



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

(43) Date of publication:
31.12.2014 Bulletin 2015/01

(51) Int Cl.:
C23C 26/00 ^(2006.01) **B23H 1/00** ^(2006.01)
C25D 5/26 ^(2006.01)

(21) Application number: **13751445.1**

(86) International application number:
PCT/JP2013/054412

(22) Date of filing: **21.02.2013**

(87) International publication number:
WO 2013/125657 (29.08.2013 Gazette 2013/35)

(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

- **BABA, Kazuhiko**
Tokyo 100-0011 (JP)
- **NORO, Hisato**
Tokyo 100-0011 (JP)
- **WATANABE, Seiichi**
Sapporo-shi
Hokkaido 060-8628 (JP)
- **YOSHIDA, Souki**
Sapporo-shi
Hokkaido 060-8628 (JP)

(30) Priority: **24.02.2012 JP 2012038556**
24.02.2012 JP 2012038560

(71) Applicant: **JFE Steel Corporation**
Tokyo, 100-0011 (JP)

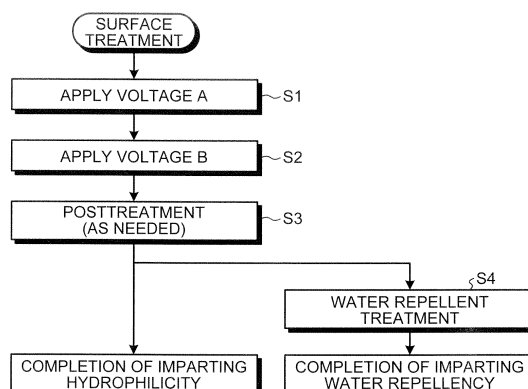
(74) Representative: **Stebbing, Timothy Charles**
Haseltine Lake LLP
Lincoln House, 5th Floor
300 High Holborn
London WC1V 7JH (GB)

(72) Inventors:
• **NAGOSHI, Masayasu**
Tokyo 100-0011 (JP)
• **SATO, Kaoru**
Tokyo 100-0011 (JP)

(54) **METAL MATERIAL SURFACE TREATMENT METHOD, AND METAL MATERIAL**

(57) A metal material surface treatment method, includes: immersing, as a cathode electrode, a target material that is made of the metal material and that has a target surface, and an anode electrode, in an electrolyte solution; applying a voltage A that is 70 V or more and in a voltage range in which the cathode electrode is not oxidized or does not melt, between the cathode electrode and the anode electrode; and applying a voltage B that is in the voltage range and that differs from the voltage A by 5 V or more, between the cathode electrode and the anode electrode. This method can add a new function to the surface of a metal material without requiring a lot of labor and high cost.

FIG.1



Description

Field

5 **[0001]** The present invention relates to a metal material surface treatment method to add a new function to the surface of the metal material and relates to a metal material subjected to surface treatment by the surface treatment method.

Background

10 **[0002]** When the surfaces of metal materials are utilized as functional materials, an important factor is wettability of the surfaces of the metal materials, in other words, hydrophilicity and water repellency of the metal materials. Various characteristics can be imparted to metal materials by controlling the factor. For example, metal materials used for heat exchangers require an affinity between a medium such as water and the inner and outer surfaces of the metal heat exchanger tube, in other words, wettability of the surfaces of the metal materials, to increase heat conduction. Imparting hydrophilicity to the surfaces provides many advantages, for example, that self-cleansing effect of washing deposit of dirt and the like away with water can be expected. Techniques to impart hydrophilicity to metal surfaces are thus disclosed as follows: for example, Patent Literature 1 discloses a technique to form a porous oxide layer using corona discharge; and Patent Literature 2 discloses a method of forming a hydrophilic film by etching a surface to form a film thereon and then removing the film.

20 **[0003]** However, the technique using corona discharge is a technique to form an oxide layer on a surface, and once the oxide layer has removed due to peeling or the like, the function disappears. The method in which a hydrophilic film is combined with etching is expensive because of its complicated processes involving film formation. Moreover, once the hydrophilic coating has removed in use, the effect decreases and is not recovered, for example. On the other hand, as for water repellency on the surfaces of metal materials, for example, metal materials such as steel materials react with water to corrode in an environment containing water. Water repellency imparting techniques to prevent metal materials from corroding have been thus proposed in recent years. In the techniques, the surfaces of the metal materials are formed to have water repellency (hydrophobicity), which reduces wet areas on the surfaces of the metal materials or allows water in contact with the metal surfaces to readily run off the metal surfaces.

