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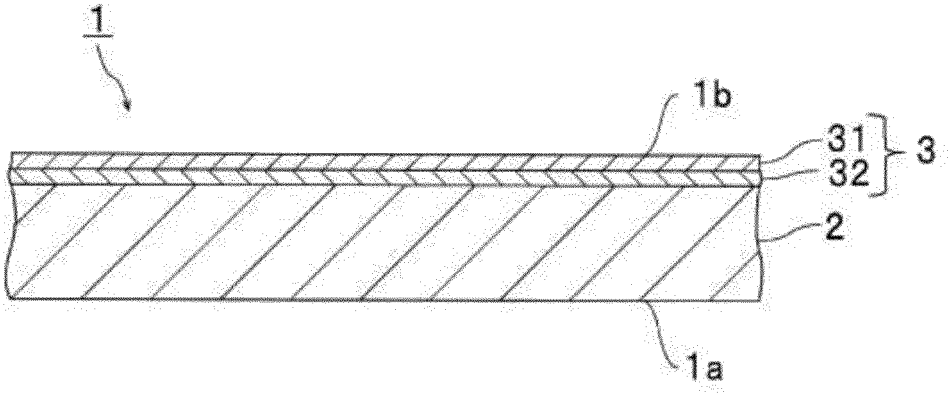
(54) **LAYERED SHEET**

(57) Provided is a layered sheet which can provide a metallic luster favorably while maintaining design of a surface of a carbonaceous substrate and can suppress a change in color tone. The layered sheet according to the present invention includes a carbonaceous substrate, a metal layer disposed on a surface of the carbonaceous substrate, and a metal oxide layer disposed on a surface of the metal layer opposite to the carbonaceous substrate.

[FIG. 1.]



EP 3 733 400 A1

Description

TECHNICAL FIELD

[0001] The present invention relates to a layered sheet using a carbonaceous substrate.

BACKGROUND ART

[0002] The carbonaceous substrate is lightweight and has excellent strength. Thus, the carbonaceous substrate is used in various fields such as the aviation field, space field, motorcycle field, automobile field, building field, civil engineering field, sports field and leisure field.

[0003] The surface of the carbonaceous substrate is generally black. In order to enhance the design of the carbonaceous substrate, the carbonaceous substrate may be colored.

[0004] A carbonaceous substrate subjected to coloring treatment is disclosed in Patent Document 1 below. Patent Document 1 below discloses carbon fibers (colored carbonaceous substrate) having a lightness L* of 20 or more in an L*a*b* color system measured using a reflection spectrum in a visible region at an incident angle of 60 degrees and a light receiving angle of 45 degrees. In Patent Document 1, a paint containing a pigment or a dye is used for the coloring treatment.

Related Art Document

Patent Document

[0005] Patent Document 1: JP 2010-229587A

SUMMARY OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0006] When a paint containing a pigment or dye is applied to the surface of a carbonaceous substrate, a colored layer is formed on the surface of the carbonaceous substrate. As a result, the luster of the carbonaceous substrate may be impaired at the portion where the surface of the carbonaceous substrate is covered with the colored layer. The unique design of the carbonaceous substrate may be impaired.

[0007] By forming a metal layer on the surface of the carbonaceous substrate, a metallic luster may be imparted. However, simply forming the metal layer may change the color of the metal layer and change a color tone on the metal layer side. When the metal layer is exposed to a high temperature or exposed to the atmosphere for a long period of time, the color of the metal layer may further change, and the color tone on the metal layer side may further change.

[0008] An object of the present invention is to provide a layered sheet which can provide a metallic luster favorably while maintaining design of a surface of a carbonaceous substrate and can suppress a change in color tone.

MEANS FOR SOLVING THE PROBLEMS

[0009] According to a broad aspect of the present invention, there is provided a layered sheet including a carbonaceous substrate, a metal layer disposed on a surface of the carbonaceous substrate, and a metal oxide layer disposed on a surface of the metal layer opposite to the carbonaceous substrate.

[0010] In a specific aspect of the layered sheet according to the present invention, a metal element contained in the metal layer is titanium, silver, or aluminum.

[0011] In a specific aspect of the layered sheet according to the present invention, an average thickness of the metal oxide layer is 3 nm or more.

[0012] In a specific aspect of the layered sheet according to the present invention, the average thickness of the metal oxide layer is less than 40 nm.

[0013] In a specific aspect of the layered sheet according to the present invention, a metal oxide contained in the metal oxide layer is TiO_2 or SiO_2.

EFFECT OF THE INVENTION

[0014] The present invention can provide a layered sheet which can provide a metallic luster favorably while maintaining design of a surface of a carbonaceous substrate and can suppress a change in color tone.

BRIEF DESCRIPTION OF DRAWINGS

[0015] [Fig. 1] Fig. 1 is a schematic cross-sectional view showing a layered sheet according to a first embodiment of the present invention.

MODE FOR CARRYING OUT THE INVENTION

[0016] Hereinafter, the present invention will be described in detail.

[0017] A layered sheet according to the present invention is a layered sheet including a carbonaceous substrate, a metal layer disposed on a surface of the carbonaceous substrate, and a metal oxide layer disposed on a surface of the metal layer opposite to the carbonaceous substrate. In the layered sheet according to the present invention, a color tone may be changed on the metal layer and the metal oxide layer side. Thus, in this specification, a layer in which the metal layer and the metal oxide layer are stacked may be referred to as a color tone adjusting layer. The layered sheet according to the present invention includes a carbonaceous substrate and a color tone adjusting layer disposed on a surface of the carbonaceous substrate. In the layered sheet according to the present invention, the color tone adjusting layer includes a metal layer (second color tone adjusting layer) on the carbonaceous substrate side, and a metal oxide layer (first color tone adjusting layer) on the side opposite to the carbonaceous substrate side. In the layered sheet according to the present invention, the carbonaceous substrate, the metal layer, and the metal oxide layer are stacked in this order. The layered sheet according to the present invention has a first surface and a second surface on the side opposite to the first surface. In the layered sheet according to the present invention, the carbonaceous substrate is disposed on a first surface side of the layered sheet, and the color tone adjusting layer is disposed on a second surface side of the layered sheet. In the layered sheet according to the present invention, the carbonaceous substrate is disposed on the first surface side of the layered sheet, and the metal oxide layer (first color tone adjusting layer) is disposed on the second surface side of the layered sheet.

