

DESCRIPTION

Title of Invention

COATED METAL PLATE

5 Technical Field

[0001] The present invention relates to a coated metal sheet.

Background Art

[0002] Stainless steel sheets with designability enhanced by etching, coloring, surface
10 treatment, or the like are used, for example, for door materials, control panels, and so forth
for elevators. Such stainless steel sheets are required to have a less tendency to be stained
with fingerprints and the like, high stain resistance, high scratch resistance, and so forth.
Accordingly, a coating film consisting of resin, wax, oil, or the like is commonly formed on
such a stainless steel sheet.

15 [0003] If a coating film consisting of resin is formed on the surface of a stainless steel
sheet, however, the coating film undergoes cracking, whitening, or the like through
temporal change, frequently leading to deterioration of the designability. Moreover,
re-coating is needed on regular basis for wax and oil.

[0004] Consideration has thus been made on forming a coating film consisting of an
20 inorganic material on the surface of a stainless steel sheet (for example, PTL 1). Coating
films consisting of an inorganic material have advantages of less temporal change and high
hardness.

Citation List

25 Patent Literature

[0005]

PTL 1

Japanese Patent Application Laid-Open No. 2009-1685

Summary of Invention

5 Technical Problem

[0006] If such a coating film consisting of an inorganic material is thin, however, light reflected on the surface of the metal sheet and light reflected on the surface of the coating film tend to interfere with each other, and hence color unevenness, coloring, or the like (hereinafter, also referred to as "interference patterns") is likely to occur. On the other hand, forming a thick coating film is likely to lead to loss of the texture derived from the metal sheet (such as gloss), and thus to deterioration of the designability. Although inclusion of an aggregate in a coating film is contemplated to prevent generation of interference patterns, however, such inclusion is likely to lower the transparency of the coating film and to lead to deterioration of the designability, similarly.

15 [0007] The present invention has been made in view of such circumstances. Specifically, an object of the present invention is to provide a coated metal sheet which is superior in stain resistance, does not cause interference patterns, and is superior in designability.

20 Solution to Problem

[0008] The present invention provides the following coated metal sheet.

[1] A coated metal sheet, comprising:

a metal sheet; and

a coating film formed on at least one surface of the metal sheet and substantially consisting of a composition represented by a compositional formula $K_2O \cdot xSiO_2$, where x satisfies $3.5 \leq x < 6.8$, wherein

an average value of coating rates per mm² at 10 arbitrary positions having the coating film is 1 to 90%.

[0009]

[2] The coated metal sheet according to [1], wherein the average value of the coating
5 rates is 3 to 80%.

[3] The coated metal sheet according to [1] or [2], wherein
the coating film consists of a plurality of films in a form of islands, and
an average maximum width of the films is 500 μm or smaller.

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Advantageous Effects of Invention

[0010] The present invention can provide a coated metal sheet which is superior in stain resistance, does not cause interference patterns, and is superior in designability.

15 Brief Description of Drawings

[0011]

FIG. 1A shows an SEM image of a coated metal sheet produced in Example (No. 4), and FIG. 1B shows a binarized image of the Si distribution of the region determined by EDS;

20 FIG. 2A shows an SEM image of a coated metal sheet produced in Example (No. 5), and FIG. 2B shows a binarized image of the Si distribution of the region determined by EDS;

FIG. 3A shows an SEM image of a coated metal sheet produced in Example (No. 8), and FIG. 3B shows a binarized image of the Si distribution of the region determined by
25 EDS; and

FIG. 4A shows an SEM image of a coated metal sheet produced in Example (No. 9),

and FIG. 4B shows a binarized image of the Si distribution of the region determined by EDS.

Description of Embodiments

5 [0012] The present invention relates to a coated metal sheet including: a metal sheet; and a coating film formed on the metal sheet in a discontinuous manner. The coated metal sheet can be applied, for example, to door materials and control panels for elevators, outer panels for home appliances, furniture and furnishings, and building materials.

