



(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 153(4) EPC

(43) Date of publication:
08.07.2020 Bulletin 2020/28

(51) Int Cl.:
C23C 18/24 ^(2006.01) **C25B 1/00** ^(2006.01)
C25D 5/56 ^(2006.01)

(21) Application number: **18849843.0**

(86) International application number:
PCT/JP2018/032342

(22) Date of filing: **31.08.2018**

(87) International publication number:
WO 2019/045047 (07.03.2019 Gazette 2019/10)

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME
Designated Validation States:
KH MA MD TN

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(30) Priority: **01.09.2017 JP 2017168258**

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(54) **PLATING PRETREATMENT METHOD FOR ABS RESIN SURFACE, PLATING TREATMENT METHOD FOR ABS RESIN SURFACE, AND ABS RESIN PLATED PRODUCT**

(57) A treatment device 1 has: a treatment tank 2 provided with a constant temperature heater 3 on the outer periphery; an electrolytic cell 6 continuing from a pipe 4 provided with a circulation pump 5; and a pipe 7 for supply to the treatment tank 2 from the electrolytic cell 6. Within the electrolytic cell 6 are provided a positive electrode 6A and a negative electrode 6B formed from diamond electrodes and a bipolar electrode 6C disposed between the two. The treatment tank 2 and the electrolytic cell 6 are filled with a prescribed concentration of sulfuric acid. The treatment device is configured such that a persulfate solution S such as peroxydisulfuric acid is generated by electrolysis of the sulfuric acid by making a prescribed current flow from a direct current power supply unit to the positive electrode 6A and the negative electrode 6B, and this persulfate solution S can be supplied to the treatment tank 2 via the pipe 7. A plating pretreatment method for Cr and Mn-free ABS resin surfaces that can form plating sufficiently adhering to an ABS resin

surface can be applied to this treatment device 1.

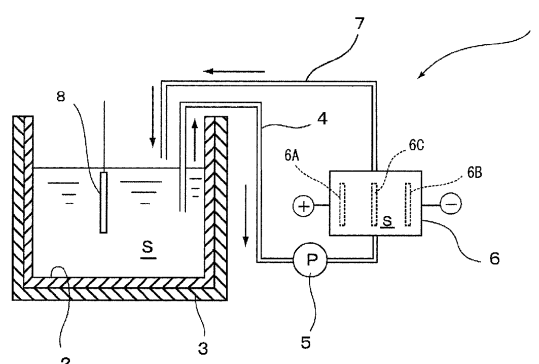


FIG. 1

Description

[Technical Field]

5 **[0001]** The present invention relates to a pretreatment method performed prior to a plating treatment of an ABS resin surface. The present invention further relates to a plating treatment method for an ABS resin surface that has been subjected to this pretreatment. The present invention still further relates to an ABS resin plated product obtained by plating the ABS resin surface that has been subjected to this pretreatment.

10 [Background Art]

15 **[0002]** Plastics are substituted for parts where metals are used as structural materials and component materials for advantages such as weight reduction, cost reduction, freedom of shape, ease of mass production, and the like. At present, they are widely used not only for decoration but also for exterior and interior parts of automobiles, home electric appliances, and the like. At this time, a plastic surface is often plated to improve rigidity, wear resistance, weather resistance, heat resistance, and the like.

20 **[0003]** Since plastics are non-conductive, it is necessary to first form a metal film serving as a conductor on a plastic before plating. Methods therefor are roughly classified into dry methods such as chemical vapor deposition (CVD) and physical vapor deposition (PVD), and wet methods such as electroless nickel plating. The wet methods have been employed so far because the dry methods mostly involve film formation in a vacuum state and therefore are not suitable for mass production or application to large components.

25 **[0004]** Among these plastic molded articles, ABS resin is widely used as the main plastic substituted for metals because it is a resin which is most easily plated. For surface roughening treatment as a pretreatment for plating the ABS resin, surface roughening treatment using a chromic acid/sulfuric acid solution is performed. Chromic acid is represented by the chemical formula: H_2CrO_4 , and in an etching liquid that is a mixed solution of chromic acid with concentrated sulfuric acid, there is an equilibrium of $2\text{CrO}_4^{2-} + 2\text{H}_3\text{O}^+ \rightarrow \text{Cr}_2\text{O}_7^{2-} + 3\text{H}_2\text{O}$, but Cr is hexavalent. Hexavalent chromium is subject to REACH regulations and the RoHS Directive, but hexavalent chromium itself is not regulated because it does not remain in products. However, in recent years, there has been a growing interest in environmental issues, and there is a strong demand for environmentally friendly technologies that do not use hexavalent chromium. In addition, there are problems in which wastewater treatment such as reduction, neutralization, and coagulation sedimentation is required for wastewater containing Cr, and the precipitate from the treatment cannot be easily disposed because it contains Cr.

