener chain was made of copper-zinc alloy (Cu: 65% by mass (65.7 at.%), Zn: 35% by mass (34.3 at.%)). The element array was a molded product obtained through pressing a Y-shaped bar annealed in an oxidative atmosphere into an element shape, and fixed to a fastener tape by calking. The fastener chain was set in a tubular furnace batch processing apparatus for gas phase reaction (ϕ75 mm quartz tube (capacity: 0.6 L)), and subjected to gas phase oxidation by using a mixed gas of air and ammonia gas under reaction conditions shown in Tables 1. After the gas phase oxidation, the fastener chain was subjected to antirust treatment in the same manner as in Test Example 1. Neither clear lacquer coating nor waxing was performed.

(Test Example 3)

[0112] Prepared was a metallic fastener chain of 200 to 250 mm in length after degreasing and water washing. The element array of the metallic fastener chain was made of copper-zinc alloy (Cu: 60% by mass (60.7 at.%), Zn: 40% by mass (39.3 at.%)). The element array was a molded product obtained through pressing a Y-shaped bar annealed in an oxidative atmosphere into an element shape, and fixed to a fastener tape by calking. The fastener chain was set in a tubular furnace batch processing apparatus for gas phase reaction (ϕ75 mm quartz tube (capacity: 0.6 L)), and subjected to gas phase oxidation by using a mixed gas of air and ammonia gas under reaction conditions shown in Tables 1. After the gas phase oxidation, the fastener chain was subjected to antirust treatment in the same manner as in Test Example 1. Neither clear lacquer coating nor waxing was performed.

(Test Example 4)

[0113] The same fastener chain as in Test Example 1 was subjected to coloring not by gas phase oxidation but by liquid phase chemical conversion treatment. Specifically, the chemical conversion treatment was performed through soaking the fastener chain after degreasing and water washing in a chemical conversion treatment solution. After the chemical conversion treatment, the fastener chain was subjected to antirust treatment in the same manner as in Test Example 1. Neither clear lacquer coating nor waxing was performed.

(Test Example 5)

[0114] The same fastener chain as in Test Example 2 was subjected to coloring not by gas phase oxidation but by liquid phase chemical conversion treatment. Specifically, the chemical conversion treatment was performed through soaking the fastener chain after degreasing and water washing in a chemical conversion treatment solution. After the chemical conversion treatment, the fastener chain was subjected to antirust treatment in the same manner as in Test Example 1. Neither clear lacquer coating nor waxing was performed.

(Test Example 6)

[0115] The same fastener chain as in Test Example 3 was subjected to coloring not by gas phase oxidation but by liquid phase chemical conversion treatment. Specifically, the chemical conversion treatment was performed through soaking the fastener chain after degreasing and water washing in a chemical conversion treatment solution. After the chemical conversion treatment, the fastener chain was subjected to antirust treatment in the same manner as in Test Example 1. Neither clear lacquer coating nor waxing was performed.

[0116] Color tones obtained in Test Examples 1 to 6 vary depending on the treatment time, the gas for treatment, and the concentration of the liquid, and change generally depending on time and concentration in the order of yellow → reddish brown → brown → blackish brown. The estimated composition of the oxide film at this time is oxidized copper including Cu_2O and CuO.

<Tests on various performances>

[0117] Results of performance evaluation on mechanical properties for the metallic fastener chain samples of Test Examples 1 to 6 are shown in Tables 1.

[0118] "L-class durability test" refers to a test in a method in accordance with JIS S 3015: 2007 (repeated opening and closing durability test). All of the samples were rated as "500 cycles cleared". The rating "500 cycles cleared" means that a fastener chain to which a slider, stops, and so forth have been attached functions as a slide fastener without any abnormality even after the slider is reciprocally moved against the fastener chain in 500 cycles.

[0119] For "rubbing fastness", tests were conducted for the elements with methods in accordance with JIS L 0803: 2011 and JIS L 0849: 2013, which relate to tests for stained tape. After testing, evaluation of rubbing fastness was performed based on the presence or absence of a stain (due to attachment and peeling) in visual observation of the surface of elements and the surface of a test cloth after testing.
Without stain: ○-mark (a circle)
With stain: X-mark

<Analysis of oxide layer in depth direction>

[0120] The element surface of each of the metallic fastener chain samples of Test Example 1 to 6, after gas phase oxidation or chemical conversion treatment but before antirust treatment, was subjected to AES analysis by using an

Auger electron spectrometer equipped with an FE electron gun to acquire depth profiles. Conditions for AES analysis were as follows: acceleration voltage of electron gun: 10 kV; electric current: 3 × 10^{-8} A; beam diameter: 50 μm; inclination of sample: 30°. An Ar monomer ion gun with 2 kV was used for etching. Sputtering time was converted with a standard etching speed of 8.0 nm/min for SiO_2 standard material to calculate detection depths. The etching speed was a value calculated by dividing 100 nm by duration until the intensity of O in SiO_2 standard material (a 100-nm thermal oxide film on an Si substrate) reached half the original value.