[0013] As described above, consideration has been made on forming a coating film
10 consisting of an inorganic material on the surface of a metal sheet for the purpose of enhancing the stain resistance or the like of a metal sheet, and so forth. However, forming a relatively thin coating film on the surface of a metal sheet is likely to result in generation of interference patterns. Forming a thick coating film, on the other hand, is likely to deteriorate the designability of the metal sheet. For conventional coated metal sheets, a
15 coating film with uniform thickness is evenly formed on the surface for stain resistance or the like.

[0014] The present inventors found, in contrast, that a coating film formed in a discontinuous manner less causes interference patterns, and further found that a coating film substantially consisting of a composition represented by the compositional formula
20 $K_2O \cdot xSiO_2$ ($3.5 \leq x < 6.8$) can provide sufficient stain resistance, even if the coating film is discontinuous.

[0015] The mechanism that stain resistance is developed even if the coating film covering the metal sheet is discontinuous is inferred as follows. In the coating film consisting of the above composition, a trace amount of potassium is dissolved out on the
25 surface. Potassium ions then attract moisture in the atmosphere through hydration therewith. As a result, not only regions with the coating film formed but also regions in a

gap of the coating film, in other words, regions where the metal sheet is exposed are covered with a thin water film. Therefore, even when an oil stain of sebum, oil-based ink, or the like attaches to the surface of the coated metal sheet, the stain floats on the water film and can be easily removed by wiping or the like.

5 [0016] In most cases, it becomes difficult with time to remove a stain attaching to the surface of a coated metal sheet because some of the components of the stain are impregnated into the coating film or the metal sheet. In the coated metal sheet according to the present invention, in contrast, a water film with a sufficient thickness is present on the surface, which makes the permeation of the stain components into the coated metal
10 sheet difficult. In addition, the high hydrophilicity of the coating film facilitates the permeation of water into a space between the surface of the coated metal sheet and the stain. Therefore, stains attaching to the surface of the coated metal sheet can be peeled off, for example, by wiping with a damped cloth.

[0017] The coating film may be formed only on one surface or on both surfaces of the
15 metal sheet. The coating film may be formed only in some regions of the metal sheet, or in the entire region of one surface or both surfaces of the metal sheet.

[0018] Here, the average value of coating rates per mm^2 at 10 arbitrary positions having the coating film (hereinafter, also referred to as "average coating rate") is 1 to 90%, preferably 3 to 80%, more preferably 10 to 80%, and even more preferably 15 to 80%. If
20 the average coating rate is within the range, interference patterns are less likely to be generated and development of stain resistance is facilitated. The shape of each of the regions (1 mm^2) to determine coating rates is not limited and may be any shape, for example, a rectangle such as a square and an oblong square, or a circle; however, the shape is typically a rectangle. The average coating rate is determined in the following manner.

25 [0019] Ten arbitrary positions (regions of 1 mm^2) in regions with the coating film formed therein are subjected to SEM (scanning electron microscopy)/EDS (energy dispersive

X-ray spectrometry) to determine Si element distribution. Subsequently, the Si distribution images acquired are binarized by using image processing software. In the binarization, regions with any increase in Si from a reference Si detection value in a part without the coating film formed therein (metal sheet) are assumed as regions with the coating film for processing. From each of the resulting binarized images, the number of pixels in regions with increase in Si (regions with the coating film) is obtained, which is divided by the total number of pixels to calculate the coating rate. The average value of the coating rates is used as the average coating rate.

[0020] Here, the coating film preferably consists of a plurality of films in a form of islands. The films in a form of islands refer to films formed in a discontinuous manner and separated to each other. Such films in a form of islands are likely to be formed if the average coating rate is 50% or lower. In typical cases, the peripheral length of each film is 1,600 μm or smaller. The shape of each film and intervals between films are not limited. The plurality of films formed may be uniform in shape or non-uniform in shape.