30 **[0005]** Accordingly, as an environmentally friendly technology that replaces chromic acid, Patent Literature 1 proposes etching using a mixed solution of permanganate and an inorganic salt. Patent Literature 2 and Patent Literature 3 disclose a pretreatment method for electroless plating in which a surface of a plastic molded article is roughened using ozone-dissolved water.

[Citation List]

[Patent Literature]

40

[0006]

[Patent Literature 1]

Japanese Patent Laid-Open No. 2008-31513

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[Patent Literature 2]

Japanese Patent Laid-Open No. 2002-121678

[Patent Literature 3]

Japanese Patent Laid-Open No. 2012-52214

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[Summary of Invention]

[Technical Problem]

55 **[0007]** However, the method of etching with the mixed solution of permanganate and an inorganic salt disclosed in Patent Literature 1 has problems that the surface treatment of the ABS resin is difficult, and adhesiveness to the metal is poor. In addition, it is said that manganese (Mn) will also become subject to REACH regulations and the RoHS Directive in the future in the same manner as Cr, and therefore it is desirable not to use it. Furthermore, in the plating pretreatment method for a plastic surface disclosed in Patent Literature 2 and Patent Literature 3, since ozone has a high decomposition

rate, it is necessary to produce high-concentration ozone water and maintain a high concentration. Therefore, not only is large-scale equipment required, but there is also a problem that unevenness is likely to occur in treatment due to a local difference in ozone concentration.

[0008] The present invention has been made in view of the above problems, and an objective thereof is to provide a plating pretreatment method for a Cr- and Mn-free ABS resin surface which is a plating pretreatment method for an ABS resin surface by which plating sufficiently adhered to an ABS resin surface can be formed. Another objective of the present invention is to provide a plating treatment method in which plating is favorably adhered to the ABS resin surface that has been subjected to such a pretreatment method. Still another object of the present invention is to provide an ABS resin plated product obtained by plating the ABS resin surface that has been subjected to this pretreatment.

[Solution to Problem]

[0009] In order to achieve the above-mentioned objectives, firstly, the present invention provides a plating pretreatment method for an ABS resin surface (Invention 1), the method including treating ABS resin with a solution obtained by electrolysis of sulfuric acid.

[0010] According to this invention (Invention 1), when an ABS resin surface is roughened by dissolving a butadiene component on the surface through a strong oxidizing action of persulfuric acid generated by electrolysis of sulfuric acid, a specific surface area increases and hydrophilic functional groups are exposed. Therefore, when ABS resin is subjected to plating treatment after this treatment, a sufficiently adhered plating can be obtained. In the present specification, "ABS resin" refers to not only the case of an acrylonitrile-butadiene-styrene copolymer resin (ABS resin) alone, but also a blend resin of this ABS resin and another resin, specifically, a mixed resin of ABS resin and polycarbonate (PC resin). In particular, "ABS resin" also includes a PC/ABS mixed resin in which a content of PC resin is 20% to 70% by weight with respect to a total of 100% by weight of ABS resin and PC resin.

[0011] In the above invention (Invention 1), a concentration of sulfuric acid in the solution is preferably 60% to 87% by weight (Invention 2).

[0012] According to this invention (Invention 2), a specific surface area is increased by suitably roughening an ABS resin surface with a persulfate solution obtained by electrolysis of sulfuric acid at this concentration, whereby adhesiveness of plating can be improved. In addition, by varying a concentration of sulfuric acid within the above range, it is possible to adjust a degree of treatment of an ABS resin surface.

[0013] In the above inventions (Inventions 1 and 2), a temperature in the treatment is preferably 50°C to 80°C (Invention 3).

[0014] According to this invention (Invention 3), a specific surface area is increased by suitably roughening an ABS resin surface while inhibiting decomposition of persulfuric acid, whereby adhesiveness of plating can be further improved.

[0015] In the above inventions (Inventions 1 to 3), a concentration of persulfuric acid in the solution is preferably 3 g/L or more (Invention 4).