[0121] Atomic concentrations of Cu, Zn, and O were calculated by using relative sensitivity coefficients of Cu: 1, Zn: 1, O: 1. Used for each of the mean Zn concentration, mean Cu concentration, and mean O concentration of an oxide layer was the mean of the corresponding measurements at depths of 10 to 20 nm from the surface of the oxide layer; used for each of the mean Zn concentration and mean Cu concentration in the surface of a base material was the mean of the corresponding measurements from the boundary between an oxide layer and the base material (the surface of the base metal), where the O concentration reached 5 at.% or less, to a depth of 20 nm therefrom. For reference, the depth profiles for Test Examples 3 and 6 are shown in Figures 3 and 4, respectively.

[Table 1-1]

		Gas phase (antique gold color)		
Test No.		Test Example 1	Test Example 2	Test Example 3
Element composition: Cu/Zn mass ratio		85/15	65/35	60/40
Reaction conditions	NH_3 concentration (%)^{*1}	5	8	8
	Furnace temperature (°C)	20	20	20
	Treatment time (sec)	60	60	60
Zn/Cu in oxide layer: A (Mean zinc concentration (at.%) of oxide layer / mean copper concentration of oxide layer (at.%))		0.244 (12.33/50.52)	0.523 (20.63/39.45)	0.736 (25.03/34.00)
Zn/Cu in surface of base material: B (Mean zinc concentration (at.%) in surface of base material / mean copper concentration in surface of base material (at.%))		0.0962 (8.42/87.51)	0.232 (17.92/77.37)	0.256 (19.53/76.20)
A/B		2.54	2.25	2.88
Mean oxygen concentration of oxide layer (at.%)		37.15	39.92	40.97
Rubbing fastness		○	○	○
L-class durability test		500 cycles cleared	500 cycles cleared	500 cycles cleared
*1: Ammonia concentration: 100% ammonia gas Vol / (air + 100% ammonia gas) Vol × 100				

[Table 1-2]

		Gas phase (antique gold color)		
Test No.		Test Example 4	Test Example 5	Test Example 6
Element composition: Cu/Zn mass ratio		85/15	65/35	60/40
Reaction conditions	NH_3 concentration (%)^{*1}	-	-	-
	Furnace temperature (°C)	-	-	-
	Treatment time (sec)	-	-	-
Zn/Cu in oxide layer: A (Mean zinc concentration (at.%) of oxide layer / mean copper concentration of oxide layer (at.%))		0.0331 (2.85/86.12)	0.0549 (4.56/83.00)	0.0801 (6.67/83.23)
Zn/Cu in surface of base material: B		0.0827	0.230	0.248

(continued)

	Gas phase (antique gold color)		
Test No.	Test Example 4	Test Example 5	Test Example 6
(Mean zinc concentration (at.%) in surface of base material / mean copper concentration in surface of base material (at.%))	(7.30/88.31)	(17.82/77.37)	(18.91/76.29)
A/B	0.400	0.239	0.323
Mean oxygen concentration of oxide layer (at.%)	11.03	12.44	10.1
Rubbing fastness	X	X	X
L-class durability test	500 cycles cleared	500 cycles cleared	500 cycles cleared
*1: Ammonia concentration: 100% ammonia gas Vol / (air + 100% ammonia gas) Vol × 100			

[0122] The results shown in Tables 1 demonstrate that although the results of the L-class durability test for the samples of Test Examples 1 to 3 were comparable to those in the case of the conventional chemical conversion treatment (Test Examples 4 to 6), the samples of Test Examples 1 to 3 were superior in rubbing fastness to the samples of Test Examples 4 to 6.

<Analysis of oxide layer in depth direction for samples including finishing layer>

[0123] Each of the above-described metallic fastener chain samples of Test Examples 1 to 3 after gas phase oxidation was subjected to antirust treatment followed by clear lacquer coating. After drying, each sample was soaked in a release agent (S-BACK H-300: produced by SASAKI CHEMICAL CO., LTD.) at normal temperature overnight to remove the clear lacquer coating and the antirust treatment layer from the sample, exposing the oxide layer of the element surface. Subsequently, the oxide layer was analyzed in the depth direction in the above-described manner, and test results substantially the same as those before formation of the finishing layer were obtained for any of the samples.

Reference Signs List

[0124]

10, 20	Article
11	Base material
12	Oxide layer
13	Finishing layer
110, 210, 310	Gas phase oxidation device
118	Controller
112	Ammonia gas decomposer
113	Blower (gas aspirator)
114	Gas phase oxidation gas-feeding system
115	Gas phase reaction chamber
116	Water seal unit
120	Fastener chain
122	Conveyor
30	Tone-treatment system
31	Degreasing device
32	Water-washing device
34	Gas phase oxidation device
35	Water-washing device
36	Antirust-treatment device
37	Dryer
38	Surface-treatment device
39	Dryer

41 Slide fastener part

Claims

1. An article comprising: a base material 11 with at least a surface composed of a zinc-containing copper alloy; and an oxide layer 12 adjacent to the surface of the base material 11, wherein a ratio A of a mean zinc concentration to a mean copper concentration in a depth range of 10 nm to 20 nm with reference to a surface of the oxide layer 12 is higher than a ratio B of a mean zinc concentration to a mean copper concentration in the surface of the base material 11.