[0018] According to the above configuration of the present invention, a metallic luster can be provided favorably while maintaining design of a surface of a carbonaceous substrate, and in addition, a change in color tone can be suppressed.

[0019] The carbonaceous substrate may have a luster or may have a surface pattern due to an uneven shape. The surface of the carbonaceous substrate is generally black. In the present invention, a metallic luster can be favorably provided without impairing the surface pattern of the carbonaceous substrate. Moreover, in the present invention, a change in color tone on the metal layer side can be suppressed.

[0020] In the layered sheet according to the present invention, since the metal layer is provided, the metallic luster can be favorably imparted to the layered sheet. In the layered sheet according to the present invention, since the metal oxide layer is provided, the change of the color of the metal layer can be suppressed, and the change in color tone on the metal layer side of the layered sheet can be suppressed. Moreover, in the layered sheet according to the present invention, since both the metal layer and the metal oxide layer are provided, a metallic luster can be provided favorably while maintaining design of the surface of the carbonaceous substrate, and in addition, the change in color tone on the metal layer side of the layered sheet can be suppressed.

[0021] In the layered sheet according to the present invention, since the metal oxide layer is provided, a color tone of the layered sheet can be adjusted.

[0022] Further, in the present invention, the angular dependence of color tone can be imparted to the layered sheet. Therefore, the color tone can be changed depending on an angle at which the layered sheet is viewed.

[0023] A mechanism in which the color tone such as a metallic luster is imparted to the layered sheet according to the present invention is considered a cause of (1) the effect of the color (reflection spectrum) of the metal layer, (2) the effect of light absorption by the metal oxide layer, and (3) the effect of optical interference generated by the metal layer and the metal oxide layer. The mechanism in which the color tone such as a metallic luster is imparted to the layered sheet according to the present invention is not limited to the above (1) to (3).

[0024] Simply forming the metal layer on the surface of the carbonaceous substrate may change the color of the metal layer and change the color tone on the metal layer side of the layered sheet. When the metal layer is exposed to high temperatures or exposed to the atmosphere for a long period of time, the color of the metal layer may further change, and the color tone on the metal layer side of the layered sheet may further change. The present inventor has found that the change in color tone on the metal layer side of the layered sheet can be suppressed by daringly forming the metal oxide layer on the surface of the metal layer. According to the above configuration of the present invention, the change in color tone on the metal layer side of the layered sheet can be suppressed.

[0025] A color tone of the second surface of the layered sheet can be adjusted by changing an average thickness of the metal oxide layer. Since the color tone can be precisely adjusted by finely adjusting the thickness of the metal oxide layer, the color tone suitable for user's purpose can be imparted to the layered sheet.

[0026] In the layered sheet according to the present invention, the color tone adjusting layer is preferably a layer having a property that makes the color tone of the second surface of the layered sheet different from the color tone of the surface

of the carbonaceous substrate. That is, in the layered sheet according to the present invention, the color tone adjusting layer is preferably a layer that imparts the color tone different from the color tone of the surface of the carbonaceous substrate to the second surface of the layered sheet.

[0027] The color tone adjusting layer may have or may not have optical transparency. From the viewpoint of further maintaining design of the surface of the carbonaceous substrate, the color tone adjusting layer preferably has optical transparency. From the viewpoint of effectively imparting a metallic luster to the layered sheet, the color tone adjusting layer preferably does not have optical transparency.

[0028] The metal layer may have or may not have optical transparency. From the viewpoint of further maintaining design of the surface of the carbonaceous substrate, the metal layer preferably has optical transparency. From the viewpoint of more effectively imparting a metallic luster to the layered sheet, the metal layer preferably does not have optical transparency.

[0029] The metal oxide layer may have or may not have optical transparency. From the viewpoint of further maintaining design of the surface of the carbonaceous substrate, the metal oxide layer preferably has optical transparency.

[0030] The color tone adjusting layer (the metal layer, the metal oxide layer) having optical transparency means that the surface pattern (uneven shape) of the carbonaceous substrate is visually recognized through the color tone adjusting layer (the metal layer, the metal oxide layer) on the second surface of the layered sheet. When the color tone adjusting layer (the metal layer, the metal oxide layer) has optical transparency, it is preferable that the surface pattern (uneven shape) of the carbonaceous substrate be visually recognized through the color tone adjusting layer (the metal layer, the metal oxide layer) on the second surface of the layered sheet, and it is preferable that a luster of the carbonaceous substrate be visually recognized through the color tone adjusting layer (the metal layer, the metal oxide layer).

[0031] The metal oxide layer having optical transparency means that the surface pattern (uneven shape) of the carbonaceous substrate or the metal layer is visually recognized through the metal oxide layer on the second surface of the layered sheet. When the metal oxide layer has optical transparency, it is preferable that the surface pattern (uneven shape) of the carbonaceous substrate or the metal layer be visually recognized through the metal oxide layer on the second surface of the layered sheet, and it is preferable that a luster of the carbonaceous substrate or the metal layer be visually recognized through the metal oxide layer.

[0032] Since the layered sheet according to the present invention has the above performance, the layered sheet is suitably used as a decorative substrate sheet.

[0033] Hereinafter, specific embodiments of the present invention will be described with reference to the drawings.

[0034] Fig. 1 is a schematic cross-sectional view showing a layered sheet according to a first embodiment of the present invention.

[0035] A layered sheet 1 shown in Fig. 1 includes a carbonaceous substrate 2 and a color tone adjusting layer 3. The color tone adjusting layer 3 includes a metal oxide layer (first color tone adjusting layer) 31 and a metal layer (second color tone adjusting layer) 32. The layered sheet 1 includes the carbonaceous substrate 2, the metal oxide layer 31, and the metal layer 32. The metal layer 32 is disposed between the carbonaceous substrate 2 and the metal oxide layer 31. The metal layer 32 is disposed on a surface of the carbonaceous substrate 2. The metal oxide layer 31 is disposed on a surface of the metal layer 32 on the side opposite to the carbonaceous substrate 2.

[0036] The metal oxide layer 31 preferably has optical transparency.

[0037] The layered sheet 1 has a first surface 1a and a second surface 1b on the side opposite to the first surface 1a.