[0016] According to this invention (Invention 4), a specific surface area is increased by suitably roughening an ABS resin surface through a strong oxidizing action of persulfuric acid, whereby adhesiveness of plating can be still further improved.

[0017] Secondly, the present invention provides a plating treatment method for an ABS resin surface (Invention 5), the method including subjecting an ABS resin surface to electroless plating or electroplating after treating the surface by the plating pretreatment method for the ABS resin surface according to any one of the above inventions (Inventions 1 to 4).

[0018] According to this invention (Invention 5), by dissolving a butadiene component on an ABS resin surface through a strong oxidizing action of persulfuric acid generated by electrolysis of sulfuric acid, the surface is roughened, and hydrophilic functional groups are exposed. Therefore, when the ABS resin is subjected to plating treatment after this treatment, it is possible to precipitate plating such as chromium with favorable adhesiveness to an ABS resin surface.

[0019] Thirdly, the present invention provides an ABS resin plated product (Invention 6) which has been subjected to plating treatment by the plating treatment method for the ABS resin surface according to the above invention (Invention 5).

[0020] According to this invention (Invention 6), the ABS resin plated product is obtained by plating an ABS resin surface with chromium or the like with favorable adhesiveness.

[Advantageous Effects of Invention]

[0021] According to the plating treatment method for an ABS resin surface of the present invention, when an ABS resin surface is roughened by dissolving a butadiene component on the surface through a strong oxidizing action of persulfuric acid generated by electrolysis of sulfuric acid, a specific surface area increases and hydrophilic functional groups are exposed, and therefore, when the ABS resin is subjected to plating treatment after this treatment, a sufficiently adhered plating can be obtained.

[Brief Description of Drawings]

[0022] Fig. 1 is a schematic diagram showing a configuration of a treatment device which is suitable for a plating pretreatment method for an ABS resin surface according to an embodiment of the present invention can be applied.

[Description of Embodiments]

[0023] Fig. 1 shows a treatment device which is suitable for a plating pretreatment method for an ABS resin surface according to an embodiment of the present invention can be applied. In Fig. 1, a treatment device 1 includes a treatment tank 2 provided with a constant temperature heater 3 on an outer periphery, an electrolytic cell 6 continuing from a pipe 4 having a circulation pump 5, and a pipe 7 for supply from the electrolytic cell 6 to the treatment tank 2. The electrolytic cell 6 has an anode 6A and a cathode 6B formed from diamond electrodes, and a bipolar electrode 6C disposed therebetween. The treatment tank 2 may have a stirring means such as an air diffuser for stirring the inside of the tank as needed.

[0024] Such a treatment device 1 is configured such that the treatment tank 2 and the electrolytic cell 6 are filled with sulfuric acid of a predetermined concentration in an initial state, a sulfate solution S containing persulfuric acid (an oxidizing agent) such as peroxodisulfuric acid (hereinafter referred to as a persulfate solution in the present specification) is generated by making a predetermined current to be supplied from a direct current power supply unit to the anode 6A and the cathode 6B, and by electrolysis of sulfuric acid, this persulfate solution S can be supplied to the treatment tank 2 via the pipe 7. The device 1 is configured such that the persulfate solution S refluxes from the treatment tank 2 to the electrolytic cell 6 via the pipe 4 by the circulation pump 5, and thereby the persulfate solution S is circulated. In the treatment tank 2, an ABS resin plate 8 to be treated is suspended in a vertical direction.

[0025] In the persulfate solution S, a concentration of sulfuric acid is preferably 60% to 87% by weight, particularly 70% to 83% by weight. When the concentration of sulfuric acid is less than 60% by weight, a concentration of sulfuric acid in a resulting persulfate solution S becomes too low, a surface of the ABS resin plate 8 therefore cannot be sufficiently roughened, and an effect of improving adhesiveness of plating cannot be sufficiently obtained, whereas even when the concentration exceeds 87% by weight, not only can the effect not be further improved, but a handling property also deteriorates, which is not preferable.

[0026] Next, a plating pretreatment method for an ABS resin surface using the treatment device 1 as described above will be described. First, when sulfuric acid is put into the treatment tank 2 and heated with the constant temperature heater 3 and is supplied to the electrolytic cell 6 using the circulation pump 5, and a predetermined current is applied from a direct current power supply unit to electrolyze the sulfuric acid. Thereby, the persulfate solution S such as peroxodisulfuric acid is generated, and this persulfate solution S is supplied to the treatment tank 2 via the pipe 7 and circulated.

