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(54) **MULTI-STAGE RESIN SURFACE ETCHING METHOD, AND PLATING METHOD ON RESIN USING SAME**

MEHRSTUFIGES HARZBEREICHENÄTZVERFAHREN UND PLATTIERUNGSVERFAHREN AUF HARZ DAMIT

PROCÉDÉ DE GRAVURE DE SURFACE DE RÉSINE À PLUSIEURS ÉTAPES, ET PROCÉDÉ DE PLACAGE SUR UNE RÉSINE METTANT EN UVRE LEDIT PROCÉDÉ

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(73) Proprietor: **JCU Corporation**

Tokyo 1100015 (JP)

(72) Inventors:

- **KURAMOCHI, Yasuyuki**
Michigan 48393 (US)
- **ISHIZUKA, Hiroshi**
Kawasaki-shi
Kanagawa 215-0033 (JP)

- **IZUMITANI, Miyoko**
Kawasaki-shi
Kanagawa 215-0033 (JP)

(74) Representative: **Blodig, Wolfgang**

Wächtershäuser & Hartz
Patentanwaltspartnerschaft mbB
Weinstrasse 8
80333 München (DE)

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Description

Technical Field

5 **[0001]** The present invention relates to a multi-stage resin surface etching method, and a plating method on a resin using the same.

Background Art

10 **[0002]** Conventionally, it is known that when a plastic surface is subjected to a metallization treatment by plating, in order to enhance adhesion of the plastic surface to a plating film, an etching treatment for roughening the plastic surface with a mixed liquid of chromic acid and sulfuric acid is performed before a plating treatment.

[0003] However, in the etching treatment, the operation is performed at a high temperature of 60°C or higher using harmful hexavalent chromium, and therefore, there was a problem that the operation environment is deteriorated, and further, attention is needed also for a waste water treatment thereof.

15 **[0004]** Further, recently, a technique for etching a plastic surface using permanganic acid has also been reported (PTL 1), however, permanganic acid may sometimes be promptly decomposed depending on use conditions, and it was sometimes problematic for industrial use.

[0005] Thereafter, in order to suppress decomposition of the etching solution using permanganic acid described above, a composition for an etching treatment containing permanganic acid, a specific inorganic acid, and further one component selected from a halogen oxoacid, a halogen oxoacid salt, a persulfate, and a bismuthate has also been reported (PTL 2), however, the above-mentioned component is used in a large amount, and therefore, the cost is high, and this was also problematic for industrial use.

20 **[0006]** Further, in order to suppress decomposition of the etching solution using permanganic acid described above, a technique in which a resin is swollen with an aqueous dispersion or an aqueous solution containing a specific organic compound, and thereafter the resin is brought into contact with an aqueous solution containing permanganic acid, and further brought into contact with an aqueous solution containing an acid or the like has also been reported (PTL 3), however, a swelling step is essential, adhesion of plating after etching is sometimes low, etc., and this was also problematic for industrial use.

25 **[0006]** Further, in order to suppress decomposition of the etching solution using permanganic acid described above, a technique in which a resin is swollen with an aqueous dispersion or an aqueous solution containing a specific organic compound, and thereafter the resin is brought into contact with an aqueous solution containing permanganic acid, and further brought into contact with an aqueous solution containing an acid or the like has also been reported (PTL 3), however, a swelling step is essential, adhesion of plating after etching is sometimes low, etc., and this was also problematic for industrial use.

30 **[0006]** Further, in order to suppress decomposition of the etching solution using permanganic acid described above, a technique in which a resin is swollen with an aqueous dispersion or an aqueous solution containing a specific organic compound, and thereafter the resin is brought into contact with an aqueous solution containing permanganic acid, and further brought into contact with an aqueous solution containing an acid or the like has also been reported (PTL 3), however, a swelling step is essential, adhesion of plating after etching is sometimes low, etc., and this was also problematic for industrial use.

Citation List

Patent Literature

35 **[0007]**

PTL 1: WO 2005/094394

PTL 2: Japanese Patent No. 5177426

PTL 3: JP-A-2007-100174

40 **[0008]** EP 2657367 A1 discloses a pre-etching composition and an etching process for plastic substrates.

[0009] JP H08 337880 A discloses a method for roughening an adhesive layer for electroless plating made of an amino resin and a heat resistant resin.