2. The article according to claim 1, wherein the mean zinc concentration in the surface of the base material 11 is 5 to 50 at.%.

3. The article according to claim 1 or 2, wherein a ratio A/B of the ratio A to the ratio B is 2.0 or higher.

4. The article according to any one of claims 1 to 3, wherein a whole of the base material 11 is composed of the zinc-containing copper alloy.

5. The article according to claim 4, wherein the mean zinc concentration in the depth range of 10 nm to 20 nm with reference to the surface of the oxide layer 12 is 5 to 80 at.%.

6. The article according to any one of claims 1 to 5, wherein the article is a slide fastener member.

7. A slide fastener comprising the article according to claim 6.

8. A tone-treatment method for an article, comprising subjecting an article comprising a base material with at least a surface composed of a zinc-containing copper alloy to gas phase oxidation at least in a presence of oxygen.

9. The tone-treatment method for an article according to claim 8, wherein the tone-treatment method comprises forming an oxide layer adjacent to the surface of the base material through gas phase oxidation, wherein a ratio A of a mean zinc concentration to a mean copper concentration in a depth range of 10 nm to 20 nm with reference to a surface of the oxide layer is higher than a ratio B of a mean zinc concentration to a mean copper concentration in the surface of the base material.

10. The tone-treatment method according to claim 8 or 9, wherein the gas phase oxidation is performed in a presence of ammonia.

11. The tone-treatment method according to any one of claims 8 to 10, wherein tone control through the gas phase oxidation is performed by changing one or more selected from a group consisting of ammonia concentration, oxygen concentration, another reactive gas concentration, humidity in a reaction system, temperature in a reaction system, treatment time, and article temperature.

12. The tone-treatment method according to any one of claims 8 to 11, wherein the article is a fastener member.

13. The tone-treatment method according to any one of claims 8 to 12, wherein the gas phase oxidation is performed at an atmosphere temperature of 20 to 80°C.

14. The tone-treatment method according to any one of claims 8 to 13, wherein the gas phase oxidation is performed under negative pressure.

15. The tone-treatment method according to any one of claims 8 to 14, wherein the tone-treatment method comprises performing activation treatment followed by water washing of the surface of the base material before performing the gas phase oxidation.

16. The tone-treatment method according to any one of claims 8 to 15, wherein the tone-treatment method comprises degreasing followed by water washing of the surface of the base material before performing the gas phase oxidation.

17. The tone-treatment method according to any one of claims 8 to 14, wherein the tone-treatment method comprises performing at least one or more surface treatments selected from a group consisting of clear coating, antirust treatment, and waxing, on the surface of the oxide layer formed through the gas phase oxidation.

18. A gas phase oxidation device for performing a tone-treatment method, the gas phase oxidation device comprising: a gas phase reaction chamber 115 for performing gas phase oxidation including an inlet 115in and an outlet 115out; a conveyor 122 that allows an elongated member at least partly including a portion with at least a surface composed of a metal to enter the inlet, pass through the gas phase reaction chamber 115, and continuously exit from the outlet; a discharge port 114c for feeding a gas phase oxidation gas into the gas phase reaction chamber 115; and a suction port 121 for discharging a gas in the gas phase reaction chamber 115 out of the chamber 115.

19. The gas phase oxidation device according to claim 18, wherein a water seal unit 116 for blocking the gas in the gas phase reaction chamber 115 is provided on either one or both of an outlet 115out side and an inlet 115in side of the gas phase reaction chamber 115.

20. The gas phase oxidation device according to claim 19, wherein the water seal unit 116 for blocking the gas in the gas phase reaction chamber 115 from an outside is provided only on the outlet 115out side of the gas phase reaction chamber 115.

21. The gas phase oxidation device according to claim 20, wherein the gas phase oxidation device comprises a gas flow controller for controlling the gas phase oxidation gas fed into the gas phase reaction chamber 115 to flow from the inlet 115in side to the outlet 115out side.

22. The gas phase oxidation device according to claim 21, wherein the gas flow controller includes: one or more discharge ports 114c for feeding the gas phase oxidation gas placed in the gas phase reaction chamber 115; and one or more suction ports 121 for discharging the gas in the chamber 115 out of the chamber 115, wherein all of the one or more suction ports 121 are disposed closer to the outlet side than all of the one or more discharge ports.

23. The gas phase oxidation device according to claim 22, wherein the conveyor 122 is configured to allow the article to pass through the gas phase reaction chamber 115 in a direction including either one or both of a substantially vertically upward direction and a substantially vertically downward direction.

24. The gas phase oxidation device according to claim 23, wherein the gas phase reaction chamber 115 includes: a first chamber 115a placed on the inlet 115in side; a second chamber 115b placed on the outlet 115out side; and a third chamber 115c placed between the first chamber 115a and the second chamber 115b, and the conveyor 122 is configured to allow the article to sequentially pass through the first chamber 115a, the third chamber 115c, and the second chamber 115b, and configured to allow the article to pass through the third chamber 115c in a direction including either one or both of the substantially vertically upward direction and the substantially vertically downward direction.