[0038] The carbonaceous substrate 2 is disposed on a first surface side 1a of the layered sheet 1. The second color tone adjusting layer 3 is disposed on a second surface side 1b of the layered sheet 1. In the color tone adjusting layer 3, the metal oxide layer 31 is disposed on the second surface side 1b of the layered sheet 1, and the metal layer 32 is disposed on the second surface side 1b of the layered sheet 1. The carbonaceous substrate 2, the metal layer 32, and the metal oxide layer 31 are arranged in this order.

[0039] The layered sheet 1 includes one metal oxide layer 31 and one metal layer 32. Each of the metal oxide layer and the metal layer may be a single layer or a multilayer.

[0040] Hereinafter, details of the respective layers constituting a layered sheet will be described.

(Carbonaceous substrate)

[0041] The carbonaceous substrate is disposed on a first surface side of the layered sheet in the layered sheet. The material of the carbonaceous substrate is a carbonaceous material, and the carbonaceous material is generally black. One kind of the carbonaceous materials may be used alone, and two or more kinds thereof may be used in combination. The shape of the carbonaceous substrate may be a flat sheet. The carbonaceous substrate may be a woven fabric or a knitted fabric. When the shape of the carbonaceous substrate is a flat sheet, a pattern may be present on the surface of the carbonaceous substrate.

[0042] The carbonaceous substrate generally contains 90% by mass or more and 100% by mass or less of carbon atoms in 100% by mass of the carbonaceous substrate.

[0043] From the viewpoint of enhancing design of the surface of the carbonaceous substrate, the carbonaceous material is preferably carbon fiber. The carbonaceous substrate is preferably a carbon fiber substrate.

[0044] The carbon fiber substrate is preferably a carbon fiber woven fabric, a carbon fiber knitted fabric, or a carbon fiber nonwoven fabric. As the carbon fiber substrate, only one of carbon fiber woven fabric, carbon fiber knitted fabric, and carbon fiber nonwoven fabric may be used, or two or more of them may be used in combination.

[0045] The basis weight of the carbon fiber is not particularly limited, but is preferably 50 g/m^2 or more, more preferably 100 g/m^2 or more, and preferably 700 g/m^2 or less, more preferably 500 g/m^2 or less.

[0046] The filament diameter of the carbon fiber is not particularly limited, but is preferably 1 μm or more, more preferably 2 μm or more, and preferably 50 μm or less, more preferably 20 μm or less.

[0047] When the carbonaceous material is carbon fiber, the density of the carbon fiber is not particularly limited, but is preferably 1/inch or more, more preferably 2/inch or more, and preferably 50/inch or less, more preferably 20/inch or less.

[0048] When the carbonaceous substrate is a carbon fiber woven fabric, the weaving method is not particularly limited, but plain weaving or twill weaving is preferable.

[0049] When the carbonaceous substrate is a carbon fiber substrate, particularly when the carbonaceous substrate is a carbon fiber woven fabric, a carbon fiber knitted fabric, or a carbon fiber nonwoven fabric, unique design of the carbon fiber, such as an uneven shape, a pattern, and a luster can be imparted to the layered sheet. Formation of a specific color tone adjusting layer can achieve visual recognition of the unique design even if the color tone adjusting layer is disposed on the surface of the carbon fiber substrate. When the carbonaceous material is carbon fiber, a layered sheet that is lightweight and excellent in strength can be obtained. In a preferred embodiment of the present invention, from the viewpoint of remarkably expressing an uneven shape and pattern of the carbonaceous substrate, the carbon fiber substrate is preferably a carbon fiber woven fabric or carbon fiber knitted fabric.

[0050] In one embodiment of the present invention, from the viewpoint of increasing the strength of the layered sheet, the layered sheet may be made into a carbon fiber-reinforced plastic. The carbon fiber-reinforced plastic includes the layered sheet. The carbon fiber-reinforced plastic preferably includes the layered sheet and plastic. The layered sheet may be used as a material of a carbon fiber-reinforced plastic. The carbon fiber substrate may be used as a material of a carbon fiber-reinforced plastic. When the carbon fiber substrate is used as the material of the carbon fiber-reinforced plastic, unique design of the carbon fiber substrate, such as an uneven shape, a pattern, and a luster can be imparted to the carbon fiber-reinforced plastic. Formation of a specific color tone adjusting layer can achieve visual recognition of the unique design after the carbon fiber-reinforced plastic is molded even if the color tone adjusting layer is disposed on the surface of the carbon fiber substrate. Moreover, by using the carbon fiber substrate as the material of the carbon fiber-reinforced plastic, a layered sheet that is lightweight and excellent in strength can be obtained.

(Color tone adjusting layer)

[0051] The color tone adjusting layer is a layer disposed on the surface of the carbonaceous substrate. The color tone adjusting layer is disposed on a second surface side of the layered sheet in the layered sheet. The color tone adjusting layer is preferably a layer having a property that makes the color tone of the second surface of the layered sheet different from the color tone of the surface of the carbonaceous substrate.

[0052] The color tone adjusting layer includes a metal oxide layer and a metal layer disposed between the metal oxide layer and the carbonaceous substrate. The layered sheet includes a metal oxide layer and a metal layer.

[0053] From the viewpoint of favorably imparting a color to the layered sheet, the color tone adjusting layer preferably has a property that makes a spectral reflectance curve in visible light of the second surface of the layered sheet different from a spectral reflectance curve in visible light of the surface of the carbonaceous substrate.

[0054] From the viewpoint of more favorably imparting a color to the layered sheet, the metal oxide layer preferably has a property that makes the spectral reflectance curve in visible light of the second surface of the layered sheet different from the spectral reflectance curve in visible light of the surface of the carbonaceous substrate.

[0055] From the viewpoint of more favorably imparting a color to the layered sheet, the metal layer preferably has a property that makes the spectral reflectance curve in visible light of the second surface of the layered sheet different from the spectral reflectance curve in visible light of the surface of the carbonaceous substrate.

[0056] From the viewpoint of suppressing a decrease in optical transparency (for example, visible light transmittance) of the color tone adjusting layer, the color tone adjusting layer preferably does not substantially contain a pigment. From the viewpoint of suppressing a decrease in optical transparency (for example, visible light transmittance) of the color tone adjusting layer, the color tone adjusting layer preferably does not substantially contain a dye. When the color tone adjusting layer not substantially containing a pigment is formed, or when the color tone adjusting layer not substantially containing a dye is formed, unique design of the carbonaceous substrate such as an uneven shape, a surface pattern, and a luster can be effectively prevented from being impaired on the second surface of the layered sheet. Formation of the color tone adjusting layer not substantially containing both a pigment and a dye can more effectively prevent unique design of the carbonaceous substrate such as an uneven shape, a surface pattern, and a luster from being imparted

on the second surface of the layered sheet. In addition, formation of the color tone adjusting layer not substantially containing both the pigment and the dye can improve adhesion between the carbonaceous substrate and the metal layer.

