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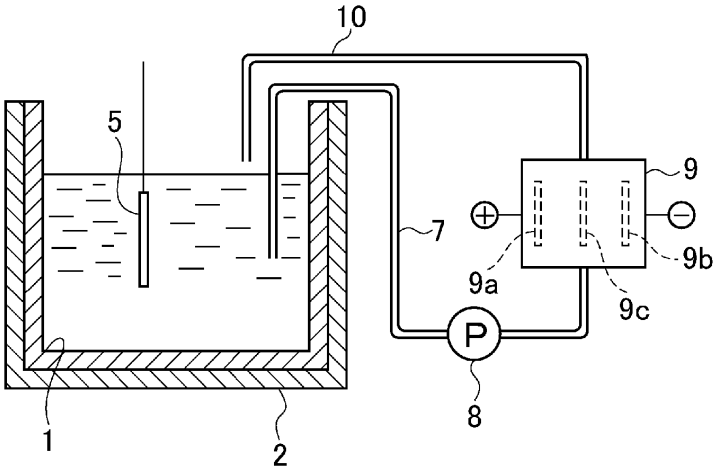
(54) PLASTIC SURFACE TREATMENT METHOD

(57) Provided is a Cr-free plastic surface treatment method which can provide a plating film sufficiently adhered to a plastic surface. The plastic surface treatment method comprises treating plastic with a solution obtained by electrolyzing sulfuric acid. It is preferable that the sulfuric acid concentration of the sulfuric acid solution is 50 to 92 wt%, the persulfuric acid concentration is not less than 3 g/L, and the treatment temperature is not lower than 80°C, for example, 80 to 140°C, particularly 100 to 130°C. By immersing plastic in this sulfuric acid solution for 1 minute to 10 minutes, hydrophilic functional groups are exposed on the surface of the plastic.

Fig. 1



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Description

Technical Field

[0001] The present invention relates to a method for treating a surface of a plastic (resin molded product), the method being performed prior to metallization of a surface of a plastic.

Background Art

[0002] In portions of structural materials and component materials where metals are used, plastics are substituted for the metals utilizing advantages of the plastics, such as weight saving, reduction in cost, freedom of shape and ease of mass production. At present, plastics are widely used not only for decoration but also for exterior or interior trim parts, home appliances, and the like. In such uses, the plastic surface is subjected to plating in many cases in order to enhance rigidity, abrasion resistance, weathering resistance, heat resistance, etc.

[0003] Plastics are non-conductive, and therefore, in order to carry out plating, it is necessary to form a metal film, which becomes a conductor, on plastics first. The methods are broadly classified into dry methods such as CVD and PVD and wet methods such as electroless nickel plating. In most of the dry methods, film formation is carried out under vacuum, and they are not suitable for mass production or application to large components, so that the wet methods have been adopted so far.

[0004] Pretreatment of an ABS resin and a PEEK resin has been heretofore thought to be difficult, and in the etching process for them, a chromic acid-sulfuric acid solution has been used to thereby achieve the purpose.

[0005] Chromic acid is H_2CrO_4, and in the etching solution that is a mixed solution of chromic acid and concentrated sulfuric acid, equilibrium of

$$2CrO_4^{2-} + 2H_3O^+ \rightarrow Cr_2O_7^{2-} + 3H_2O$$

is present, but Cr is hexavalent in any case. Although hexavalent Cr is an object of REACH regulation and RoHS regulation, hexavalent Cr does not remain in the products and is not subject to regulation. In recent years, however, concern about environmental issues is increasing, and environmentally friendly technology using no hexavalent Cr has been strongly desired.

[0006] As environmentally friendly technology substituted for chromic acid, it is described in a PTL 1 that etching with a mixed solution of permanganate and an inorganic salt is carried out. In the method of this PTL 1, however, surface treatment of a PEEK resin and an ABS resin is difficult, and there occurs a problem in adhesion to a metal.

Citation List

Patent Literature

[0007] PTL 1: JP 2008-31513 A

Summary of Invention

Technical Problem

[0008] It is an object of the present invention to provide a Cr-free pre-plating treatment method which can provide a plating film sufficiently adhered to a surface of a plastic.

[0009] In order to solve the above problem, the present inventors have intensively studied, and as a result, they have completed the present invention comprising treating a plastic surface with a sulfuric acid solution containing persulfuric acid (oxidizing agent) obtained by electrolyzing sulfuric acid which thereby can provide a plating film sufficiently adhered to the plastic surface when the subsequent plating treatment is performed.