25. The gas phase oxidation device according to claim 24, wherein the third chamber 115c includes: a third chamber upper portion 115c1 located at the same height as the first chamber 115a and the second chamber 115b; and a third chamber lower portion 115c2 located below the third chamber upper portion 115c1, and the conveyor 122 is configured to allow the article to pass through the first chamber 115a, the third chamber upper portion 115c1, the third chamber lower portion 115c2, and the second chamber 115b.

26. The gas phase oxidation device according to claim 24 or 25, wherein the gas phase oxidation device comprises: at least one of the discharge ports 114c in the third chamber lower portion 115c2; and at least one of the suction ports 121 in the second chamber 115b.

27. The gas phase oxidation device according to any one of claims 24 to 26, wherein the conveyor 122 is configured to allow the article to pass through the third chamber 115c in a direction including both of the substantially vertically upward direction and the substantially vertically downward direction.

Figure 1

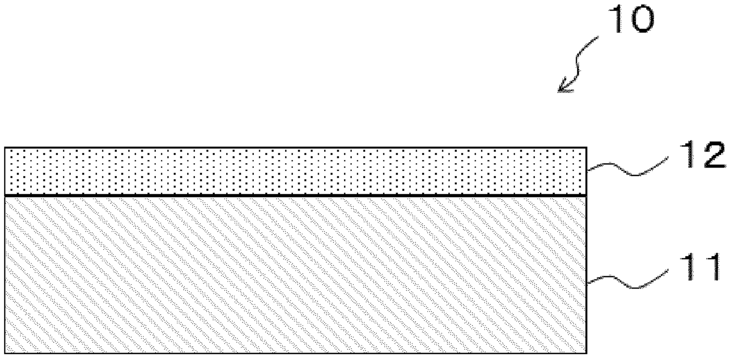


Figure 2

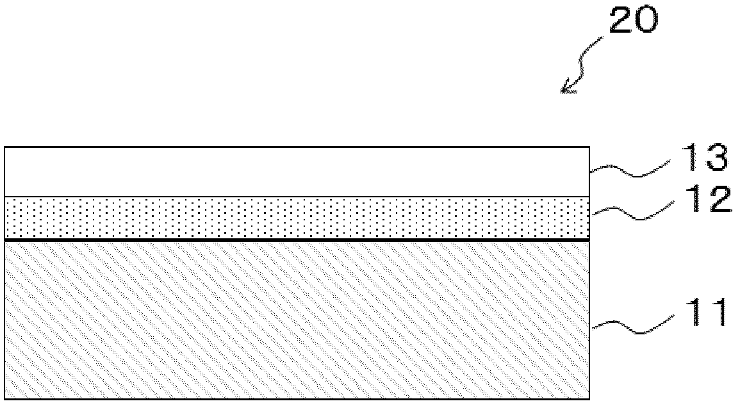


Figure 3

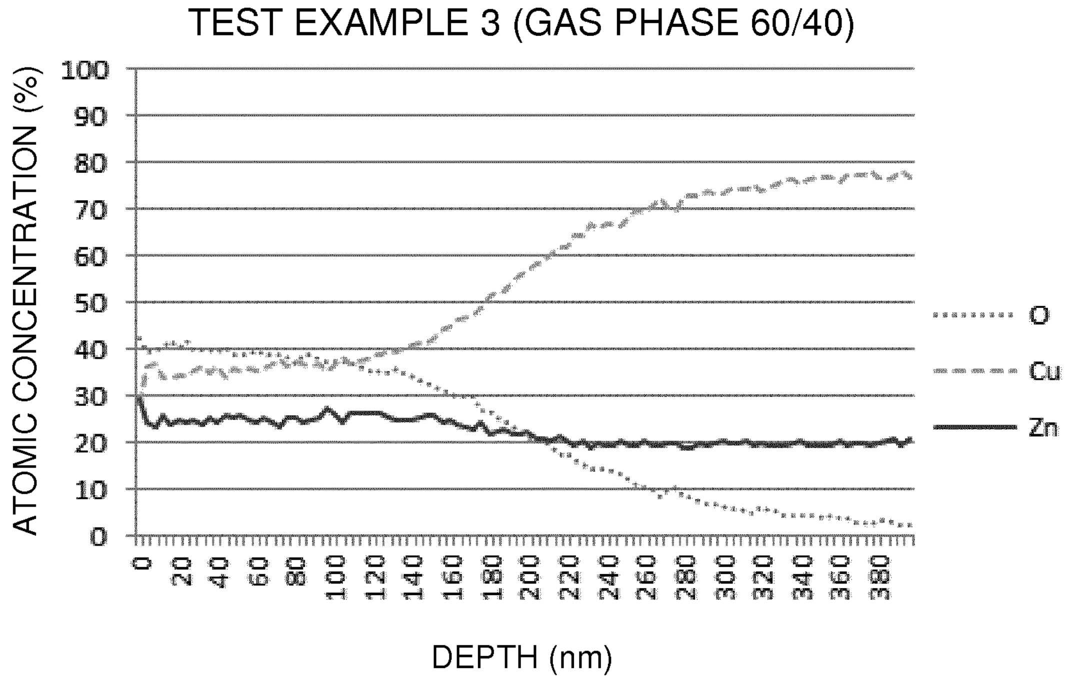
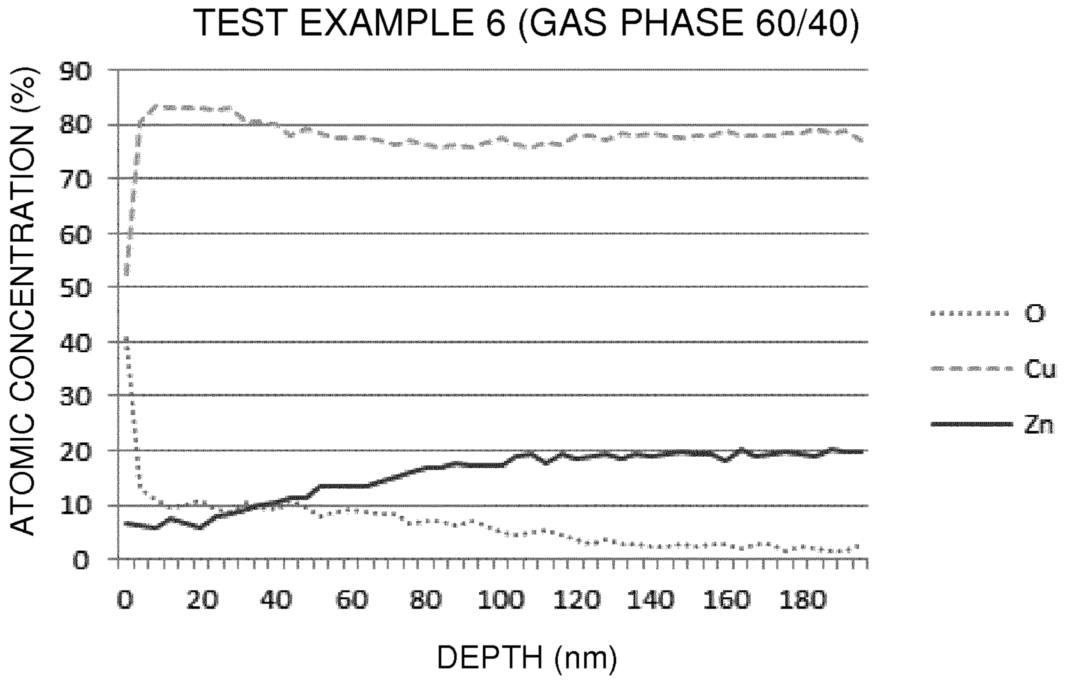