[0057] The metal layer contains or does not contain a pigment. The metal layer contains or does not contain a dye. When the metal layer contains a pigment, the content of the pigment in 100% by weight of the metal layer is preferably 0.1% by weight or less, more preferably 0.01% by weight or less. When the metal layer contains a dye, the content of the dye in 100% by weight of the metal layer is preferably 0.1% by weight or less, more preferably 0.01% by weight or less.

[0058] The metal oxide layer contains or does not contain a pigment. The metal oxide layer contains or does not contain a dye. When the metal oxide layer contains a pigment, the content of the pigment in 100% by weight of the metal oxide layer is preferably 0.1% by weight or less, more preferably 0.01% by weight or less. When the metal oxide layer contains a dye, the content of the dye in 100% by weight of the metal oxide layer is preferably 0.1% by weight or less, more preferably 0.01% by weight or less.

[0059] In a color tone adjusting layer containing a pigment and a color tone adjusting layer containing a dye, generally, the optical transparency is low, and the surface of the carbonaceous substrate is hardly visually recognized. In a color tone adjusting layer containing a pigment and a color tone adjusting layer containing a dye, generally, the optical transparency is low, and the surface pattern of the carbonaceous substrate is hardly visually recognized. In the color tone adjusting layer containing the pigment and the color tone adjusting layer containing the dye, generally, a metallic luster is hardly imparted.

[0060] The metal oxide layer includes a metal oxide. The metal oxide layer preferably contains a metal oxide represented by MO_x, and is preferably a metal oxide layer represented by MO_x. M in MO_x represents an n-valent metal, and x represents a number of n/2.5 or more and n/2 or less. In MO_x, O represents oxygen. One kind of the metal oxide may be used alone, and two or more kinds thereof may be used in combination.

[0061] The metal layer includes a metal element. The metal layer may contain a small amount of oxygen atoms. However, in this case, the metal layer contains a compound represented by MO_x in which M in MO_x represents an n-valent metal, and x is greater than 0 and less than n/2.5 (preferably less than n/20). Such a metal layer containing a small amount of oxygen atoms is also called a metal layer. When the metal layer contains metals alone, the metal layer contains a compound represented by M, and M represents a metal.

[0062] One kind of the metal element contained in the metal layer may be used alone, and two or more kinds thereof may be used in combination.

[0063] When the metal oxide layer is not provided, or when a metal layer is provided instead of the metal oxide layer, the metal layer may be oxidized. When metal contained in the metal layer is oxidized, the color of the metal layer may change, and the color tone on the metal layer side of the layered sheet may change.

[0064] In the present invention, since the metal layer is provided, the metallic luster can be favorably imparted to the layered sheet. In the present invention, since the metal oxide layer is provided, the change of the color of the metal layer due to oxidation of metal can be suppressed, and the change in color tone on the metal layer side of the layered sheet can be suppressed. In the present invention, since the metal oxide layer is provided, the color tone of the layered sheet can be adjusted. In the present invention, since both the metal layer and the metal oxide layer are provided, a metallic luster can be favorably imparted to the layered sheet while maintaining design of the surface of the carbonaceous substrate, and in addition, the change in color tone can be suppressed.

[0065] When M in MO_x represents an n-valent metal and x represents a number of n/2.5 or more and less than n/2, MO_x is an incomplete oxide of metal. Such an incomplete oxide of metal is also called a metal oxide. It is better that x is as close as possible to n/2.

[0066] From the viewpoint of effectively suppressing the change in color tone on the metal layer side of the layered sheet, x is preferably n/2.5 or more, more preferably n/2.2 or more, and further preferably n/2.

[0067] When M in MO_x represents an n-valent metal and x represents a number of n/2, MO_x is a complete oxide of metal.

[0068] More preferably, M in MO_x represents an n-valent metal, and x represents a number of n/2. That is, it is more preferable that the metal oxide layer contain a complete oxide of metal. In this case, since metal contained in the metal oxide layer is not oxidized, the change of the color imparted to the layered sheet can be suppressed. Even if the metal oxide layer is exposed to high temperatures or exposed to the atmosphere for a long period of time, the change of the imparted color can be significantly suppressed.

[0069] Regarding the valence of oxygen atoms, for example, a cross section of a layer containing MO_x is subjected to elemental analysis by FE-TEM-EDX (for example, "JEM-ARM200F" manufactured by JEOL Ltd.), and x is calculated from an element ratio of M and O per area of the cross section of the layer containing MO_x, whereby the valence of oxygen atoms can be calculated.

[0070] From the viewpoint of more effectively suppressing the change in color tone on the metal layer side of the layered sheet and favorably adjusting the color tone of the layered sheet, M in MO_x is preferably silicon, zinc, silver, gold, titanium, aluminum, tin, copper, iron, molybdenum, niobium, or indium. M in MO_x may contain only one kind of these metal elements, or may contain two or more kinds. From the viewpoint of much more effectively suppressing the change in color tone on the metal layer side of the layered sheet and favorably adjusting the color tone of the layered

sheet, M in MO_x is more preferably silicon, zinc, titanium, aluminum, tin, niobium, or indium, further preferably silicon or titanium.

[0071] The metal oxide contained in the metal oxide layer is preferably TiO_y, SiO_y, ZnO, Al_2O_y, Nb_2O_y, SnO_y, or In_2O_y, more preferably TiO_y or SiO_y. y is any number that becomes a complete oxide of metal or an incomplete oxide of metal. The metal oxide contained in the metal oxide layer is preferably TiO_2, SiO_2, ZnO, Al_2O_3, Nb_2O_5, SnO_2, or In_2O_3, more preferably TiO_2 or SiO_2. These metal oxides are complete oxides of metals. The metal oxide layer may contain only one kind of these metal oxides, or may contain two or more kinds. When the metal oxide layer contains the above preferable metal oxide, the change in color tone can be suppressed more effectively, and the color tone of the layered sheet can be adjusted favorably.