45 Summary of Invention

Technical Problem

50 **[0010]** An object of the present invention is to provide a novel technique that is a resin etching technique without using chromic acid and can be operated at an industrial level.

Solution to Problem

55 **[0011]** The present inventors made intensive studies for achieving the above object, and as a result, they unexpectedly found that by dividing an etching step using an oxidizing agent for a resin into two stages and further repeatedly performing the step, a resin surface can be sufficiently etched even without performing a resin swelling step, and therefore, by the subsequent plating, high adhesion is obtained, and thus completed the present invention.

[0012] The present invention relates to the subject matter of claims 1 to 3. That is, the present invention is directed to

a resin surface etching method, characterized in that, in etching a resin surface, the method consists of step (a), step (b) and step (c), wherein in step (c) the set of steps (a) and (b) is repeated one or more times:

(a) a step of treating the resin surface with a solution containing an oxidizing agent and adsorbing the oxidizing agent on the resin surface, wherein the oxidizing agent used is permanganic acid or a salt thereof; and
 (b) a step of activating the oxidizing agent adsorbed on the resin surface in the step (a), wherein the activation of the oxidizing agent is performed by a treatment with a solution containing one type or two or more types of activating agents selected from the group consisting of sulfuric acid, phosphoric acid, hydrochloric acid, nitric acid, methanesulfonic acid, hydrogen peroxide, peroxodisulfate, periodic acid, perchloric acid, and perbromic acid, wherein the content of the activating agent in the solution is 0.05 mol/L or more,

wherein after step (a) water washing may be performed, and after step (b) a neutralization and reduction treatment or a conditioner treatment may be performed, and

wherein the resin is selected from the group consisting of acrylonitrile-butadiene-styrene (ABS), polycarbonate/acrylonitrile-butadiene-styrene (PC/ABS), acrylonitrile-styrene-acrylate (ASA), silicon-based composite rubber-acrylonitrile-styrene (SAS), NORYL, polypropylene, polycarbonate (PC), acrylonitrile-styrene, polyacetate, polystyrene, polyethylene, polyether ketone, polyethylene terephthalate, polybutylene terephthalate, polysulfone, polyether ether sulfone, polyether imide, modified polyphenylene ether, polyphenylene sulfide, polyamide, polyimide, liquid crystal polymers, and copolymers of these polymers.

[0013] Further, the present invention is directed to a plating method on a resin, characterized in that, in plating a resin, the plating is performed after the resin is etched by the above-mentioned resin surface etching method.

Advantageous Effects of Invention

[0014] The resin surface etching method of the present invention can suppress decomposition of an oxidizing agent used for etching. Further, in the resin surface etching method of the present invention, the etching step is repeatedly performed, however, etching can be more efficiently performed in a shorter time than when the etching step is performed in one stage for a long time. In addition, by the resin surface etching method of the present invention, the resin surface can be sufficiently etched, and therefore, it is not necessary to perform a resin swelling step that was conventionally required.

[0015] Therefore, when a resin is plated after performing the above-mentioned etching method, a plated product that has high adhesion and can particularly withstand also a severe heat shock test can be obtained.

Description of Embodiments

[0016] In the resin surface etching method of the present invention (hereinafter referred to as "method of the present invention"), one set of the following steps (a) and (b) is performed two or more times. Incidentally, even if sufficient etching cannot be achieved by a certain number of sets, sufficient etching can be achieved by increasing the number of sets.

(a) a step of treating the resin surface with a solution containing an oxidizing agent and adsorbing the oxidizing agent on the resin surface

(b) a step of activating the oxidizing agent adsorbed on the resin surface in the step (a)

[0017] Incidentally, the resin may be subjected to a treatment such as degreasing, or surface conditioning, before performing the method of the present invention. However, a swelling step for facilitating resin etching is not performed. Water washing or hot water washing may be performed before or after the treatment such as degreasing, or surface conditioning.