Figure 4



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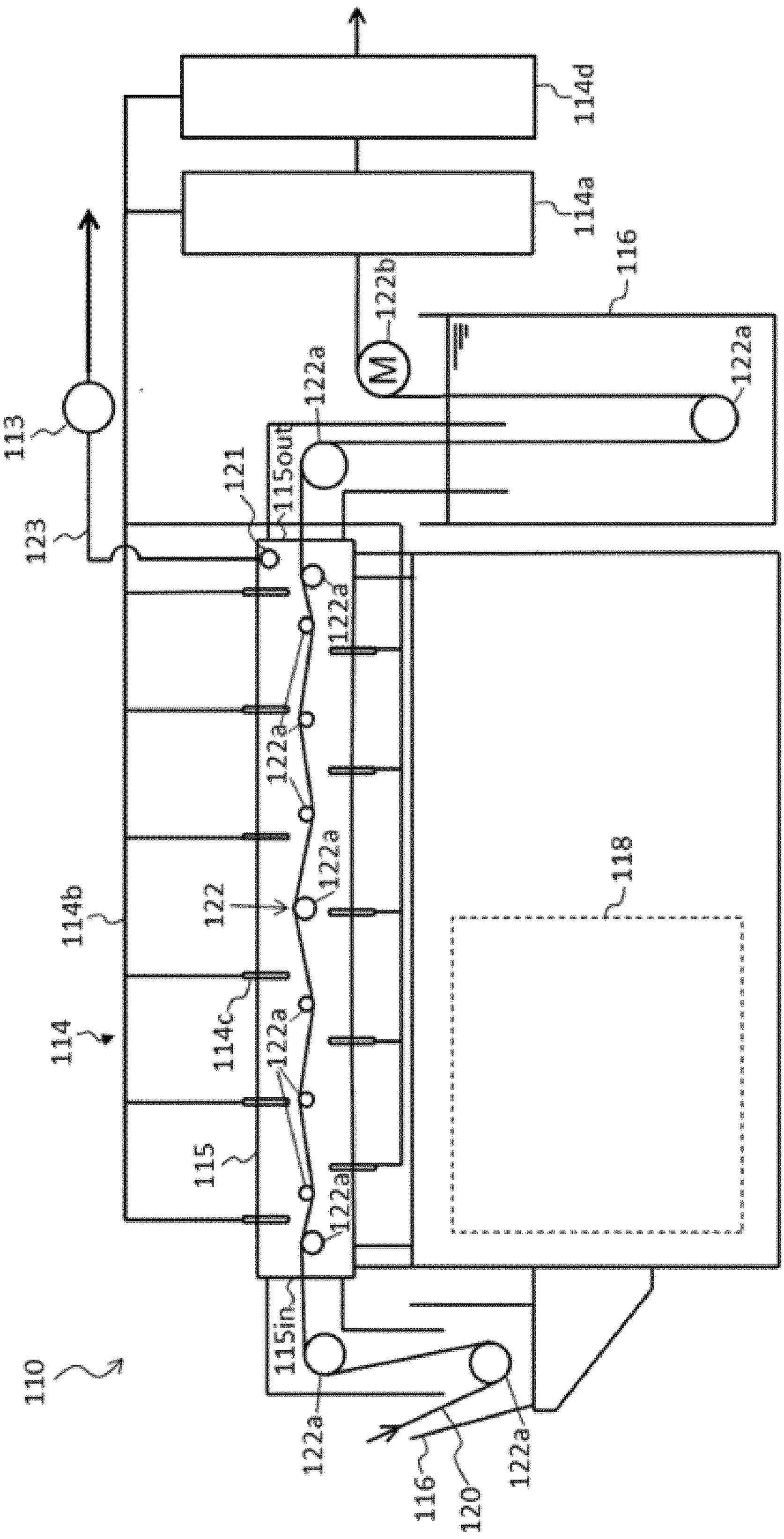
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Figure 6