[0027] At this time, it is preferable to heat the persulfate solution S with the constant temperature heater 3 such that a temperature of the persulfate solution S becomes 50°C to 80°C. When the temperature of the persulfate solution S is less than 50°C, the surface of the ABS resin plate 8 cannot be sufficiently roughened, and therefore the effect of improving adhesiveness of plating cannot be sufficiently obtained, whereas when the temperature exceeds 80°C, decomposition of persulfuric acid is promoted, which reduces treatment efficiency.

[0028] In addition, it is sufficient for electrolysis of sulfuric acid in the electrolytic cell 6 to be performed under such conditions in which a concentration of persulfuric acid such as peroxodisulfuric acid generated by the electrolysis is 3 g/L or more, particularly 3 to 20 g/L. When the concentration of persulfuric acid is less than 3 g/L, the effect of improving adhesiveness of plating cannot be obtained sufficiently, whereas even when the concentration exceeds 20 g/L, the above effect cannot be further improved, and it is not economical.

[0029] When the persulfate solution S in the treatment tank 2 reaches the above-mentioned temperature and concentration of persulfuric acid, the surface of the ABS resin plate 8 is treated by immersing the degreased ABS resin plate 8 in the treatment tank 2. At this time, it is preferable that the ABS resin plate 8 be subjected to wet treatment in advance in order to suppress air bubbles adhering to the plate when the plate is immersed in the persulfate solution S.

[0030] By immersing the ABS resin plate 8 in the persulfate solution S in the treatment tank 2 for 5 to 20 minutes, hydrophilic functional groups are exposed on the surface of the ABS resin plate 8. Accordingly, hydroxyl groups, carbonyl groups, aldehyde groups, and carboxyl groups of the ABS resin appear on the ABS resin surface. Thereby, adhesiveness of plating can be improved in the subsequent plating treatment.

[0031] After activating the functional groups developed on the resin surface of the ABS resin plate 8 in the above steps, neutralization and/or reduction treatment, conditioning treatment, and the like may be performed as necessary.

[0032] The surface of the ABS resin plate 8 can be etched by the pretreatment method of the present embodiment described above. In addition, after the plating pretreatment method of the present embodiment, it is possible to apply a conventionally known plating method for a resin such as an electroless plating method and a direct plating method.

[0033] For example, a catalyst is applied to the ABS resin plate 8 that has been treated by the pretreatment method

of the present embodiment using a catalyst application treatment liquid. The catalyst application treatment liquid is not particularly limited as long as it is a liquid generally used for applying a catalyst in a plating step, but it preferably contains a noble metal, more preferably contains palladium, and particularly preferably contains a palladium/tin mixed colloid catalyst solution. In order to apply these catalysts to a resin surface, a temperature of the catalyst application treatment liquid is preferably set to 10°C to 60°C, particularly 20°C to 50°C, and the ABS resin plate 8 is immersed therein and treated for 1 to 20 minutes, preferably 2 to 5 minutes. Next, the resin surface to which the catalyst has been applied is metallized by a metal plating treatment such as electroless plating or electroplating (direct plating).

[0034] In a case where electroless plating is used for metallization of a resin surface, treatment may be further performed with an activation treatment liquid containing hydrochloric acid or sulfuric acid after a catalyst is applied with the catalyst application treatment liquid. A concentration of hydrochloric acid or sulfuric acid in this activation treatment liquid is 0.5 mol/L or more, preferably 1 to 4 mol/L. In order to treat a resin surface with these activation treatment liquids, a temperature of the activation treatment solution is preferably set to 0°C to 60°C, particularly 30°C to 45°C, and the ABS resin plate 8 is immersed therein and treated for preferably 1 to 20 minutes, particularly 2 to 5 minutes.

[0035] The ABS resin plate 8 to which the catalyst has been applied and which has been subjected to activation treatment as described above is then subjected to electroless plating treatment. The electroless plating treatment can be performed according to a general method using electroless plating such as known electroless nickel plating liquid, electroless copper plating liquid, electroless cobalt plating liquid, or the like. Specifically, in the case of performing plating treatment to a resin surface with the electroless nickel plating liquid, the ABS resin plate 8 is immersed in the electroless nickel plating liquid at a pH of 8 to 10 and a liquid temperature of 30°C to 50°C for 5 to 15 minutes.