Solution to Problem

[0010] The present invention is based on such knowledge, and the gist of the present invention is as follows.

[1] A method for treating a surface of a plastic comprising treating a plastic with a solution obtained by electrolyzing sulfuric acid.

[2] The method for treating a surface of a plastic according to [1], wherein the solution has a concentration of the

sulfuric acid of 50 to 92 wt%.

[3] The method for treating a surface of a plastic according to [1] or [2], wherein a treatment temperature is 80 to 140°C.

[4] The method for treating a surface of a plastic according to any one of [1] to [3], wherein the solution contains persulfuric acid at a concentration of 3 to 20 g/L.

[5] The method for treating a surface of a plastic according to any one of [1] to [4], the plastic being treated in a treatment equipment comprising a treatment tank for storing a sulfuric acid-containing treatment solution and an electrolytic cell for forming persulfuric acid, the sulfuric acid-containing treatment solution being circulated between the treatment tank and the electrolytic cell, wherein the plastic is immersed in the treatment tank to treat the surface of the plastic.

Advantageous Effects of Invention

[0011] According to the method for treating a surface of a plastic of the present invention, a plating film sufficiently adhered to the plastic surface can be obtained.

Brief Description of Drawing

[0012] [Fig. 1] Fig. 1 is a structural view of a pretreatment equipment.

Description of Embodiments

[0013] In the method for treating a surface of a plastic of the present invention, the plastic of interest is not particularly limited, and examples thereof include plastics having high difficulty in etching, which can not be etched unless a chromic acid-sulfuric acid solution is used, such as acrylonitrile-butadienestyrene (ABS) resin, polyether ether ketone (PEEK) resin, polyethylene naphthalate (PEN) resin, polyethylene terephthalate (PET) resin and polyphenylene sulfide (PPS) resin.

[0014] In the present invention, the plastic is degreased first, and thereafter, the plastic is immersed in a sulfuric acid solution obtained by electrolyzing sulfuric acid, thereby treating the plastic surface. It is preferable that the sulfuric acid concentration of this sulfuric acid solution be 50 to 92 wt%, particularly 70 to 85 wt%, the persulfuric acid concentration be not less than 3 g/L, for example, 3 to 20 g/L, particularly 3 to 10 g/L, and the treatment temperature be not lower than 80°C, for example, 80 to 140°C, particularly 100 to 130°C. By the immersion in this sulfuric acid solution for 1 to 10 minutes, hydrophilic functional groups are exposed on the surface of the plastic. In the case of a PEEK resin, hydroxyl groups and carboxyl groups appear on the plastic surface.

[0015] Fig. 1 is a schematic sectional view showing an example of electrolysis equipment suitable for carrying out electrolysis of such sulfuric acid.

[0016] On the outer periphery of a treatment tank 1, a thermostatic heater 2 is provided. In the tank 1, a plastic plate 5 is arranged as a plastic to be treated in such a manner that the respective plate surfaces are directed upward and downward. In the treatment tank 1, a stirring means to stir the solution, such as a diffuser tube, may be installed.

[0017] The solution in the treatment tank 1 is circulated through a pipe 7, a pump 8, an electrolytic cell 9 and a pipe 10. In the electrolytic cell 9, an anode 9a and a cathode 9b each of which is formed of a diamond electrode, and a bipolar electrode 9c arranged between them are installed. To the anode 9a and the cathode 9b, a predetermined current is allowed to flow from a power supply unit, and sulfuric acid is electrolyzed, thereby forming persulfuric acid such as peroxodisulfuric acid.

[0018] Using the equipment shown in Fig. 1, the surface treatment of the plastic plate 5 is carried out by placing sulfuric acid in the treatment tank 1, operating the pump 8 and the electrolytic cell 9 to form a sulfuric acid and persulfuric acid-containing treatment solution having a sulfuric acid concentration and a persulfuric acid concentration in the above ranges, and thereafter immersing the plastic plate 5 in the treatment solution in the treatment tank 1 for a predetermined time while operating the pump 8 and the electrolytic cell 9.

[0019] The plastic plate 5 taken out of the treatment tank 1 is subjected to washing with water and drying, and then subjected to plating treatment. As plating treatment methods, there are electroless plating with autocatalysis and electroless plating without autocatalysis, and any of them is available. A metal for plating may be any of nickel, copper, cobalt and alloys thereof.