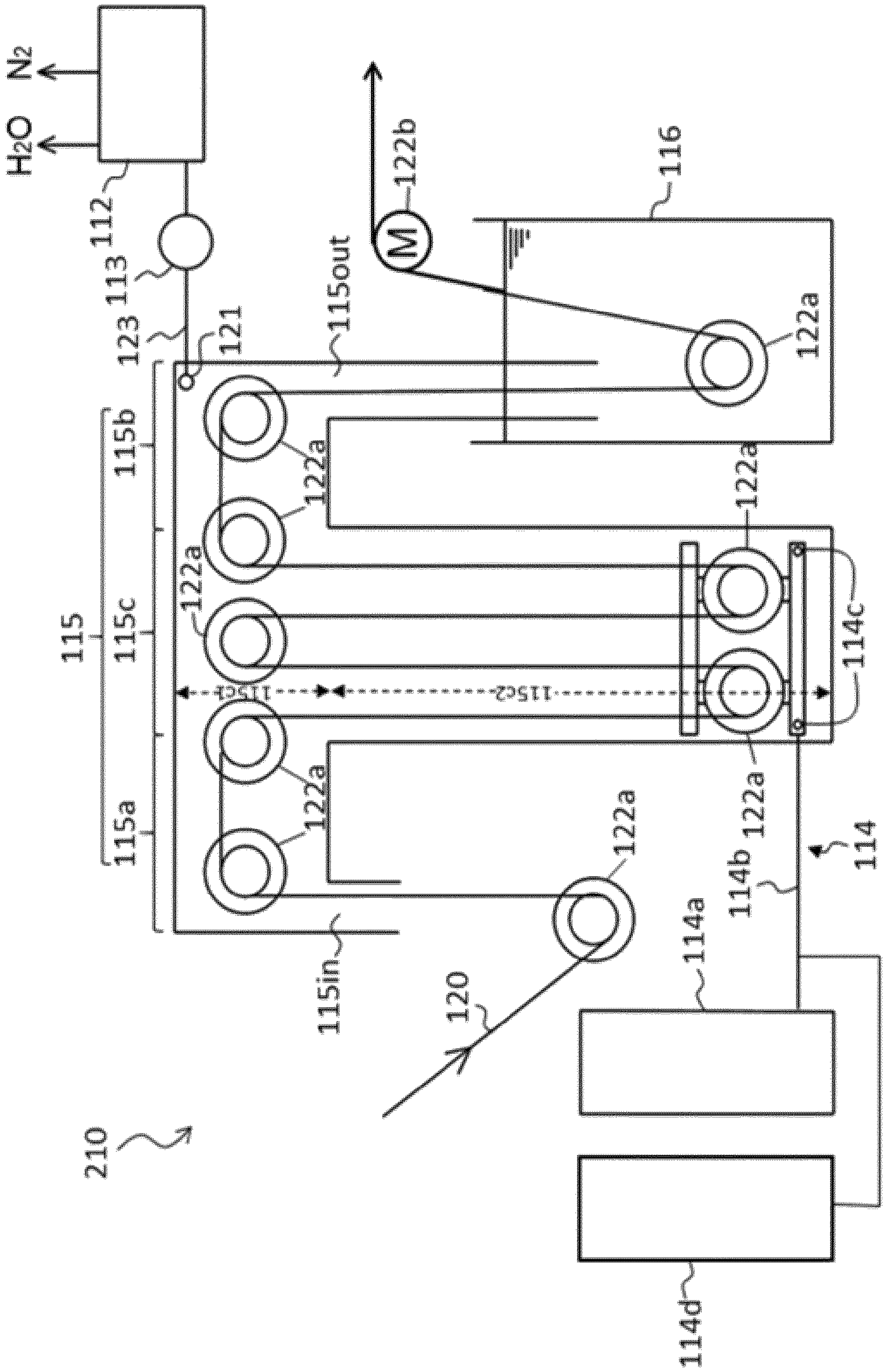
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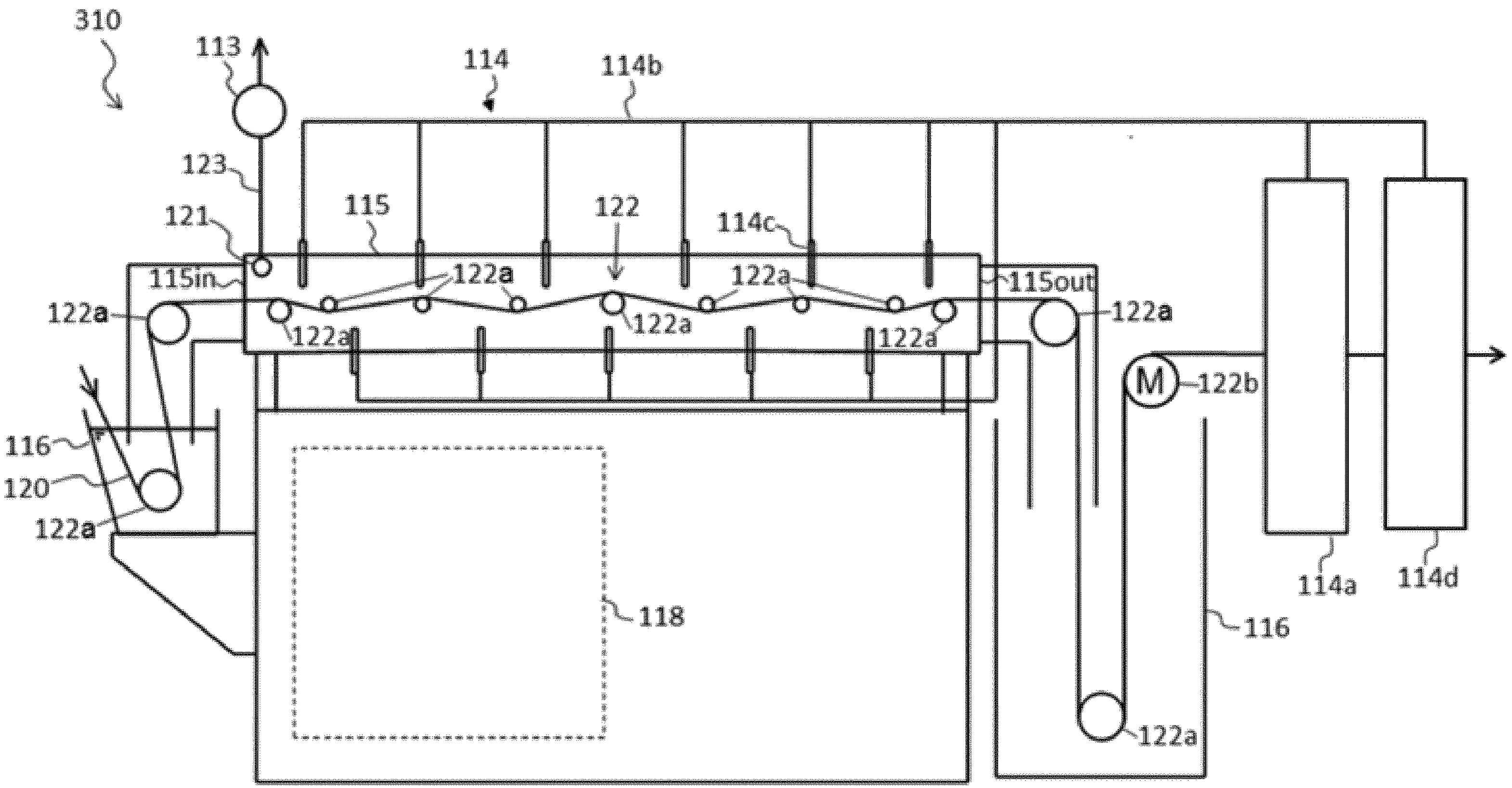