[0036] In addition, in the case of using electroplating (direct plating) for metallization of a resin surface, a catalyst is applied with a catalyst application treatment liquid, and thereafter, treatment can be further performed with an activation treatment liquid containing copper ions at a pH of 7 or more. The origin of the copper ions contained in the activation treatment liquid is not particularly limited, and examples thereof include copper sulfate. In order to treat a resin surface with these activation treatment liquids, a temperature of the activation treatment solution is preferably set to 0°C to 60°C, particularly 30°C to 50°C, and the ABS resin plate 8 is immersed therein and treated for preferably 1 to 20 minutes, particularly 2 to 50 minutes.

[0037] The ABS resin plate 8 to which the catalyst has been applied and subjected to activation treatment as described above is subsequently immersed in a general-purpose copper electroplating bath such as a copper sulfate bath, and treated in general conditions, for example, 1 to 5 A/dm² for 2 to 10 minutes. In addition, sufficient washing with water or hot water is performed between treatments. As described above, the surface of the ABS resin plate 8 is subjected to metal plating such as electroless plating or electroplating, and if necessary, the surface of the metallized ABS resin plate 8 may further be subjected to various plating such as copper electroplating, nickel electroplating, and chrome electroplating. It is sufficient for these metal platings to enable acquirement of a film as plating, and examples thereof include nickel, copper, chromium, cobalt, tin, zinc, iron, silver, gold, and alloys thereof.

[0038] Such a treatment may be performed continuously while replacing the ABS resin plate 8, but it is desirable that the circulation pump 5 be continuously driven to continuously replenish the treatment tank 2 with fresh persulfate solution S from the electrolytic cell 6 via the pipe 7, because persulfuric acid of the persulfate solution S in the treatment tank 2 decomposes with the progress of the treatment, which decreases a concentration of persulfuric acid. In addition, when the concentration of sulfuric acid decreases, the treatment tank 2 may be appropriately replenished with sulfuric acid, and when the concentration of sulfuric acid increases, the treatment tank 2 may be appropriately replenished with water. A sulfuric acid concentration system can be installed in the treatment tank 2 so that this operation can be performed automatically.

[0039] Prior to the pretreatment of the present embodiment as described above, the ABS resin plate 8 may be subjected to treatment for imparting wettability, if necessary. This treatment may be performed by, for example, sufficiently immersing the ABS resin plate 8 in a wet treatment tank to impart wettability to the surface of the resin substrate. In addition, a surfactant may be contained in the wet treatment tank. The surfactant is not particularly limited, but for example, it is possible to use an amine salt type surfactant, a quaternary amine salt type surfactant, an amino acid type surfactant, a betaine type surfactant, a carboxylate type surfactant, a sulfonate type surfactant, a sulfate ester type surfactant, a phosphate ester type surfactant, an ether type surfactant, an ester type surfactant, a nitrogen-containing surfactant, a fluorine-containing surfactant, and the like. One kind of these surfactants may be used, or two or more kinds thereof may be used.

[0040] The ABS resin plate 8 pretreated as above can be subjected to electroless plating or electroplating by a general method. Accordingly, it is possible to obtain an ABS resin plated product in which the surface of the ABS resin plate 8 is plated with chromium or the like with favorable adhesiveness.

[0041] The plating treatment method for an ABS resin surface according to the present invention has been described above based on the above-described embodiment. However, the present invention is not limited to the above-described examples, and various modifications can be made. For example, the present invention is applicable not only to batch treatment as in the present embodiment but also to continuous treatment. In addition, the ABS resin plate is not limited

to the plate as in the present embodiment, but can also be applied to molded articles of various shapes.

Examples

5 **[0042]** Hereinafter, the present invention will be described more specifically with reference to Examples and Comparative Examples. However, the present invention is not limited by these descriptions. In the following Examples and Comparative Examples, measurement of a concentration of persulfuric acid and an adhesiveness test were performed as follows.

10 <Method for measuring concentration of persulfuric acid>

[0043] First, a concentration of a total oxidizing agent contained in a treatment liquid (a persulfate solution S) was measured by iodine titration. This iodine titration is a method in which KI is added to the persulfate solution S to release I_2 , this I_2 is titrated with a sodium thiosulfate standard solution to determine an amount of I_2 , and a concentration of an oxidizing agent is obtained from the amount of I_2 . Next, only a concentration of hydrogen peroxide in the persulfate solution S was obtained by potassium permanganate titration, and a concentration of persulfuric acid was calculated by subtracting a value of potassium permanganate titration from a value of iodine titration.