[0072] The metal element contained in the metal oxide layer and the metal element contained in the metal layer may be the same or different. From the viewpoint of effectively making the color tone of the second surface of the layered sheet different from the color tone of the surface of the carbonaceous substrate, a metal element contained most in the metal oxide layer is preferably different from a metal element contained most in the metal layer.

[0073] From the viewpoint of imparting a specific surface color and a metallic luster to the layered sheet, the metal element contained in the metal layer is preferably titanium, silver, aluminum, copper, chromium, or palladium, more preferably titanium, silver, or aluminum. The metal layer may contain only one kind of these metal elements, or may contain two or more kinds.

[0074] From the viewpoint of adjusting the color tone of the layered sheet and more favorably providing a metallic luster, the metal element contained most in the metal layer is preferably silver or aluminum. When the metal element contained most in the metal layer is silver or aluminum, between the second surface of the layered sheet and the surface of the carbonaceous substrate, a color difference ΔE^* ab in an L*a*b* color system measured in accordance with JIS Z8781-4: 2013 can be increased.

[0075] From the viewpoint of more favorably imparting a metallic luster to the layered sheet, the metal element contained most in the metal layer is preferably titanium.

[0076] From the viewpoint of much more favorably imparting a metallic luster to the layered sheet and much more effectively suppressing the change in color tone on the metal layer side of the layered sheet, the metal oxide contained most in the metal oxide layer is preferably TiO_2 or SiO_2, and the metal element most contained in the metal layer is preferably titanium, silver, or aluminum.

[0077] The visible light transmittance of the metal oxide layer is preferably 5% or more, more preferably 8% or more, and preferably 100% or less, more preferably 90% or less. When the visible light transmittance of the metal oxide layer is the above lower limit or more and the above upper limit or less, the uneven shape and luster of the carbonaceous substrate are hardly impaired, and a metallic luster can be favorably imparted to the layered sheet.

[0078] The visible light transmittance is an average value of measured values obtained when a transmittance in a wavelength range of 380 nm to 780 nm is measured at intervals of 5 nm. The visible light transmittance can be measured using, for example, a spectrophotometer (for example, "U-4100" manufactured by Hitachi High-Technologies Corporation). An integrating sphere can be used as a detector.

[0079] The visible light transmittance may be measured by preparing a metal oxide layer having an average thickness equivalent to that of the metal oxide layer of the layered sheet.

[0080] Examples of the respective formation methods of the metal oxide layer and the metal layer include sputtering (reactive sputtering method, RF sputtering method), and vapor deposition methods (plasma vapor deposition method, vacuum vapor deposition method (EB vapor deposition method, ion plating method, IAD method)). From the viewpoint of further inhibiting impairment of the design of the carbonaceous substrate such as an uneven shape and a luster, the metal oxide layer and the metal layer are each preferably formed by sputtering and are each preferably a sputtering film. When the metal oxide layer is a sputter layer, the thickness of the metal oxide layer can be finely adjusted, and therefore, the color tone of the layered sheet can be precisely adjusted, so that the color tone suitable for user's purpose can be imparted to the layered sheet.

[0081] The average thicknesses of the metal oxide layer and the metal layer are changed, so that the visible light transmittances of the metal oxide layer and the metal layer can be changed, or the color tone of the second surface of the layered sheet can be changed to various colors.

[0082] The surface of the color tone adjusting layer opposite to the carbonaceous substrate side is preferably not flat. The surface of the color tone adjusting layer opposite to the carbonaceous substrate side preferably has concavoconvexes. The layered sheet preferably has, on the surface of the color tone adjusting layer opposite to the carbonaceous substrate side, concavoconvexes corresponding to concavoconvexes of the surface of the carbonaceous substrate on the color tone adjusting layer side. Such concavoconvexes of the color tone adjusting layer can be favorably formed by sputtering or the like. On the other hand, when the color tone adjusting layer is formed on the carbonaceous substrate by applying a paint containing a dye or a paint containing a pigment, the surface of the color tone adjusting layer is usually flat.

[0083] The average thickness of the metal oxide layer is preferably 3 nm or more, more preferably 5 nm or more, and

further preferably 10 nm or more. The average thickness of the metal oxide layer is preferably 50 nm or less, more preferably 40 nm or less, further preferably less than 40 nm, particularly preferably 30 nm or less. When the average thickness of the metal oxide layer is the above lower limit or more, the change in color tone on the metal layer side of the layered sheet can be effectively suppressed. When the average thickness of the metal oxide layer is the above upper limit or less or less than the above upper limit, the design of the carbonaceous substrate such as an uneven shape and a luster are more hardly impaired. When the average thickness of the metal oxide layer is the above upper limit or less or less than the above upper limit, the surface roughness, refraction resistance, etc. of the carbonaceous substrate are hardly impaired. Moreover, when the average thickness of the metal oxide layer is the above upper limit or less or less than the above upper limit, the color tone and texture of the metal derived from the metal layer can be maintained while maintaining the luster and color tone of the metal layer.

[0084] In general, when a layer containing a metal alone is exposed to the atmosphere or the like, whereby the surface of the layer is naturally oxidized, the thickness of the metal oxide layer to be formed is less than 3 nm.

[0085] The average thickness of the metal layer is preferably 10 nm or more, more preferably 20 nm or more, further preferably 30 nm or more, particularly preferably 40 nm or more, most preferably 50 nm or more. The average thickness of the metal layer is preferably 200 nm or less, more preferably 190 nm or less, further preferably 180 nm or less, particularly preferably 170 nm or less, most preferably 150 nm or less. When the average thickness of the metal layer is the above lower limit or more, a metallic luster can be favorably imparted to the layered sheet. When the average thickness of the metal layer is the above upper limit or less, the design of the carbonaceous substrate such as an uneven shape and a luster are hardly impaired. Further, when the average thickness of the metal layer is the above upper limit or less, the surface roughness, refraction resistance, etc. of the carbonaceous substrate are hardly impaired.

[0086] The average thickness can be measured, for example, by observing a cross section of each of the metal oxide layer and the metal layer with FE-TEM (for example, "JEM-ARM200F" manufactured by JEOL Ltd.). From a cross-sectional TEM image obtained by FE-TEM, arbitrary 5 points or more separated by a distance of 100 nm or more are selected, and an average value of thicknesses measured at the respective points is defined as the average thickness.