[0018] The resin that can be treated with the etching solution of the present invention is selected from the group consisting of acrylonitrile-butadiene-styrene (ABS), polycarbonate/acrylonitrile-butadiene-styrene (PC/ABS), acrylonitrile-styrene-acrylate (ASA), silicon-based composite rubber-acrylonitrile-styrene (SAS), NORYL, polypropylene, polycarbonate (PC), acrylonitrile-styrene, polyacetate, polystyrene, polyethylene, polyether ketone, polyethylene terephthalate, polybutylene terephthalate, polysulfone, polyether ether sulfone, polyether imide, modified polyphenylene ether, polyphenylene sulfide, polyamide, polyimide, liquid crystal polymers, and copolymers of the above-mentioned respective polymers. Among these resins, particularly ABS and PC/ABS are preferred. Further, the shape of the resin is not particularly limited.

[0019] The oxidizing agent used in the step (a) of the method of the present invention is permanganic acid or a salt

thereof, examples thereof include permanganates such as potassium permanganate, or sodium permanganate. Optionally manganese salts such as manganese sulfate, manganese nitrate, manganese carbonate, manganese chloride, manganese acetate, manganese dioxide, sodium manganate, or potassium manganite may be used in addition. Further, among these oxidizing agents, one type or two or more types can be used.

5 **[0020]** As the solution containing the oxidizing agent, for example, a solution obtained by dissolving the oxidizing agent in a solvent such as water is exemplified. The content of the oxidizing agent in this solution is not particularly limited, but is, for example, 0.0005 mol/L or more, preferably from 0.005 to 2.0 mol/L.

10 **[0021]** Further, in the solution containing the oxidizing agent, a pH buffer agent or a surfactant may be incorporated in such an amount that the performance of the pH buffer agent or the surfactant is exhibited as long as the oxidizing action of this solution is not impaired. Incidentally, the pH of the solution containing the oxidizing agent is not particularly limited, but is preferably from 3.0 to 10.0.

[0022] The pH buffer agent is not particularly limited, however, examples thereof include phosphates, citrates, borates, carbonates, acetates, diethylbarbiturates, tris(hydroxymethyl)aminomethane, hydroxyethylpiperazine ethanesulfonic acid, or ethylenediaminetetraacetic acid. Among these pH buffer agents, one type or two or more types can be used.

15 **[0023]** The surfactant is not particularly limited, however, examples thereof include amine salt type surfactants, quaternary amine salt type surfactants, amino acid type surfactants, betaine type surfactants, carboxylate type surfactants, sulfonate type surfactants, sulfuric acid ester salt type surfactants, phosphoric acid ester salt type surfactants, ether type surfactants, ester type surfactants, nitrogen-containing type surfactants, or fluorine-containing type surfactants. Among these surfactants, one type or two or more types can be used. By using the surfactant, the throwing power of plating can be improved.

20 **[0024]** A method for treating the resin with a solution containing the oxidizing agent and adsorbing the oxidizing agent on the resin surface is not particularly limited, and for example, the resin may be immersed in the solution containing the oxidizing agent. Conditions for immersing the resin are also not particularly limited, and for example, the resin may be immersed in the solution at 0 to 100°C, preferably at 60 to 70°C for 30 seconds or more, preferably for 1 to 5 minutes.

25 **[0025]** After adsorbing the oxidizing agent on the resin surface in the step (a), water washing may be performed as needed. Thereafter, the oxidizing agent adsorbed on the resin surface is activated in the step (b).

[0026] A method for activating the oxidizing agent is not particularly limited, and for example, the resin may be immersed in a solution containing one type or two or more types of activating agents.

30 **[0027]** The activating agents are selected from the group consisting of sulfuric acid, hydrochloric acid, nitric acid, phosphoric acid, methanesulfonic acid, hydrogen peroxide, peroxydisulfate, periodic acid, perchloric acid, and perbromic acid. Among these activating agents, hydrogen peroxide, phosphoric acid, and sulfuric acid are preferred. Such an activating agent is prepared as a solution by being dissolved in a solvent such as water. The content of the activating agent in this solution is 0.05 mol/L or more, preferably from 0.5 to 17 mol/L.

35 **[0028]** Further, in the solution containing the activating agent, a surfactant may be incorporated in such an amount that the performance of the surfactant is exhibited as long as the activating action of this solution is not impaired. The surfactant is not particularly limited, however, examples thereof include amine salt type surfactants, quaternary amine salt type surfactants, amino acid type surfactants, betaine type surfactants, carboxylate type surfactants, sulfonate type surfactants, sulfuric acid ester salt type surfactants, phosphoric acid ester salt type surfactants, ether type surfactants, ester type surfactants, nitrogen-containing type surfactants, and fluorine-containing type surfactants. Among these surfactants, one type or two or more types can be used. By using the surfactant, the throwing power of plating can be improved.

