



(11) **EP 3 633 066 A1**

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

(43) Date of publication:
08.04.2020 Bulletin 2020/15

(51) Int Cl.:
C23C 18/30 *(2006.01)*

(21) Application number: **18810479.8**

(86) International application number:
PCT/JP2018/010095

(22) Date of filing: **15.03.2018**

(87) International publication number:
WO 2018/220946 (06.12.2018 Gazette 2018/49)

(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

(72) Inventors:
• **KURAMOCHI Yasuyuki**
Michigan 48393 (US)
• **ISHIZUKA Hiroshi**
Kawasaki-shi
Kanagawa 215-0033 (JP)
• **IZUMITANI Miyoko**
Kawasaki-shi
Kanagawa 215-0033 (JP)

(30) Priority: **01.06.2017 PCT/JP2017/020426**

(71) Applicant: **JCU Corporation**
Tokyo 110-0015 (JP)

(74) Representative: **Blodig, Wolfgang**
Wächtershäuser & Hartz
Patentanwaltspartnerschaft mbB
Weinstrasse 8
80333 München (DE)

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

(57) A novel technique that is a resin etching technique without using chromic acid and can be operated at an industrial level is provided by a resin surface etching method characterized in that, in etching a resin surface, one set of the following steps (a) and (b) is performed two or more times without performing a resin swelling

step: (a) a step of treating the resin surface with a solution containing an oxidizing agent and adsorbing the oxidizing agent on the resin surface, and (b) a step of activating the oxidizing agent adsorbed on the resin surface in the step (a).

EP 3 633 066 A1

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.

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

Citation List

Patent Literature

35 **[0007]**

PTL 1: WO 2005/094394

PTL 2: Japanese Patent No. 5177426

PTL 3: JP-A-2007-100174

40

Summary of Invention

Technical Problem

45 **[0008]** 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

50 **[0009]** 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.

55 **[0010]** That is, the present invention is directed to a resin surface etching method, characterized in that, in etching a resin surface, one set of the following steps (a) and (b) is performed two or more times without performing a resin swelling step:

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

agent on the resin surface; and

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

[0011] 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 without performing a resin swelling step.

Advantageous Effects of Invention

[0012] 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.

[0013] 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

[0014] 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)

[0015] Incidentally, the resin may be subjected to a treatment such as degreasing, surface conditioning, and the like 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, surface conditioning, and the like.

[0016] The resin that can be treated with the etching solution of the present invention is not particularly limited, but examples thereof include 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, polyamide, aromatic polyamides, polyethylene, polyether ketone, polyethylene terephthalate, polybutylene terephthalate, polysulfone, polyether ether sulfone, polyether imide, modified polyphenylene ether, polyphenylene sulfide, polyamide, polyimide, epoxy resins, liquid crystal polymers, and the like, and copolymers of the above-mentioned respective polymers, and the like. Among these resins, particularly ABS and PC/ABS are preferred. Further, the shape of the resin is also not particularly limited.

[0017] The oxidizing agent used in the step (a) of the method of the present invention is not particularly limited, however, examples thereof include permanganates such as potassium permanganate, sodium permanganate, and the like, and manganese salts such as manganese sulfate, manganese nitrate, manganese carbonate, manganese chloride, manganese acetate, manganese dioxide, sodium manganate, potassium manganite, and the like. Among these oxidizing agents, particularly permanganates are preferred. Further, among these oxidizing agents, one type or two or more types can be used.

[0018] 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.

[0019] 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.

[0020] The pH buffer agent is not particularly limited, however, examples thereof include phosphates, citrates, borates, carbonates, acetates, diethylbarbiturates, tris(hydroxymethyl)aminomethane, hydroxyethylpiperazine ethanesulfonic acid, ethylenediaminetetraacetic acid, and the like. Among these pH buffer agents, one type or two or more types can be used.

[0021] 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, fluorine-containing type surfactants, and the like. 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.

[0022] 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.

[0023] 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).

[0024] 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 selected from the group consisting of an inorganic acid, an organic acid, hydrogen peroxide, a halogen oxoacid, a halogen oxoacid salt, and a persulfate.