The plurality of films may be formed at uniform intervals or at non-uniform intervals. However, the plurality of films is preferably formed on the metal sheet with a generally uniform density. If the films are formed with a biased formation density, the above-described effects may be insufficient. If the area of each film is excessively large, the presence or absence of a film is visually noticeable. For these reasons, in the case that the coating film consists of a plurality of films in a form of islands, the average maximum width of the films is preferably 500 μm or smaller, and more preferably 10 to 200 μm . The maximum width of each film can be determined from the above-described binarized image, and the average of the maximum widths for 10 arbitrary films is used as the average maximum width.

[0021] The average thickness of the coating film is preferably 0.05 to 3 μm , and more preferably 0.1 to 0.6 μm . If the average thickness of the coating film is 0.05 μm or larger,

it is easy to achieve the above-described effect sufficiently. If the average thickness of the coating film is 3 μm or smaller, the visual light transmission of the coating film is sufficiently high, and the texture derived from the metal sheet is less likely to be deteriorated. To determine the average thickness of the coating film, the coated metal sheet is arbitrarily cut out and the cross-section is observed. Specifically, a test piece cut out of the coated metal sheet is embedded in resin, from which an appropriate cross-section is then produced by polishing or the like, and ion milling or the like is further performed for the cross-section to produce a cross-section for precise observation. Ten arbitrary positions with the coating film are observed through SEM or TEM, and the average of thicknesses at the 10 positions is used as the average thickness.

[0022] Here, the metal sheet in the coated metal sheet according to the present invention is not limited, and, for example, austenitic stainless steel such as SUS304 and SUS316, or ferritic stainless steel such as SUS430 can be used. For applications requiring mechanical strength, it is preferred to use a material made of austenitic or ferritic stainless steel hardened through cold rolling, a sheet of martensitic stainless steel such as SUS410 and SUS420, or a sheet of precipitation-hardened stainless steel such as SUS631. In addition to stainless steel sheets, copper, carbon steel, iron-nickel alloy, various plated steel sheets, and aluminum sheets may be used.

[0023] These metal sheets may have been subjected to surface processing according to a conventional method, for example, smooth surface finish such as BA finish and mirror finish, polishing to give linear patterns such as HL finish for designability and functionality, polishing to give curved patterns such as vibration polishing, embossing to give dots, or coloring with various techniques such as oxidation coloring and coloring by sputtering.

[0024] The coating film substantially consists of a composition represented by the compositional formula $\text{K}_2\text{O} \cdot x\text{SiO}_2$ ($3.5 \leq x < 6.8$), and can be a film obtained by applying a mixed solution of potassium silicate ($\text{K}_2\text{O} \cdot n\text{SiO}_2$ ($2 \leq n \leq 4$)) and colloidal silica (SiO_2) and

drying the mixed solution. The compositional formula $K_2O \cdot xSiO_2$ represents not the state of the elements in the coating film but the ratio of the constituent elements. In the coating film, SiO_2 is typically forming siloxane bonds. On the other hand, potassium is present as potassium ions, electrically attracting and attracted by silicate ions not forming a siloxane bond. The coating film exhibits high hydrophilicity as described above, and the hydrophilicity is inferred to develop by virtue of the high hydration ability of a trace amount of potassium ions dissolved out on the surface of the coating film and the hydrophilicity of silanol groups.

[0025] The ratio of silicon oxide (SiO_2) to potassium oxide (K_2O), which is represented by x in the above compositional formula, is required to be 3.5 or higher and lower than 6.8; however, the ratio is preferably 3.8 or higher and 5.2 or lower. If the value represented by x is lower than 3.5, potassium ions are excessively dissolved out on the surface of the coating film. The potassium ions dissolved out tend to react with carbon dioxide in the atmosphere to precipitate as carbonate, which is the phenomenon of efflorescence. Further, if the value represented by x is lower than 3.5, formation of the coating film is likely to be insufficient, and the average coating rate attained may be out of a desired range. If the value represented by x is 6.8 or higher, on the other hand, it is required to mix a large amount of colloidal silica in forming the coating film. As a result, the film-forming capability is lowered, and the average coating rate attained may be out of a desired range or insufficient strength for films may be provided. The composition of the coating film can be adjusted, for example, through the mixing ratio between potassium silicate and colloidal silica. The composition of the coating film can be confirmed by EDS, XRF, EPMA, or the like, and the state of chemical bonding of Si can be confirmed by XPS, IR, or the like.