20 <Plating adhesiveness test>

[0044] This test is for examining adhesiveness by performing thermal shock by heating and rapidly cooling a sample, in which, after performing 40 cycles of the shock at 70°C and -30°C, that is, a temperature difference of 100°C, for 1 hour at each temperature, conditions such as the presence or absence of peeling, cracks, swelling, and the like on a plating surface were observed and evaluated on a three-point scale of classifications 1 to 3 below.

25 Classification 1: No peeling, cracks, wrinkles, or swelling on plating was observed.
Classification 2: Peeling, cracks, wrinkles, and swelling on plating were observed in less than 25% of the sample area.
Classification 3: Peeling, cracks, wrinkles, and swelling on plating were observed in 25% or more of the sample area.

30 [Example 1]

[0045] A surface treatment of the ABS resin plate 8 was performed using the device shown in Fig. 1. Specifications and conditions of a treatment tank are as follows.

35 <Treatment tank>

[0046] Volume of the treatment tank 2: 40 L
Size of the ABS resin plate 8: 500 mm × 500 mm × 5 mm thick

40 <Properties of persulfate solution S and conditions of surface treatment>

[0047] Concentration of sulfuric acid: 75% by weight
Concentration of persulfuric acid: 10 g/L
Treatment temperature: 75°C
45 Treatment time: 15 minutes

<Electrolytic cell 6 for generation of persulfuric acid and electrolysis conditions>

[0048] Cell volume: 0.5 L
50 Anode and cathode: Diamond electrode (150 mm diameter)
Bipolar electrode material: Same as the anode and the cathode
Current density: 50 A/dm²
Liquid circulation volume: 2.5 L/min
Concentration of sulfuric acid: 75% by weight
55 Concentration of persulfuric acid: 10 g/L
Treatment temperature: 75°C

[0049] The ABS resin plate 8 was first immersed in a wet treatment tank containing a surfactant for 10 minutes, and then was immersed in the treatment tank 2 filled with the persulfate solution S for 10 minutes. Thereafter, the plate was

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removed from the treatment tank 2, washed with tap water, and then subjected to electroless nickel plating through an activation step and a catalyst application step. Thereafter, chromium plating was finally performed on the plate. Tables 1 and 2 show the treatment conditions in the plating step. In addition, plating adhesiveness of the chrome-plated ABS resin plate 8 was evaluated by the above method. Table 3 shows results together with conditions for the electrolytic sulfuric acid treatment.

[Table 1]

Treatment name	Bath composition	Concentration	Treatment temperature (°C)	Treatmenttime (minutes)
Wet	Sulfuric acid	20 mL/L	50	10
	ENILEX WE* 1	10 mL/L		
Electrolytic sulfuric acid	Electrolytic sulfuric acid solution	78% by weight of sulfuric acid	60	10
Washing	Tap water	-	55	10
Activation	Hydrochloric acid	100 mL/L	Room temperature	1
Catalyst application	Hydrochloric acid	150 mL/L	35	4
	ENILEX CT-580*2	30 mL/L		
Activation	Hydrochloric acid	80 mL/L	35	4
Electroless nickel plating	ENILEX Ni-100AM*3	160 mL/L	35	10
	ENILEX Ni-100BM*4	160 mL/L		
	Ammonia water	pH = 9.5		
Activation	EBAVATE V-345*5	60 g/L	Room temperature	0.5
Nickel strike plating	Nickel sulfate	240 g/L	55	3
	Nickel chloride	30 g/L		
	Boric acid	30 g/L		
Activation	EBAVATE V-345*5	60 g/L	Room temperature	0.5
Copper replacement	Activator PDC*6	10 mL/L	Room temperature	0.5
	Sulfuric acid	10 mL/L		
Copper plating	Copper sulfate	225 g/L	Room temperature	40
	Sulfuric acid	55 g/L		
	Concentrated hydrochloric acid (as chlorine ion)	0.15 mL/L (60 mg/L)		
	CU-BRITE EP-30A*6	1 mL/L		
	CU-BRITE EP-30B*7	0.3 mL/L		
	CU-BRITE EP-30C*8	4 mL/L		
*1~*8: names of products manufactured by JCU Corporation				

[Table 2]