40 **[0029]** A method for activating the oxidizing agent adsorbed on the resin surface is not particularly limited, and for example, when a solution containing the activating agent is used, the resin may be immersed in the solution at, for example, 0 to 100°C, more preferably at 60 to 70°C for 30 seconds or more, more preferably for 1 to 5 minutes.

45 **[0030]** The above-mentioned steps (a) and (b) constitute one set, however, after this step (b), a neutralization and reduction treatment, or a conditioner treatment may be performed as needed. Further, each of the steps (a) and (b) is performed for preferably 30 seconds or more, more preferably 1 to 5 minutes.

[0031] By the method of the present invention described above, a resin surface can be etched. Incidentally, the method of the present invention can be used for etching a resin surface in a conventionally known plating method on a resin, and in the other steps, a conventionally known plating method on a resin can be used.

50 **[0032]** Examples of the conventionally known plating method on a resin include an electroless plating method and a direct plating method.

[0033] Hereinafter, a plating method on a resin using the method of the present invention will be described.

55 **[0034]** To a resin etched by the method of the present invention, subsequently, a catalyst is imparted using a catalyst imparting treatment solution. This catalyst imparting treatment solution is not particularly limited as long as it is generally used for imparting a catalyst in a plating step, but is preferably a solution containing a noble metal, more preferably a solution containing palladium, and particularly preferably a palladium/tin mixed colloidal catalyst solution. In order to impart such a catalyst to the resin surface, the treatment may be performed by setting the temperature of the catalyst imparting treatment solution to 10 to 60°C, preferably 20 to 50°C and immersing the resin therein for 1 to 20 minutes,

preferably 2 to 5 minutes.

[0035] The resin surface to which the catalyst is imparted in this manner is subsequently subjected to metal plating such as electroless metal plating or metal electroplating (direct plating), thereby metallizing the resin surface.

[0036] When electroless metal plating is used for metallization of the resin surface, after the catalyst is imparted using the catalyst imparting treatment solution, a treatment may be further performed using an activation treatment solution containing hydrochloric acid or sulfuric acid. The concentration of hydrochloric acid or sulfuric acid in this activation treatment solution is 0.5 mol/L or more, preferably from 1 to 4 mol/L. In order to treat the resin surface with such an activation treatment solution, the treatment may be performed by setting the temperature of the activation treatment solution to 0 to 60°C, preferably 30 to 45°C and immersing the resin therein for 1 to 20 minutes, preferably 2 to 5 minutes.

[0037] The resin subjected to the catalyst impartment and activation treatments as described above is subsequently subjected to an electroless metal plating treatment. The electroless metal plating treatment can be performed according to a usual method using a known electroless metal plating solution such as an electroless nickel plating solution, an electroless copper plating solution, or an electroless cobalt plating solution. Specifically, when the resin surface is subjected to a plating treatment with an electroless nickel plating solution, the treatment may be performed by immersing the resin in the electroless nickel plating solution at pH 8 to 10 and at a liquid temperature of 30 to 50°C for 5 to 15 minutes.

[0038] Further, when metal electroplating (direct plating) is used for metallization of the resin surface, after imparting a catalyst using a catalyst imparting treatment solution, a treatment may be further performed using an activation treatment solution containing copper ions at pH 7 or higher, preferably 12 or higher. A source of the copper ions contained in this activation treatment solution is not particularly limited, and for example, copper sulfate is exemplified. In order to treat the resin surface with the activation treatment solution, the treatment may be performed by setting the temperature of the activation treatment solution to 0 to 60°C, preferably 30 to 50°C and immersing the resin therein for 1 to 20 minutes, preferably 2 to 50 minutes.

[0039] The resin subjected to the catalyst impartment and activation treatments as described above is subsequently immersed in a widely used copper electroplating bath such as a copper sulfate bath, and may be subjected to a treatment under usual conditions, for example, at 1 to 5 A/dm² for 2 to 10 minutes.

[0040] Further, the plastic surface metallized by subjecting the resin surface to metal plating such as electroless plating or metal electroplating as described above can also be additionally subjected to various types of copper electroplating or nickel electroplating or chromium electroplating according to need.