Figure 7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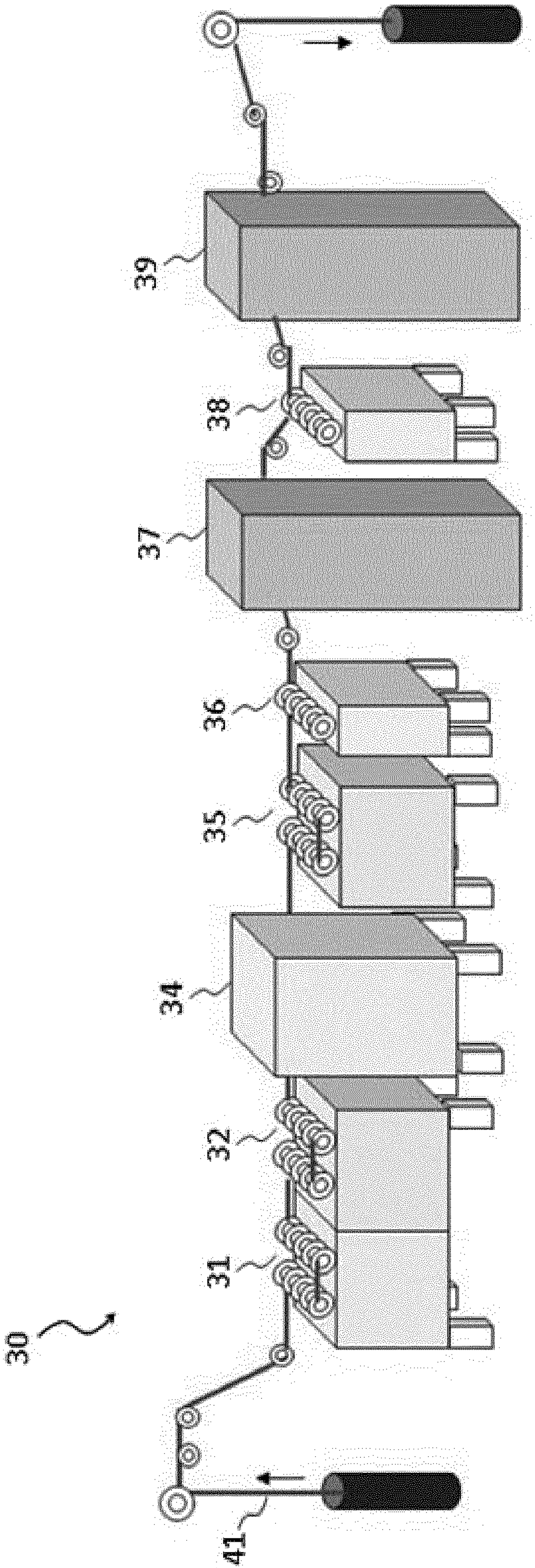