Examples

[0020] Hereinafter, the present invention will be more specifically described with reference to the examples and the comparative examples. However, the present invention is in no way limited by these descriptions. In the examples and the comparative examples below, the persulfuric acid concentration measurement and the adhesion test were carried

out in the following manner.

< Measuring method for persulfuric acid concentration >

[0021] First, the total concentration of oxidizing agents contained in the treatment solution was measured by iodometric titration. This iodometric titration is a method in which KI is added to liberate I_2, then I_2 is titrated with a sodium thiosulfate standard solution to determine the amount of I_2, and from the amount of I_2, an oxidizing agent concentration is determined. Next, only the hydrogen peroxide concentration was determined by potassium permanganate titration, and the potassium permanganate titration value was subtracted from the iodometric titration value, thereby determining the persulfuric acid concentration.

<Adhesion test>

[0022] On the surface, 6 cuts penetrating down to the PEEK resin are perpendicularly made at intervals of 2 mm in each direction, and using a prescribed transparent pressure-sensitive adhesive tape, the degree of peeling is checked. The peeled portion is compared with the illustrated example and subjected to six-grade evaluation of classes 0 to 5. The class 0 means that most excellent adhesion without any peeling is exhibited. The cuts are made at 3 positions.

Example 1

[0023] Using the equipment shown in Fig. 1, surface treatment of a PEEK resin plate was carried out. The specification of the treatment tank and the conditions are as follows.

<Treatment tank>

[0024] Volume of treatment tank 1: 40 L
Size of PEEK resin plate: 500 mm × 500 mm × thickness 5 mm

<Electrolytic cell for forming persulfuric acid>

[0025] Cell volume: 0.5 L
Anode and cathode: diamond electrode (diameter 150 mm)
Bipolar electrode material: same as anode and cathode
Current density: 50 A/dm^2
Solution flow rate: 52 L/h

<Surface treatment conditions>

[0026] Sulfuric acid concentration: 85 wt%
Persulfuric acid concentration: 10 g/L
Treatment temperature: 120°C
Treatment time: 51 minutes

[0027] First, a sulfuric acid solution of 85 wt% was placed in the treatment tank 1, and after the persulfuric acid concentration became not less than 3 g/L by operating the pump 8 and the electrolytic cell 9, the PEEK resin plate was immersed. After the resin plate was immersed for 5 minutes, the resin plate was taken out of the treatment tank 1, washed with pure water, then dried, and subjected to electroless nickel plating by way of a catalyst application process and an activation process. The treatment conditions of each process are shown in Table 1.

[0028] From the electroless nickel-plated plate, a sample of 150 mm × 100 mm was cut out, and the adhesion was examined by the aforementioned method.

[Table 1]

Process name	Bath composition	Concentration	Treatment temperature (°C)	Treatment time (min)
Catalyst application	hydrochloric acid	100 mL/L	60	10
	tin chloride	20 g/L		
	palladium chloride	0.2 g/L		
Activation	sulfuric acid	300 mL/L	50	10
Electroless nickel plating	Top Nicolon TOM-S	200 mL/L	60	10
	aqueous ammonia	adjusted to pH=8		

Example 2 to Comparative Example 5

[0029] A test was carried out in the same manner as in Example 1, except that the surface treatment conditions were set as shown in Table 2. The results are shown in Table 2. In Table 2, the results of Example 1 are also shown.

[Table 2]

Example	Sulfuric acid concentration (50 to 92 wt%)	Treatment temperature (100 to 130°C)	Persulfuric acid concentration (not less than 3 g/L)	Treatment time (1 to 10 min)	Adhesion test result
Ex. 1	85	120	10	1	class 0
Ex. 2	75	130	5	10	class 0
Ex. 3	92	100	3	2	class 0
Com p. Ex. 1	85	140	5	3	class 1
Com p. Ex. 2	45	100	10	10	class 3
Comp. Ex. 3	85	120	1	10	class 4
Comp. Ex. 4	96	100	0	10	class 4
Comp. Ex. 5	96	100	10	1	class 3

[0030] As shown in Table 2, it is seen that excellent adhesion is obtained according to the example method.