[0087] From the viewpoint of favorably imparting a color to the layered sheet, between the second surface of the layered sheet and the surface of the carbonaceous substrate, the color difference ΔE* ab in the L*a*b* color system measured in accordance with JIS Z8781-4: 2013 is preferably 10 or more, more preferably 15 or more, further preferably 20 or more. The color difference ΔE* ab between the second surface of the layered sheet and the surface of the carbonaceous substrate may be 50 or less.

[0088] From the viewpoint of favorably imparting a color to the layered sheet, in the measurement of a lightness L* in the L*a*b* color system measured in accordance with JIS Z8781-4: 2013, the lightness L* of the second surface of the layered sheet is higher than the lightness L* of the surface of the carbonaceous substrate by preferably 5 or more, more preferably 6 or more, further preferably 7 or more. A difference between the lightness L* of the second surface of the layered sheet and the lightness L* of the surface of the carbonaceous substrate may be 50 or less.

[0089] When the color difference ΔE* ab and the lightness L* of the surface of the carbonaceous substrate are measured, the carbonaceous substrate before arrangement of the color tone adjusting layer may be used. When the surfaces on both sides of the carbonaceous substrate are the same, the measurement may be performed on the surface of the carbonaceous substrate opposite to the color tone adjusting layer side.

[0090] From the viewpoint of effectively suppressing the change in color tone on the metal layer side of the layered sheet, between the second surface of the layered sheet and the second surface of the layered sheet allowed to stand for 240 hours under the conditions of a temperature of 85°C and a humidity of 85% RH, the color difference ΔE* ab in the L*a*b* color system measured in accordance with JIS Z8781-4: 2013 is preferably 10 or less, more preferably 5 or less, further preferably 3 or less.

[0091] The present invention will be described below in more detail by way of Examples and Comparative Examples. The present invention is not limited to the following Examples.

(Example 1)

Formation of second color tone adjusting layer (metal layer):

[0092] As a carbonaceous substrate, a carbon fiber substrate ("TR3523 M" manufactured by Mitsubishi Chemical Corporation, thickness of 0.21 mm) which was a fabric in which carbon fibers (basis weight of 200 g/m^2, filament diameter of 7 μm) were woven in a twill weave was used. The carbonaceous substrate was placed in a vacuum apparatus and evacuated to 5.0×10^{-4} Pa or less. Subsequently, argon gas was introduced, and a DC magnetron sputtering method was used to form a Ti layer (average thickness of 50 nm) as the second color tone adjusting layer on the surface of the carbonaceous substrate, thus obtaining a laminate of the carbonaceous substrate and the second color tone adjusting layer.

Formation of first color tone adjusting layer (metal oxide layer):

[0093] A laminate of the carbonaceous substrate and the second color tone adjusting layer was placed in a vacuum apparatus and evacuated to 5.0×10^{-4} Pa or less. Subsequently, argon gas and oxygen gas were introduced, and a DC magnetron sputtering method was used to form a TiO_2 layer (average thickness of 1 nm) as the first color tone adjusting layer on a surface opposite to the carbonaceous substrate of the second color tone adjusting layer, thus obtaining a layered sheet.

(Examples 2 to 6)

[0094] A layered sheet was obtained in the same manner as in Example 1 except that the average thickness of the first color tone adjusting layer was changed as shown in Table 1.

(Examples 7 to 10)

[0095] A layered sheet was obtained in the same manner as in Example 1 except that the average thickness of the first color tone adjusting layer and the material of the second color tone adjusting layer were changed as shown in Tables 1 and 2.

(Examples 11 to 14)

[0096] A layered sheet was obtained in the same manner as in Example 1 except that the material and the average thickness of the first color tone adjusting layer were changed as shown in Table 2.

(Example 15)

[0097] A layered sheet was obtained in the same manner as in Example 1 except that the average thickness of the first color tone adjusting layer was changed as shown in Table 2.

(Examples 16, 17)

[0098] A layered sheet was obtained in the same manner as in Example 1 except that the average thickness of the first color tone adjusting layer and the material of the second color tone adjusting layer were changed as shown in Table 2.

(Comparative Example 1)

[0099] The carbon fiber substrate in Example 1 ("TR3523 M" manufactured by Mitsubishi Chemical Corporation, thickness of 0.21 mm) was used as an evaluation target of Comparative Example 1. In Comparative Example 1, neither the first color tone adjusting layer nor the second color tone adjusting layer was formed.

(Comparative Example 2)

[0100] A Ti layer (average thickness of 50 nm) was formed as the second color tone adjusting layer in the same manner as in Example 1 to obtain a layered sheet. In Comparative Example 2, the first color tone adjusting layer was not formed.

(Comparative Example 3)

[0101] A carbon fiber substrate in Example 1 was prepared. A paint containing a blue pigment was applied to one side of the carbon fiber substrate to form a colored layer (color tone adjusting layer having no optical transparency, average thickness of 15 μm), thus obtaining a layered sheet in which the colored layer was disposed on the second surface side.

(Comparative Example 4)

[0102] An Ag layer (average thickness of 50 nm) was formed as the second color tone adjusting layer in the same manner as in Example 1 to obtain a layered sheet. In Comparative Example 4, the first color tone adjusting layer was not formed.

(Comparative Example 5)

[0103] An Al layer (average thickness of 50 nm) was formed as the second color tone adjusting layer in the same manner as in Example 1 to obtain a layered sheet. In Comparative Example 5, the first color tone adjusting layer was not formed.

(Evaluation)

(1) Uneven shape (surface pattern)

[0104] When the second surface of the obtained layered sheet was observed, whether the uneven shape (surface pattern) of the carbon fiber substrate used for the carbonaceous substrate was not impaired was confirmed visually. In Comparative Example 1, since neither the first color tone adjusting layer nor the second color tone adjusting layer was formed, the uneven shape (surface pattern) was not evaluated.

[Assessment criteria for uneven shape (surface pattern)]

[0105] o: Uneven shape is not impaired
×: Uneven shape is impaired

(2) Metallic luster

[0106] When the second surface of the obtained layered sheet and the surface of the carbonaceous substrate (Comparative Example 1) were observed, whether the surfaces have a metallic luster was confirmed visually.

[0107] The surface of the carbonaceous substrate of Comparative Example 1 corresponds to the surfaces (the first surface of the layered sheet) of the carbonaceous substrates in the layered sheets obtained in Examples 1 to 17 and Comparative Examples 2 to 5.