[0025] Among the activating agents, as the inorganic acid, for example, sulfuric acid, hydrochloric acid, nitric acid, phosphoric acid, hydrofluoric acid, and the like are exemplified, as the organic acid, for example, acetic acid, methanesulfonic acid, and the like are exemplified, as the halogen oxoacid and the halogen oxoacid salt, for example, potassium perchlorate, sodium periodate, perbromic acid, and the like are exemplified, and as the persulfate, for example, sodium peroxodisulfate, ammonium peroxodisulfate, and the like are exemplified. 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 not particularly limited, but is, for example, 0.05 mol/L or more, preferably from 0.5 to 17 mol/L.

[0026] 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.

[0027] 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.

[0028] The above-mentioned steps (a) and (b) constitute one set, however, after this step (b), a neutralization and reduction treatment, a conditioner treatment, or the like 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.

[0029] 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.

[0030] Examples of the conventionally known plating method on a resin include an electroless plating method and a direct plating method.

[0031] Hereinafter, a plating method on a resin using the method of the present invention will be described.

[0032] 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.

[0033] 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.

[0034] 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.

[0035] 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. [0036] 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.

[0037] 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.

[0038] 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.

[0039] Incidentally, after performing the method of the present invention, water washing or hot water washing may be performed between respective steps.

[0040] The thus obtained resin plating has high adhesion.

Examples

[0041] 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>

[0042] 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.

[0043] 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.

[0044] Incidentally, the etching solution used in the etching step shown in Table 1 is as follows.

[0045] 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

[0046]

Step (a) 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 cyc	80 cyc
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
Comparative Method 3	1	2	2	1.1	B	B
Comparative Method 4	1	10	20	1.0	B	B
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.

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)
Example Method 4*	13.0	1.1	A
Example Method 5	12.0	1.2	A
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
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

[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.

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 $50 \times 180 \times 3$ 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
Example Method 11*	non	good
Example Method 12	fluorine-containing type surfactant MISTSHUT PF (manufactured by JCU Corporation): 2 ml/L	good

(continued)

	Surfactant	Appearance
Example Method 13	cationic surfactant PB-117 (manufactured by JCU Corporation): 2 ml/L	good
Example Method 14	anionic surfactant #82 (manufactured by JCU Corporation): 2 ml/L	good
Example Method 15	nonionic surfactant CHT-111A (manufactured by JCU Corporation): 2 ml/L	good
Example Method 16	amphoteric surfactant Gulanlubu SE (manufactured by JCU Corporation): 2 ml/L	good
*: The set of the steps (a) and (b) was performed five times.		

[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

[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

1. A resin surface etching method, **characterized in that**, in etching a resin surface, one set of the following steps (a) and (b) is performed two or more times without performing a resin swelling step:
 - (a) a step of treating the resin surface with a solution containing an oxidizing agent and adsorbing the oxidizing agent on the resin surface; and
 - (b) a step of activating the oxidizing agent adsorbed on the resin surface in the step (a).
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.
3. The resin surface etching method according to claim 1, wherein the oxidizing agent used in the step (a) is permanganic acid or a salt thereof.
4. The resin surface etching method according to claim 1, wherein the activation of the oxidizing agent in the step (b) 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 an inorganic acid, an organic acid, hydrogen peroxide, a halogen oxoacid, a halogen oxoacid salt, and a persulfate.
5. The resin surface etching method according to claim 1, wherein the activation of the oxidizing agent in the step (b) is performed by a treatment with a solution containing one type or two or more types 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.
6. 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 any one of claims 1 to 5 without performing a resin swelling step.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2018/010095

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl. C23C18/30 (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. C23C18/30

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.
A	JP 2007-100174 A (OKUNO CHEMICAL INDUSTRIES CO., LTD.) 19 April 2007, claims, paragraphs [0043]-[0056], [0079]-[0096] (Family: none)	1-6
A	JP 8-319574 A (MATSUSHITA ELECTRIC WORKS, LTD.) 03 December 1996, claims, paragraphs [0004]-[0022] (Family: none)	1-6

☐ 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

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"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

"I" 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
26.04.2018Date of mailing of the international search report
15.05.2018Name and mailing address of the ISA/
Japan Patent Office
3-4-3, Kasumigaseki, Chiyoda-ku,
Tokyo 100-8915, Japan

Authorized officer

Telephone No.

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- WO 2005094394 A [0007]
- JP 5177426 B [0007]
- JP 2007100174 A [0007]