[0026] To obtain the coating film, a mixed solution of potassium silicate and colloidal silica is applied onto a metal sheet to give the above-described average coating rate by using a given method, and dried. The potassium silicate and colloidal silica to form the

coating film may be each a common reagent or an industrial chemical. Examples of commercially available products of potassium silicate include "Potassium Silicate A" and "Potassium Silicate 2K" produced by Nippon Chemical Industrial CO., LTD.; "Potassium Silicate No. 2" produced by Fuji Kagaku CORP.; and "SNOWTEX K2" produced by Nissan Chemical Corporation. Examples of commercially available products of colloidal silica include "ADELITE AT" produced by ADEKA CORPORATION, "SNOWTEX" produced by Nissan Chemical Corporation, and "SILICADOL" produced by Nippon Chemical Industrial CO., LTD.

[0027] To the mixed solution to form the coating film, a solvent, a leveling agent, a defoamer, and so forth may be added, as necessary, together with potassium silicate and colloidal silica. The solid content concentration of the mixed solution to form the coating film is appropriately selected in accordance with the method of forming the coating film, and is preferably in a relatively low range, preferably 1 to 10mass%, to form the film in a discontinuous manner and control the film thickness to be small.

[0028] To apply the mixed solution to form the coating film, any method may be used which is capable of forming the coating film with the average coating rate falling within the above-described range. For example, a spray gun, an electrostatic atomizer, an inkjet apparatus, or a gravure roll transfer apparatus can be used for the method for applying the mixed solution. In the case that the coating film is formed by using a spray gun or an electrostatic atomizer, it is preferred to take some measures for adjustment of the average coating rate, for example, to reduce the discharge nozzle diameter of the spray gun or electrostatic atomizer or to adjust the atomization pressure.

[0029] To dry the mixed solution, any method may be used which is capable of sufficiently volatilizing the solvent. For example, drying may be performed at normal temperature, and heating may be performed to 80 to 300°C. Heating promotes drying of water, as the solvent, and film formation is promoted. Further, heating to 200°C or higher

can promote formation of siloxane bonds to provide a robust coating film in a short period of time. However, care should be taken in heating not to cause discoloration (temper color) due to oxidation of the raw material sheet. The drying time is typically 10 to 30 minutes with heating, and a drying time of 24 hours is enough even in drying at normal temperature.

Examples

[0030] Hereinafter, the present invention will be described in detail with reference to Examples; however, the present invention is not limited to Examples.

10 [0031] Coated metal sheets were produced by using the following methods, and surface stain resistance and the presence or absence of interference patterns were determined for each of the coated metal sheets. The metal sheets used were metal sheets A to E listed in Table 1.

[0032] [Table 1]

Metal sheet	Steel species	Surface finish
A	SUS316	vibration polishing
B	SUS304	hairline polishing
C	SUS430	shot blasting
D	SUS316	vibration polishing + coloring by sputtering
E	SUS304	hairline polishing + oxidation coloration

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[0033] [Production of coated metal sheets]

Potassium silicate (product name: Potassium Silicate No. 2, $K_2O \cdot nSiO_2$ ($n = 3.61$), produced by Fuji Kagaku CORP., or product name: Potassium Silicate No. 1, $K_2O \cdot nSiO_2$ ($n = 2.04$), produced by Fuji Kagaku CORP.) and colloidal silica (product name: SILICADOL, produced by Nippon Chemical Industrial CO., LTD.) were mixed together with mass ratios in terms of solid contents as shown in Table 2 to afford mixed solutions. The mixed