[Assessment criteria for metallic luster]

[0108] o: The surface has a metallic luster.
×: The surface does not have a metallic luster.

(3) Color difference

[0109] L*, a*, and b* in the L*a*b* color system of the second surface of the layered sheet (Examples 1 to 17 and Comparative Examples 2 to 5) and the surface of the carbonaceous substrate (Comparative Example 1) were determined in accordance with JIS Z8781-4: 2013, using a spectrophotometer ("U-4100" manufactured by Hitachi High-Technologies Corporation).

[0110] The surface of the carbonaceous substrate of Comparative Example 1 corresponds to the surfaces (the first surface of the layered sheet) of the carbonaceous substrates in the layered sheets obtained in Examples 1 to 17 and Comparative Examples 2 to 5.

[0111] The color difference ΔE^* ab in the L*a*b* color system between the second surface of the layered sheet and the surface of the fiber substrate of the layered sheet was determined from L*, a*, and b* in accordance with JIS Z8781-4: 2013.

(4) Color difference (after endurance test)

[0112] The obtained layered sheet was allowed to stand for 240 hours in a thermo-hygrostat (temperature of 85°C, humidity of 85% RH). After allowing it to stand, L*, a*, and b* in the L*a*b* color system of the second surface of the obtained layered sheet were determined in accordance with JIS Z8781-4: 2013, using a spectrophotometer ("U-4100" manufactured by Hitachi High-Technologies Corporation).

[0113] The color difference ΔE^* ab in the L*a*b* color system between the second surface of the layered sheet obtained in (3) described above and the second surface of the layered sheet allowed to stand was determined from L*, a*, and b* in accordance with JIS Z8781-4: 2013. In Comparative Example 1, since neither the first color tone adjusting layer nor the second color tone adjusting layer was formed, the color difference (after endurance test) was not evaluated.

[Assessment criteria for color difference (after endurance test)]

[0114] oo: Color difference ΔE * ab is 3 or less.
o: Color difference ΔE * ab is more than 3 and 5 or less.
Δ: Color difference ΔE * ab is more than 5 and 10 or less.
×: Color difference ΔE * ab is more than 10.

(5) Color difference of second surface of layered sheet by presence and absence of metal oxide layer

[0115] In the layered sheet obtained in Example, a metal oxide layer (first color tone adjusting layer) and a metal layer (second color tone adjusting layer) are arranged as color tone adjusting layers. In the layered sheets obtained in Comparative Examples 2, 4, and 5, only a metal layer (second color tone adjusting layer) is disposed as a color tone adjusting layer, and no metal oxide layer (first color tone adjusting layer) is disposed. In a combination of the layered sheet obtained in Example in which the material and average thickness of the second color tone adjusting layer (metal layer) were the same and the layered sheet obtained in Comparative Example, the color difference ΔE* ab in the L*a*b* color system was determined from L*, a*, and b* of the second surface of each layered sheet in accordance with JIS Z8781-4: 2013. Specifically, the color difference ΔE* ab on the second surface of the layered sheet was determined for the following combinations of the layered sheets.

(i) The color difference between the second surface of the layered sheet obtained in Examples 1 to 6 and 11 to 15 (metal layer: Ti layer, metal oxide layer: TiO_2 layer or SiO_2 layer) and the second surface of the layered sheet obtained in Comparative Example 2 (metal layer: Ti layer)
(ii) The color difference between the second surface of the layered sheet obtained in Examples 7, 8, and 16 (metal layer: Ag layer, metal oxide layer: TiO_2 layer) and the second surface of the layered sheet obtained in Comparative Example 4 (metal layer: Ag layer)
(iii) The color difference between the second surface of the layered sheet obtained in Examples 9, 10, and 17 (metal layer: Al layer, metal oxide layer: TiO_2 layer) and the second surface of the layered sheet obtained in Comparative Example 5 (metal layer: Al layer)

[Assessment criteria for color difference of second surface of layered sheet by presence and absence of metal oxide layer]

[0116]

A: Color difference ΔE* ab is 3 or less.
B: Color difference ΔE* ab is more than 3 and 10 or less.
C: Color difference ΔE* ab is more than 10 and 20 or less.
D: Color difference ΔE* ab is more than 20.

[0117] The configurations and results of the layered sheets are shown in Tables 1 to 3 below.

[Table 1]

[Table 2]

[Table 3]

			Example 9	Example 10	Example 11	Example 12	Example 13	Example 14	Example 15	Example 16	Example 17
Layered sheet	First color tone adjusting layer (Metal oxide layer)	Contained metal oxide	TiO_2	TiO_2	SiO_2	SiO_2	SiO_2	SiO_2	TiO_2	TiO_2	TiO_2
		Average thickness (nm)	5	10	5	10	15	20	40	40	40
	Second color tone adjusting layer (Metal layer)	Contained main metal element	Al	Al	Ti	Ti	Ti	Ti	Ti	Ag	Al
		Average thickness (nm)	50	50	50	50	50	50	50	50	50
	Material of carbonaceous substrate		Carbon fiber	Carbon fiber	Carbon fiber	Carbon fiber	Carbon fiber	Carbon fiber	Carbon fiber	Carbon fiber	Carbon fiber
Evaluation	Uneven shape (surface pattern)		○	○	○	○	○	○	○	○	○
	Metallic luster		○	○	○	○	○	○	○	○	○
	Second surface of layered sheet	L*	54.7	52.9	49.5	47.2	45.9	46.1	47.5	51.8	50.5
		a*	1.3	1.3	1.3	1.5	1.7	1.8	2.2	1.6	1.1
		b*	7.3	8.2	6.1	7.2	11.9	18.5	24.6	9.8	9.5
	Surface of fiber substrate	L*	32.8	32.8	32.8	32.8	32.8	32.8	32.8	32.8	32.8
		a*	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
		b*	4.4	4.4	4.4	4.4	4.4	4.4	4.4	4.4	4.4
	Color difference ΔE* ab		22.1	20.5	16.8	14.7	15.1	19.4	25.0	19.8	18.4
	After endurance test	Second surface of layered sheet L*	53.9	51.2	51.8	49.0	48.5	45.1	47.2	50.1	50.0
		Second surface of layered sheet a*	1.2	1.5	1.3	1.3	1.2	1.2	2.2	1.6	1.2
		Second surface of layered sheet b*	5.4	7.0	5.0	6.7	12.6	16.3	23.4	9.5	9.6
		Color difference ΔE* ab	2.1	2.1	2.5	1.9	2.7	2.4	1.2	1.7	0.5
		Determination	○○	○○	○○	○○	○○	○○	○○	○○	○○
	Color difference of second surface of layered sheet by presence and absence of metal oxide layer	For comparison	Comparative Example 5	Comparative Example 5	Comparative Example 2	Comparative Example 2	Comparative Example 2	Comparative Example 2	Comparative Example 2	Comparative Example 4	Comparative Example 5
		Color difference ΔE* ab	17.0	18.9	3.1	5.6	9.7	15.4	20.8	24.8	21.4
		Determination	C	C	B	B	B	C	D	D	D

				Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5
Layered sheet	First color tone adjusting layer (Metal oxide layer)		Contained metal oxide	-	-	(Blue pigment)	-	-
			Average thickness (nm)	-	-	1500 (15μm)	-	-
	Second color tone adjusting layer (Metal layer)		Contained main metal element	-	Ti		Ag	Al
			Average thickness (nm)	-	50		50	50
	Material of carbonaceous substrate			Carbon fiber	Carbon fiber	Carbon fiber	Carbon fiber	Carbon fiber
Evaluation	Uneven shape (surface pattern)			-	○	×	○	○
	Metallic luster			×	○	×	○	○
	Second surface of layered sheet		L*	-	52.1	25.4	76.4	71.6
			a*	-	1.3	-6.1	0.3	0.1
			b*	-	4.4	-34.2	6.6	5.8
	Surface of fiber substrate		L*	32.8	32.8	32.8	32.8	32.8
			a*	1.0	1.0	1.0	1.0	1.0
			b*	4.4	4.4	4.4	4.4	4.4
	Color difference ΔE* ab			-	19.3	39.9	43.7	38.8
	After endurance test	Second surface of layered sheet	L*	-	40.6	23.1	51.9	61.8
			a*	-	1.2	-5.2	-0.3	0.6
			b*	-	8.3	-34.1	5.9	8.7
		Color difference ΔE* ab		-	12.2	2.5	24.5	10.2
		Determination		-	×	○○	×	×
	Color difference of second surface of layered sheet by presence and absence of metal oxide layer		For comparison	-	-	-	-	-
			Color difference ΔE* ab	-	-	-	-	-
			Determination	-	-	-	-	-

EXPLANATION OF SYMBOLS

[0118]

1: Layered sheet
1a: First surface
1b: Second surface
2: Carbonaceous substrate
3: Color tone adjusting layer
31: Metal oxide layer (first color tone adjusting layer)
32: Metal layer (second color tone adjusting layer)

Claims

1. A layered sheet comprising:

a carbonaceous substrate;
a metal layer disposed on a surface of the carbonaceous substrate; and
a metal oxide layer disposed on a surface of the metal layer opposite to the carbonaceous substrate.

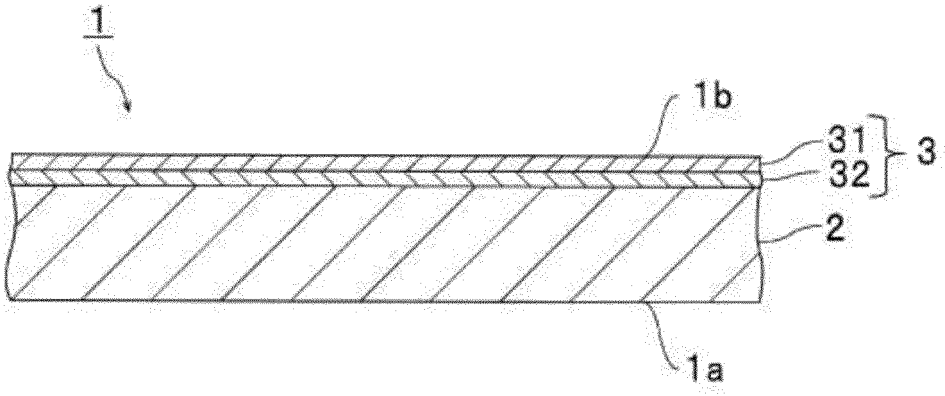
2. The layered sheet according to claim 1, wherein a metal element contained in the metal layer is titanium, silver, or aluminum.

3. The layered sheet according to claim 1 or 2, wherein an average thickness of the metal oxide layer is 3 nm or more.

4. The layered sheet according to any one of claims 1 to 3, wherein the average thickness of the metal oxide layer is less than 40 nm.

5. The layered sheet according to any one of claims 1 to 4, wherein a metal oxide contained in the metal oxide layer is TiO_2 or SiO_2.

[FIG. 1.]



INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2018/047760

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl. B32B15/04(2006.01)i, C23C14/06(2006.01)i, D01F9/12(2006.01)i, D06M11/83(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)
Int.Cl. B32B15/04, C23C14/06, D01F9/12, D06M11/83

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Published examined utility model applications of Japan	1922-1996
Published unexamined utility model applications of Japan	1971-2019
Registered utility model specifications of Japan	1996-2019
Published registered utility model applications of Japan	1994-2019

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 A	JP 61-94002 A (HITACHI CHEMICAL INDUSTRY CO., LTD.) 12 May 1986, claims, examples (Family: none)	1-3 4-5
X A	JP 2000-281469 A (NGK INSULATORS, LTD.) 10 October 2000, claims, paragraphs [0009], [0021], table 1 (Family: none)	1-3, 5 4
X	JP 60-131240 A (TOYOTA GOSEI CO., LTD.) 12 July 1985, claims, page 1, lower right column, page 2, lower left column to lower right column, page 3, upper left column, page 4, upper left column, tables (Family: none)	1-5

☒ 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	Date of mailing of the international search report
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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	KR 10-2014-0080654 A (WOOJEON & HANDAN CO., LTD.) 01 July 2014, claims, paragraphs [0024], [0029], [0032], [0052] (Family: none)	1-5
A	JP 3-82881 A (TORAY INDUSTRIES, INC.) 08 April 1991, whole document (Family: none)	1-5
A	JP 8-253874 A (KAWASAKI STEEL CORP.) 01 October 1996, whole document (Family: none)	1-5
A	JP 11-70617 A (FUJI HEAVY INDUSTRIES LTD.) 16 March 1999, whole document (Family: none)	1-5

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REFERENCES CITED IN THE DESCRIPTION

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