[0031] The present invention has been described in detail by using a specific embodiment, but it is obvious to those skilled in the art that various modifications can be made without departing from the spirit and scope of the present invention.

[0032] The present application is based on JP 2016-091178 filed with Japan Patent Office on April, 28, 2016, which is incorporated herein by reference in its entirety.

Claims

1. A method for treating a surface of a plastic comprising treating a plastic with a solution obtained by electrolyzing sulfuric acid.

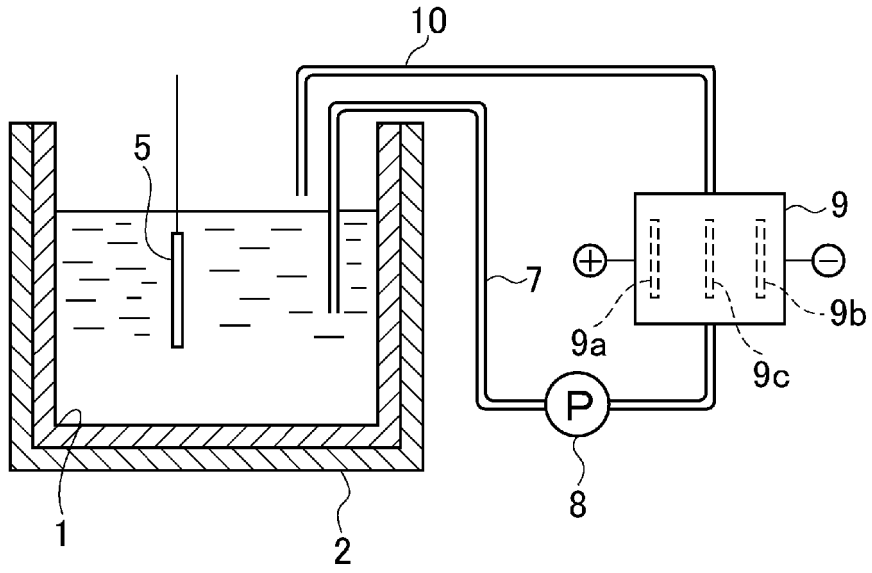
2. The method for treating a surface of a plastic according to claim 1, wherein the solution has a concentration of the sulfuric acid of 50 to 92 wt%.

3. The method for treating a surface of a plastic according to claim 1 or 2, wherein a treatment temperature is 80 to 140°C.

4. The method for treating a surface of a plastic according to any one of claims 1 to 3, wherein the solution contains persulfuric acid at a concentration of 3 to 20 g/L.

5. The method for treating a surface of a plastic according to any one of claims 1 to 4, the plastic being treated in a treatment equipment comprising a treatment tank for storing a sulfuric acid-containing treatment solution and an electrolytic cell for forming persulfuric acid, the sulfuric acid-containing treatment solution being circulated between the treatment tank and the electrolytic cell, wherein the plastic is immersed in the treatment tank to treat the surface of the plastic.

Fig. 1



INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2017/010208

A. CLASSIFICATION OF SUBJECT MATTER
C23C18/24(2006.01)i, *C25B1/30*(2006.01)i, *C25B15/08*(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)
C23C18/24, C25B1/30, C25B15/08

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Jitsuyo Shinan Koho 1922-1996 Jitsuyo Shinan Toroku Koho 1996-2017
Kokai Jitsuyo Shinan Koho 1971-2017 Toroku Jitsuyo Shinan Koho 1994-2017

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 (25.06.2015), claims; paragraphs [0030] to [0055], [0060] to [0071] & US 2013/0186774 A1 claims; paragraphs [0034] to [0065], [0068] to [0085]	1-3 4-5
A	JP 2010-189748 A (Osaka-Fu), 02 September 2010 (02.09.2010), claims; paragraphs [0131] to [0185]; fig. 1 (Family: none)	1-5

☒ 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
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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
03 April 2017 (03.04.17)	18 April 2017 (18.04.17)
Name and mailing address of the ISA/ Japan Patent Office 3-4-3,Kasumigaseki,Chiyoda-ku, Tokyo 100-8915,Japan	Authorized officer Telephone No.

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

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2017/010208

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2011-58010 A (Kurita Water Industries Ltd.), 24 March 2011 (24.03.2011), claims; paragraphs [0021] to [0036]; fig. 1 to 2 (Family: none)	1-5

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 **[0007]**
- JP 2016091178 A **[0032]**