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solutions were each applied onto one of metal sheets A to E by using an atomization spray to give an average coating rate as shown in Table 2. Thereafter, the resultants were dried at 250°C for 20 minutes to afford coating films. The average thickness of each of the coating films obtained was 0.6 μm or smaller. The average thicknesses were determined as follows. First, a test piece was cut out of a coated metal sheet, and the test piece cut out was embedded in resin, from which a cross-section was then produced by polishing. Further, ion milling or the like was performed for the cross-section to produce a cross-section for precise observation, which was observed through SEM. Thickness was measured for 10 arbitrary positions with a coating film, and the average of the thicknesses was used as the average thickness.

[0034] Average coating rates per mm² were determined as follows.

First, elemental distribution was determined for Si, a primary component of each coating film, with SEM (product name: S-3700N, produced by Hitachi High-Technologies Corporation)/EDS (product name: x-act, produced by Oxford Instruments). Ten arbitrary positions (1 mm²) in regions with a coating film formed therein were subjected to the measurement. Subsequently, the Si distribution images acquired were binarized by using image processing software (Photoshop, produced by Adobe Systems Incorporated). In the binarization, regions with any increase in Si from a reference Si detection value in a part without a coating film formed therein (metal sheet) were assumed as regions with a coating film for processing. From each of the resulting binarized images, the number of pixels in regions with increase in Si (regions with a coating film) was obtained, which was divided by the total number of pixels in the regions to calculate the coating rate. The average value of the coating rates was calculated, which was used as the average coating rate. FIGS. 1 to 4 each show an SEM image and a binarized image of the Si distribution of the region determined by EDS for Nos. 4, 5, 8, and 9, respectively.

[0035] [Evaluation]

An oil-based ink removal test (stain resistance) and determination of the presence or absence of interference patterns were performed for each of the coated metal sheets obtained in Examples and Comparative Examples. The results are shown in Table 2.

[0036] (1) Oil-based ink removal test (stain resistance)

5 On each of the coated metal sheets obtained in Examples and Comparative Examples, an image was drawn with a permanent marker (product name: magic INK (R) No. 700 black, produced by Teranishi Chemical Industry Co., Ltd.). The oil-based ink on the drawing portion was wiped with a cloth (product name: BEMCOT M3-II, produced by Asahi Kasei Corporation) impregnated with water 1 minute and 1 hour after the drawing,
10 and the state of a trace of the oil-based ink after wiping with a damped cloth was evaluated. Evaluation of a trace of the oil-based ink was based on the following criteria.

A: without any trace (100% of removal)

B: with a very slight trace (90% or higher and lower than 100% of removal)

C: with a trace (5% or higher and lower than 90% of removal)

15 D: with almost no removal (lower than 5% of removal)

[0037] (2) Checking interference patterns

The presence or absence of interference patterns was visually evaluated under a standard light source. The standard light source apparatus used was one with product name: Macbeth Judge II, produced by X-Rite Inc. TL84 was used as reference light.

20 Evaluation of interference patterns was based on the following criteria.

A: without any interference pattern (influence on design: none)

B: with a few interference patterns (influence on design: mild)

C: with significantly many interference patterns (influence on design: significant)

[0038] [Table 2]