Treatment name	Bath composition	Concentration	Treatment temperature (°C)	Treatment time (minutes)
Activation	EBAVATE V-37*9	60 g/L	Room temperature	1

(continued)

Treatment name	Bath composition	Concentration	Treatment temperature (°C)	Treatment time (minutes)
Semi-bright nickel plating	Nickel sulfate	280 g/L	55	20
	Nickel chloride	35 g/L		
	Boric acid	40 g/L		
	CF-N IIA* 10	0.5 mL/L		
	CF-24T*11	1 mL/L		
	#82-K*12	1 mL/L		
Bright nickel plating	Nickel sulfate	250 g/L	50	20
	Nickel chloride	40 g/L		
	Boric acid	40 g/L		
	#810*13	3 mL/L		
	#83*14	10 mL/L		
	#82*15	1 mL/L		
Chrome plating	Chromic acid	240 g/L	40	3
	Sulfuric acid	1 g/L		
	ECR-300L*16	10 mL/L		
	MISTSHUTNP*17	0.1 mL/L		
*9~*17: names of products manufactured by JCU Corporation				

[Examples 2 to 7]

[0050] Chromium plating was performed in the same manner as in Example 1 except that various settings of conditions for the electrolytic sulfuric acid treatment were changed as shown in Table 3, and plating adhesiveness was evaluated. Table 3 shows results together with conditions for the electrolytic sulfuric acid treatment.

[Comparative Example 1]

[0051] Chromium plating was performed in the same manner as in Example 1 except that a sulfuric acid solution having a sulfuric acid concentration of 75% by weight was used instead of the electrolytic sulfuric acid solution, and plating adhesiveness was evaluated. Table 3 shows results together with conditions for the treatment.

[Comparative Example 2]

[0052] Chromium plating was performed in the same manner as in Example 1 except that a mixed solution of sulfuric acid and hydrogen peroxide was used instead of the electrolytic sulfuric acid solution, and plating adhesiveness was evaluated. Table 3 shows results together with conditions for the treatment.

[Table 3]

Example Nos.	Concentration of sulfuric acid (% by weight)	Treatment temperature (°C)	Concentration of persulfuric acid (g/L)	Treatment time (minutes)	Result of adhesiveness test
Example 1	75	75	10	15	Classification 1
Example 2	65	80	5	20	Classification 1
Example 3	85	50	3	7	Classification 1

(continued)

Example Nos.	Concentration of sulfuric acid (% by weight)	Treatment temperature (°C)	Concentration of persulfuric acid (g/L)	Treatment time (minutes)	Result of adhesiveness test
Example 4	65	85	5	15	Classification 2
Example 5	60	80	10	20	Classification 2
Example 6	75	75	10	3	Classification 2
Example 7	85	75	2	20	Classification 2
Comparative Example 1	75	75	0	15	Classification 3
Comparative Example 2	75	75	10	15	Classification 2

[0053] As can be clearly seen from Table 3, according to the plating treatment method for an ABS resin surface of the present invention, it is possible to obtain excellent plating adhesiveness. In the plating treatment method for an ABS resin surface of Comparative Example 2, there was a problem of long-term stability of the treatment due to consumption of hydrogen peroxide.

[Reference Signs List]

[0054]

- 1 Treatment device
- 2 Treatment tank
- 3 Constant temperature heater
- 4 Pipe
- 5 Circulation pump
- 6 Electrolytic cell
- 6A Anode
- 6B Cathode
- 6C Bipolar electrode
- 7 Pipe
- 8 ABS resin plate
- S Persulfate solution

Claims

1. A plating pretreatment method for an ABS resin surface, the method comprising treating an ABS resin with a solution obtained by electrolysis of sulfuric acid.
2. The plating pretreatment method for an ABS resin surface according to claim 1, wherein a concentration of sulfuric acid in the solution is 60% to 87% by weight.
3. The plating pretreatment method for an ABS resin surface according to claim 1 or 2, wherein a temperature of treating is 50°C to 80°C.
4. The plating pretreatment method for an ABS resin surface according to any one of claims 1 to 3, wherein a concentration of persulfuric acid in the solution is 3 g/L or more.
5. A plating treatment method for an ABS resin surface, the method comprising subjecting an ABS resin surface to electroless plating or electroplating after treating the surface by the plating pretreatment method for an ABS resin surface according to any one of claims 1 to 4.

6. An ABS resin plated product which has been subjected to plating treatment by the plating treatment method for an ABS resin surface according to claim 5.