[0041] Incidentally, after performing the method of the present invention, water washing or hot water washing may be performed between respective steps.

[0042] The thus obtained resin plating has high adhesion.

Examples

[0043] Hereinafter, the present invention will be more specifically described by showing Examples and Comparative Examples. However, the invention is by no means limited to the description thereof.

Example 1

<Formation of Electroless Nickel Plating>

[0044] As a sample, a test piece (3001M, manufactured by UMG ABS, Ltd.) of an ABS resin of 50 × 100 × 3 mm was used. This sample was immersed in degreasing washing solutions PC-1 and PC-2 (manufactured by JCU Corporation) at 60°C for 10 minutes, and subsequently immersed in a surface conditioning solution at 50°C containing 10 ml/L ENILEX WE (manufactured by JCU Corporation) for 10 minutes.

[0045] The sample subjected to degreasing and surface conditioning was treated in an etching step shown in Table 1, and further immersed in a conditioner (catalyst impartment enhancing) treatment solution D-POP CDV (manufactured by JCU Corporation) at 25°C for 1 minute.

[0046] Incidentally, the etching solution used in the etching step shown in Table 1 is as follows.

Chromic acid etching (conventional method)

anhydrous chromic acid: 3.8 mol/L

sulfuric acid: 3.8 mol/L

liquid temperature: 68°C

Method of the present invention

Step (a)

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potassium permanganate: 0.3 mol/L
 fluorine-containing type surfactant MISTSHUT PF (manufactured by JCU Corporation): 2 ml/L
 boric acid/sodium tetraborate buffer solution: 10 ml/L
 liquid temperature: 68°C, pH: 6.5

Step (b)

sulfuric acid: 10 mol/L
 fluorine-containing type surfactant MISTSHUT PF (manufactured by JCU Corporation): 2 ml/L
 liquid temperature: 68°C, pH: 1.0 or lower

[0047] Subsequently, the sample was immersed in a palladium/tin mixed colloidal catalyst solution at 35°C containing 20 ml/L CT-580 (manufactured by JCU Corporation) and 2.5 mol/L hydrochloric acid for 4 minutes, thereby imparting the catalyst on the ABS resin. The sample to which the catalyst was imparted was immersed in an activation treatment solution at 35°C composed of 1.2 mol/L hydrochloric acid for 4 minutes, thereby activating the catalyst, and subsequently immersed in an electroless nickel plating solution ENILEX NI-100 (manufactured by JCU Corporation) at pH 8.8 and 35°C for 10 minutes, thereby performing electroless nickel plating until the film thickness reached 0.5 μm on the ABS resin.

<Peel Strength Measurement and Sample Preparation Method> (JIS H 8630 Appendix 6)

[0048] After the sample subjected to electroless nickel plating was sufficiently washed by water washing or hot water washing, the sample was immersed in an acid active solution V-345 (manufactured by JCU Corporation) at room temperature for 1 minute. Subsequently, according to JIS H 8630 Appendix 6, copper sulfate plating EP-30 (manufactured by JCU Corporation) was performed until the film thickness reached 20 μm. Thereafter, the resulting material was annealed at 70°C for 1 hour, and an adhesion strength was measured using a tensile strength tester AGS-H 500N (manufactured by Shimadzu Corporation).

<Heat Shock Test and Sample Preparation Method>

[0049] After the sample subjected to electroless nickel plating was sufficiently washed by water washing or hot water washing, the sample was immersed in an acid active solution V-345 (manufactured by JCU Corporation) at room temperature for 1 minute. Subsequently, copper sulfate plating CU-BRITE EP-30 (manufactured by JCU Corporation) was performed until the film thickness reached 20 μm by an electroplating method. Further, semi-glossy nickel plating CF-24T (manufactured by JCU Corporation) was performed until the film thickness reached 10 μm, and further, glossy nickel plating #88 (manufactured by JCU Corporation) was performed until the film thickness reached 10 μm, and further, microporous nickel plating MP-309 (manufactured by JCU Corporation) was performed until the film thickness reached 1 μm. Finally, glossy chromium plating EBACHROM E-300 (manufactured by JCU Corporation) was performed until the film thickness reached 0.2 μm, whereby respective plating films were sequentially formed. Thereafter, the resulting material was annealed at 70°C for 1 hour.