Figure 8

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2017/003473

A. CLASSIFICATION OF SUBJECT MATTER
C23C8/12(2006.01)i, *A44B19/00*(2006.01)i, *A44B19/42*(2006.01)i, *C23C8/02*(2006.01)i

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)
C23C8/12, A44B19/00, A44B19/42, C23C8/02

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	1996-2017
Kokai Jitsuyo Shinan Koho	1971-2017	Toroku Jitsuyo Shinan Koho	1994-2017

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 61-146422 A (Sumitomo Electric Industries, Ltd.), 04 July 1986 (04.07.1986), claims; page 3, upper left column, lines 12 to 15; page 3, upper left column, line 18 to upper right column, line 16; page 4, upper left column, lines 11 to 12; page 4, lower left column, line 10 to page 5, upper left column, line 1 (Family: none)	1-5,8-9, 14-16
Y		10,13-16
A		6-7,11-12, 17-27

☒ 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 07 March 2017 (07.03.17)	Date of mailing of the international search report 21 March 2017 (21.03.17)
Name and mailing address of the ISA/ Japan Patent Office 3-4-3,Kasumigaseki,Chiyoda-ku, Tokyo 100-8915,Japan	Authorized officer Telephone No.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2017/003473

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y A	JP 2-057674 A (The Furukawa Electric Co., Ltd.), 27 February 1990 (27.02.1990), claims; page 2, lower right column, lines 2 to 14; page 3, upper left column, lines 5 to 12; examples (Family: none)	10,12-17 1-9,11,18-27
X A	WO 2014/024293 A1 (YKK Corp.), 13 February 2014 (13.02.2014), paragraphs [0036] to [0042] & US 2015/0218674 A1 paragraphs [0039] to [0045] & EP 2883971 A1 & TW 201410887 A & CN 104284990 A	1-7 8-27
X Y A	JP 4-099859 A (The Furukawa Electric Co., Ltd.), 31 March 1992 (31.03.1992), claims; page 2, upper left column, line 16 to upper right column, line 2; examples (Family: none)	8,11,14-16 10,12-17 1-7,9,18-27
Y A	WO 2011/077567 A1 (YKK Corp.), 30 June 2011 (30.06.2011), paragraphs [0093], [0099], [0126] to [0131] & US 2012/0297583 A1 paragraphs [0102], [0108], [0137] to [0142] & EP 2517593 A1 & KR 10-2012-0073374 A & CN 102665473 A	10,12-17 1-9,11,18-27
X A	JP 62-114829 A (Hitachi Cable Ltd.), 26 May 1987 (26.05.1987), page 2, upper right column, lines 6 to 12; examples; drawings (Family: none)	18 1-17,19-27
X A	JP 56-006324 A (Fujikura Electric Wire Corp.), 22 January 1981 (22.01.1981), claims; example 2; fig. 2 (Family: none)	18-20 1-17,21-27
X A	JP 4-337059 A (Nippon Steel Corp.), 25 November 1992 (25.11.1992), claims; paragraph [0005] (Family: none)	18,21-24,27 1-17,19-20, 25-26
A	JP 63-241132 A (Nikko Aen Kabushiki Kaisha), 06 October 1988 (06.10.1988), a whole article & US 5141782 A & EP 269006 A2 & DE 3781375 A & DE 3781375 T & AU 1413288 A & KR 10-1992-0004503 B & AU 595700 B	1-27

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2017/003473

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 4-028886 A (The Furukawa Electric Co., Ltd.), 31 January 1992 (31.01.1992), a whole article (Family: none)	1-27
A	JP 2013-249522 A (Hitachi Cable Ltd.), 12 December 2013 (12.12.2013), a whole article & US 2013/0323532 A1 & CN 103451689 A	1-27

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- JP 2014205871 A **[0004] [0005]**