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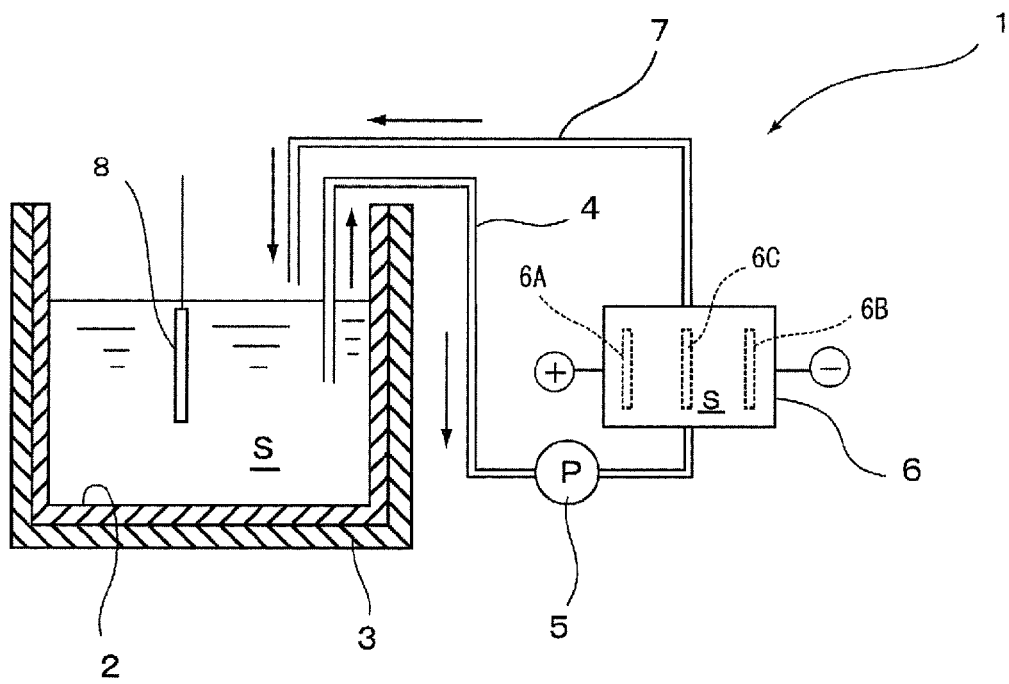


FIG. 1

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2018/032342

A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl. C23C18/24 (2006.01) i, C25B1/00 (2006.01) i, C25D5/56 (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. C23C18/24, C25B1/00, C25D5/56

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 1971-2018

Registered utility model specifications of Japan 1996-2018

Published registered utility model applications of Japan 1994-2018

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 2015-518083 A (MACDERMID ACUMEN, INC.) 25 June 2015, claims, paragraphs [0003], [0052] & WO 2013/112268 A2, claims, page 2, lines 20-27, page 11, lines 16-24 & US 2013/0186774 A1 & EP 2807290 A2 & TW 201339281 A & CA 2860845 A & KR 10-2014-0114063 A & CN 104487617 A	1-3, 5, 6 4
X A	JP 2010-138434 A (OKUNO CHEM IND CO., LTD.) 24 June 2010, claims, paragraph [0012], examples (Family: none)	1-3, 5, 6 4



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search
19.09.2018Date of mailing of the international search report
02.10.2018Name and mailing address of the ISA/
Japan Patent Office
3-4-3, Kasumigaseki, Chiyoda-ku,
Tokyo 100-8915, Japan

Authorized officer

Telephone No.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2018/032342

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 2012-132066 A (CHLORINE ENGINEERS CORP., LTD.) 12 July 2012, claims, paragraph [0002] & US 2013/0256150 A1, claims, paragraph [0001] & WO 2012/086352 A1 & EP 2657370 A1 & TW 201231730 A & CN 103380232 A & KR 10-2013-0108435 A	1-6
Y	JP 1-275769 A (NIPPON OZON KK) 06 November 1989, page 2, upper right column, lines 7-20 (Family: none)	1-6
P, A	WO 2017/187823 A1 (KURITA WATER IND LTD.) 02 November 2017, entire text & JP 2017-197831 A	1-6

Form PCT/ISA/210 (continuation of second sheet) (January 2015)

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 2008031513 A [0006]
- JP 2002121678 A [0006]
- JP 2012052214 A [0006]