[0050] The above sample was subjected to a 40-cycle (cyc) or 80-cycle heat shock test in which a step of maintaining the sample at -30°C for 30 minutes and maintaining the sample at 70°C for 30 minutes was regarded as one cycle. The sample in which swelling did not occur in the plating film was evaluated as "A", and the sample in which swelling occurred was evaluated as "B".

<Results>

[0051]

[Table 1]

	Number of etching steps	Treatment time		Peel strength (kgf/cm)	Heat shock test	
		Step (a)	Step (b)		40 eye	80 eye
Comparative Method 1	chromic acid etching for 2 min			1.1	B	B
Comparative Method 2	chromic acid etching for 10 min			1.2	A	A

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(continued)

	Number of etching steps	Treatment time		Peel strength (kgf/cm)	Heat shock test	
		Step (a)	Step (b)		40 eye	80 eye
5 Comparative Method 3	1	2	2	1.1	B	B
10 Comparative Method 4	1	10	20	1.0	B	B
15 Comparative Method 5	1	20	20	0.9	B	B
Example Method 1	2	2	2	1.2	A	B
Example Method 2	5	2	2	1.1	A	A
Example Method 3	10	2	2	1.2	A	A

[0052] It was found that the adhesion is improved by extending the treatment time in the case of chromic acid etching of the conventional method, however, the adhesion is not improved even if the treatment time is simply extended in the etching step of the method of the present invention. It was found that the adhesion is improved by repeatedly performing the etching step even in a short treatment time. Incidentally, even in the case of Example Method 1, by repeating the set of the steps (a) and (b) five times, "A" was obtained in the severer 80-cycle heat shock test.

25 Example 2

[0053] Electroless nickel plating was performed in the same manner as in Example 1 except that, in Example Method 1 of Example 1, the pH of the etching solution used in the step (a) was changed as shown in Table 2, and as the pH buffer solution, a buffer solution shown in Table 3 was used according to the pH. Incidentally, in the adjustment of the pH, sodium hydroxide and sulfuric acid were used. Further, for the electroless nickel plating, peel strength measurement and a heat shock test were performed in the same manner as in Example 1. The results are shown in Table 2.

[Table 2]

	pH	Peel strength (kgf/cm)	Heat shock test (40 cyc)
35 Example Method 4*	13.0	1.1	A
Example Method 5	12.0	1.2	A
40 Example Method 6	9.0	1.1	A
Example Method 7	6.5	1.2	A
Example Method 8	5.0	1.3	A
Example Method 9	3.0	1.1	A
45 Example Method 10	1.0	1.2	A
*: The set of the steps (a) and (b) was performed five times.			

[Table 3]

pH	pH buffer solution
10.0 or higher	carbonate/bicarbonate buffer solution
5.5 to 10.0	boric acid/sodium tetraborate buffer solution
2.5 to 5.5	acetic acid/sodium acetate buffer solution
2.5 or lower	phosphoric acid/sodium dihydrogen phosphate buffer solution

[0054] In the method of the present invention, there was no problem at any pH.

Example 3

5 [0055] Electroless nickel plating was performed in the same manner as in Example 1 except that, in Example Method 1 of Example 1, the pH buffer agent was removed from the solution used in the steps (a) and (b). When this electroless nickel plating was subjected to peel strength measurement and a heat shock test in the same manner as in Example 1, the same results as in Example Method 1 were obtained.

10 Example 4

[0056] Electroless nickel plating was performed in the same manner as in Example 1 except that, in Example Method 1 of Example 1, a test piece (3001M, manufactured by UMG ABS, Ltd.) of an ABS resin of 50 × 180 × 3 mm in a three-dimensional shape (a shape that makes air easy to remain) was used as the sample, and a surfactant shown in Table 4 was used in the solution used in the steps (a) and (b). The appearance of the electroless nickel plating was evaluated by visual observation. The results are shown in Table 4.