No.	Metal sheet	Coating film					Oil-based ink removal test		Interference patterns	Remarks	
		Potassium silicate (g)	Colloidal silica (g)	x ^{*1} (mol)	Average coating rate (%)	Shape of coating film (average maximum width)	After 1 minute	After 1 hour			
1	A			-	0	-	D	D	A		Comparative Example
2	A	100 ^{*2}	13.3	4.3	1	Films in islands (12 μm)	C	C	A		Example
3	A	100 ^{*2}	13.3	4.3	3	Films in islands (16 μm)	A	C	A		Example
4	A	100 ^{*2}	13.3	4.3	6	Films in islands (34 μm)	A	C	A		Example
5	A	100 ^{*2}	13.3	4.3	13	Films in islands (62 μm)	A	C	A		Example
6	A	100 ^{*2}	13.3	4.3	17	Films in islands (76 μm)	A	B	A		Example
7	A	100 ^{*2}	13.3	4.3	21	Films in islands (95 μm)	A	B	A		Example
8	A	100 ^{*2}	13.3	4.3	33	Films in islands (147 μm)	A	A	A		Example
9	A	100 ^{*2}	13.3	4.3	53	Discontinuous film	A	A	A		Example
10	A	100 ^{*2}	13.3	4.3	77	Discontinuous film	A	A	A		Example
11	A	100 ^{*2}	13.3	4.3	86	Discontinuous film	A	A	B		Example
12	A	100 ^{*2}	13.3	4.3	95	Discontinuous film	A	A	C		Comparative Example
13	A	100 ^{*2}	13.3	4.3	100	Continuous film	A	A	C		Comparative Example
14	A	100 ^{*2}	1.8	3.7	18	Films in islands (81 μm)	A	B	A		Example
15	A	100 ^{*2}	57.7	6.6	26	Films in islands (113 μm)	A	A	A		Example
16	A	100 ^{*3}	55.1	3.2	48	Films in islands (370 μm)	A	A	A	with efflorescence	Comparative Example
17	A	100 ^{*2}	63.5	6.9	65	Discontinuous film	-	-	-	failure in film formation	Comparative Example
18	B	100 ^{*2}	13.3	4.3	7	Films in islands (48 μm)	A	C	A		Example
19	C	100 ^{*2}	13.3	4.3	40	Films in islands (164 μm)	A	A	A		Example
20	D	100 ^{*2}	13.3	4.3	75	Discontinuous film	A	A	A		Example
21	E	100 ^{*2}	13.3	4.3	10	Films in islands (55 μm)	A	A	A		Example

^{*1} value of x in K₂O·xSiO₂ ^{*2} with Potassium Silicate No. 2 ^{*3} with Potassium Silicate No. 1

[0039] As demonstrated in Table 2, when a coating film was not formed (average coating rate : 0%), a trace of oil-based ink could not be removed in the oil-based ink removal test (No. 1). With an average coating rate of 1% or higher, in contrast, oil-based ink was successfully removed in any case (Nos. 2 to 16, and 18 to 21). With an average coating
5 rate of 95% or higher, however, interference patterns were generated (Nos. 12 and 13).

[0040] When x in the compositional formula $K_2O \cdot xSiO_2$ was lower than 3.5 for the composition constituting a coating film, efflorescence occurred and the designability of the coated metal sheet was deteriorated (No. 16). When x was 6.8 or higher, on the other hand, film formation failed (No. 17).

10 [0041] The present application claims priority to Japanese Patent Application No. 2016-181356 filed on September 16, 2016. The contents of the specification and drawings of the application are totally incorporated herein by reference.

Industrial Applicability

15 [0042] The coated metal sheet according to the present invention is superior in stain resistance, does not cause interference patterns, and is superior in designability. Accordingly, the coated metal sheet can be applied, for example, to door materials and control panels for elevators, outer panels for home appliances, furniture and furnishings, and various interior building materials.

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CLAIMS

1. A coated metal sheet, comprising:

a metal sheet; and

5 a coating film formed on at least one surface of the metal sheet and substantially consisting of a composition represented by a compositional formula $K_2O \cdot xSiO_2$, where x satisfies $3.5 \leq x < 6.8$, wherein

an average value of coating rates per mm^2 at 10 arbitrary positions having the coating film is 1 to 90%.

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2. The coated metal sheet according to claim 1, wherein the average value of the coating rates is 3 to 80%.

3. The coated metal sheet according to claim 1 or 2, wherein

15 the coating film consists of a plurality of films in a form of islands, and an average maximum width of the films is 500 μm or smaller.