[Table 4]

	Surfactant	Appearance	
20	Example Method 11*	non	good
	Example Method 12	fluorine-containing type surfactant MISTSHUT PF (manufactured hv JCU Corporation): 2 ml/L	good
25	Example Method 13	cationic surfactant PB-117 (manufactured hv JCU Corporation): 2 ml/L	good
	Example Method 14	anionic surfactant #82 (manufactured hv JCU Corporation): 2 ml/L	good
	Example Method 15	nonionic surfactant CHT-111A (manufactured hv JCU Corporation): 2 ml/L	good
30	Example Method 16	amphoteric surfactant Gulanlubu SE (manufactured hv JCU Corporation): 2 ml/L	good
*: The set of the steps (a) and (b) was performed five times.			

35 [0057] In the method of the present invention, plating was performed on the resin in a three-dimensional shape with a small number of times by using a surfactant.

Industrial Applicability

40 [0058] According to the method of the present invention, a resin surface can be etched, and therefore, the method can be used in a conventionally known plating method on a resin.

Claims

45 1. A resin surface etching method, **characterized in that**, in etching a resin surface, the method consists of step (a), step (b) and step (c), as well as optional steps (d), (e) and (f), wherein in step (c) the set of steps (a) and (b) is repeated one or more times:

50 (a) a step of treating the resin surface with a solution containing an oxidizing agent and adsorbing the oxidizing agent on the resin surface, wherein the oxidizing agent used is permanganic acid or a salt thereof; and
 (b) a step of activating the oxidizing agent adsorbed on the resin surface in the step (a), wherein the activation of the oxidizing agent is performed by a treatment with a solution containing one type or two or more types of activating agents selected from the group consisting of sulfuric acid, phosphoric acid, hydrochloric acid, nitric acid, methanesulfonic acid, hydrogen peroxide, peroxodisulfate, periodic acid, perchloric acid, and perbromic acid, wherein the content of the activating agent in the solution is 0.05 mol/L or more,
 55 wherein after step (a) water washing step (d) may be performed, and after step (b) a neutralization and reduction treatment step (e) or a conditioner treatment step (f) may be performed and,
 wherein the resin is selected from the group consisting of acrylonitrile-butadiene-styrene (ABS), polycar-

bonate/acrylonitrile-butadiene-styrene (PC/ABS), acrylonitrile-styrene-acrylate (ASA), silicon-based composite rubber-acrylonitrile-styrene (SAS), polypropylene, polycarbonate (PC), acrylonitrile-styrene polyacetate, polystyrene, polyethylene, polyether ketone, polyethylene terephthalate, polybutylene terephthalate, polysulfone, polyether ether sulfone, polyether imide, modified polyphenylene ether, polyphenylene sulfide, polyimide, liquid crystal polymers, and copolymers of these polymers.

- 5
2. The resin surface etching method according to claim 1, wherein each of the steps (a) and (b) is performed for 30 seconds or more.
- 10
3. A plating method on a resin, **characterized in that**, in plating a resin, the plating is performed after the resin is etched by the resin surface etching method according to claim 1 or 2.

Patentansprüche

- 15
1. Verfahren zum Ätzen von Harzoberflächen, **dadurch gekennzeichnet, dass** das Verfahren beim Ätzen einer Harzoberfläche aus Schritt (a), Schritt (b) und Schritt (c), sowie den optionalen Schritten (d), (e) und (f) besteht, wobei in Schritt (c) die Gruppe der Schritte (a) und (b) ein oder mehrere Male wiederholt wird:

20 (a) einen Schritt des Behandelns der Harzoberfläche mit einer Lösung, die ein Oxidationsmittel enthält, und des Adsorbierens des Oxidationsmittels auf der Harzoberfläche, wobei das verwendete Oxidationsmittel Permangansäure oder ein Salz davon ist; und

(b) einen Schritt des Aktivierens des Oxidationsmittels, das auf der Harzoberfläche im Schritt (a) adsorbiert wurde, wobei die Aktivierung des Oxidationsmittels durch eine Behandlung mit einer Lösung durchgeführt wird, die einen Typ oder zwei oder mehr Typen von Aktivierungsmitteln enthält, die aus der Gruppe ausgewählt sind, die aus Schwefelsäure, Phosphorsäure, Salzsäure, Salpetersäure, Methansulfonsäure, Wasserstoffperoxid, Peroxodisulfat, Perjodsäure, Perchlorsäure und Perbromsäure besteht, wobei der Gehalt des Aktivierungsmittels in der Lösung 0,05 mol/L oder mehr beträgt,

25 wobei nach Schritt (a) ein Waschschrift (d) mit Wasser durchgeführt werden kann und nach Schritt (b) ein Neutralisierungs- und Reduktionsbehandlungsschritt (e) oder ein Konditionierungsbehandlungsschritt (f) durchgeführt werden kann, und

30 wobei das Harz ausgewählt ist aus der Gruppe bestehend aus Acrylnitril-Butadien-Styrol (ABS), Polycarbonat/Acrylnitril-Butadien-Styrol (PC/ABS), Acrylnitril-Styrol-Acrylat (ASA), Verbundkautschuk auf Silikonbasis-Acrylnitril-Styrol (SAS), Polypropylen, Polycarbonat (PC), Acrylnitril-Styrol, Polyacetat, Polystyrol, Polyethylen, Polyetherketon, Polyethylenterephthalat, Polybutylenterephthalat, Polysulfon, Polyetherethersulfon, Polyetherimid, modifizierter Polyphenylenether, Polyphenylensulfid, Polyimid, Flüssigkristallpolymere und Copolymere dieser Polymere.

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2. Verfahren zum Ätzen von Harzoberflächen nach Anspruch 1, wobei jeder der Schritte (a) und (b) für 30 Sekunden oder länger durchgeführt wird.
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3. Verfahren zum Plattieren eines Harzes, **dadurch gekennzeichnet, dass** beim Plattieren eines Harzes das Plattieren durchgeführt wird, nachdem das Harz durch das Verfahren zum Ätzen der Harzoberfläche nach Anspruch 1 oder 2 geätzt worden ist.

Revendications

- 45
1. Procédé de gravure de surface de résine, **caractérisé en ce que**, lors de la gravure d'une surface de résine, le procédé consiste en une étape (a), une étape (b) et une étape (c), ainsi qu'en des étapes (d), (e) et (f) optionnelles, dans lequel à l'étape (c) l'ensemble des étapes (a) et (b) est répété une ou plusieurs fois :

50 (a) une étape de traitement de la surface de résine avec une solution contenant un agent oxydant et d'adsorption de l'agent oxydant sur la surface de résine, dans lequel l'agent oxydant utilisé est l'acide permanganique ou un sel de celui-ci ; et

55 (b) une étape d'activation de l'agent oxydant adsorbé sur la surface de résine à l'étape (a), dans lequel l'activation de l'agent oxydant est réalisée par un traitement avec une solution contenant un type ou deux types ou plus d'agents d'activation sélectionnés parmi le groupe constitué de l'acide sulfurique, de l'acide phosphorique, de

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l'acide chlorhydrique, de l'acide nitrique, de l'acide méthanesulfonique, du peroxyde d'hydrogène, du peroxydisulfate, de l'acide périodique, de l'acide perchlorique, et de l'acide perbromique, dans lequel la teneur en agent d'activation dans la solution est de 0,05 mol/l ou plus,

dans lequel après l'étape (a) l'étape (d) de lavage à l'eau peut être réalisée, et après l'étape (b) une étape (e) de traitement de neutralisation et de réduction ou une étape (f) de traitement de conditionnement peut être réalisée

et,

dans lequel la résine est sélectionnée parmi le groupe constitué d'acrylonitrile-butadiène-styrène (ABS), de polycarbonate/acrylonitrile-butadiène-styrène (PC/ABS), d'acrylonitrile-styrène-acrylate (ASA), de caoutchouc composite à base de silicium-acrylonitrile-styrène (SAS), de polypropylène, de polycarbonate (PC), d'acrylonitrile-styrène, de polyacétate, de polystyrène, de polyéthylène, de polyéther cétone, de téréphtalate de polyéthylène, de téréphtalate de polybutylène, de polysulfone, de polyéther éther sulfone, de polyéther imide, d'éther de polyphénylène modifié, de sulfure de polyphénylène, de polyimide, de polymères à cristaux liquides, et de copolymères de ces polymères.

2. Procédé de gravure de surface de résine selon la revendication 1, dans lequel chacune des étapes (a) et (b) est réalisée pendant 30 secondes ou plus.

3. Procédé de placage sur une résine, **caractérisé en ce que**, lors du placage d'une résine, le placage est réalisé après que la résine est gravée par le procédé de gravure de surface selon la revendication 1 ou 2.

REFERENCES CITED IN THE DESCRIPTION

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