25 **[0004]** For example, Patent Literature 3 discloses a technique to impart water repellency to the surface of a steel sheet by applying an alkoxide of Al, Zr, or another element onto the surface of the steel sheet and heating the surface at 100°C or higher. Patent Literature 4 discloses a technique to impart water repellency to the surface of a plated steel sheet by forming a coating layer of a compound for metal coupling treatment on the surface of the plated steel sheet. Patent Literature 5 discloses a technique to impart water repellency to the surface of a metal sheet by applying a water repellent coating onto the surface of the metal sheet. However, all of the above methods relate to the formation of a film on the surface using an expensive agent. This leads to disadvantages such that when such a film layer has removed due to peeling or the like, water repellency thereof is impaired, and that the process of forming the film is complicated and expensive.

30 **[0005]** In recent years, in addition to various kinds of innate performance of steel sheets, attempts have been made to add new functions to steel sheets, such as dirt resistance and deodorization properties, using photocatalysts (see Patent Literatures 6 to 9). The basic technique of such attempts is to disperse photocatalyst active particles in a coating material at a surface or in a process layer. Resin materials (see Patent Literatures 6 and 7) and an inorganic-organic composite (see Patent Literature 8) have been proposed as such a coating material. Disclosed as an attempt to directly add photocatalysts to steel sheets is a technique to produce a TiO₂ thin film on the surface of a steel sheet by a film formation method in an atomic level using plasma (plasma-enhanced atomic layer deposition) (see Non-Patent Literature 1).

Citation List

Patent Literature

50

[0006]

Patent Literature 1: Japanese Laid-open Patent Publication No. 05-179419

55

Patent Literature 2: Japanese Laid-open Patent Publication No. 2002-053977

Patent Literature 3: Japanese Laid-open Patent Publication No. 01-068477

Patent Literature 4: Japanese Laid-open Patent Publication No. 09-020983

Patent Literature 5: Japanese Laid-open Patent Publication No. 2008-075064

5 Patent Literature 6: Japanese Laid-open Patent Publication No. 2000-014755

Patent Literature 7: Japanese Laid-open Patent Publication No. 2001-131768

10 Patent Literature 8: Japanese Laid-open Patent Publication No. 2007-268761

Patent Literature 9: Japanese Laid-open Patent Publication No. 2002-053978

Non Patent Literature

15 **[0007]** Non Patent Literature 1: Chang-sooLee et al., Thin Solid Films, 518 (2010) pp.4757 - 4761

Summary

Technical Problem

20 **[0008]** The conventional hydrophilicity imparting techniques and water repellency imparting techniques are techniques to impart hydrophilicity and water repellency, respectively, to metal surfaces by forming films on the surfaces of metal materials. It is necessary for these techniques to add dissimilar metals or fine particles to the metal surfaces, which requires additional labor and cost. In addition, as for water repellency, it is insufficient to simply provide a water repellent layer onto the surface of a metal material, and special treatment is needed to be performed, such as addition of fine particles.

25 **[0009]** The conventional photocatalyst function imparting technique adds a photocatalyst function to the surfaces of steel sheets by dispersing photocatalyst active particles in a coating material or a process layer or forming a film of a photocatalyst active substance. However, the coating material and the process layer that mainly contain organic substances are decomposed with the photocatalyst active particles, and thus, the photocatalyst function cannot be expected to continue for a long time. Moreover, the use of photocatalyst active substances and organic materials leads to complicated production steps, which results in high cost. The film formation method of a TiO₂ thin film in an atomic level needs advanced technique and high cost, and thus it is difficult to industrialize the method.

30 **[0010]** In view of the above, it is an object of the present invention to provide a metal material surface treatment method that can add a new function to the surface of the metal material without requiring a lot of labor and high costs, and a metal material subjected to surface treatment by the surface treatment method.

Solution to Problem

40 **[0011]** A metal material surface treatment method according to the present invention includes: immersing, in an electrolyte solution, a target material as a cathode electrode that is made of the metal material and that has a target surface, and an anode electrode; applying a first voltage between the cathode electrode and the anode electrode; and applying a second voltage different from the first voltage between the cathode electrode and the anode electrode.

45 **[0012]** In the above-described metal material surface treatment method according to the present invention, the first voltage is 70 V or more and in a voltage range in which the cathode electrode is not oxidized or does not melt, and the second voltage is in the voltage range and differs from the first voltage by 5 V or more.

[0013] In the above-described metal material surface treatment method according to the present invention, the metal material is a stainless steel material, the first voltage is 60 V or more and in a voltage range in which the cathode electrode does not melt, and the second voltage is in the voltage range and differs from the first voltage by 5 V or more.

50 **[0014]** In the above-described metal material surface treatment method according to the present invention, the second voltage is lower than the first voltage.

[0015] The above-described metal material surface treatment method according to the present invention further includes performing one or more times of treatment at a voltage lower than the second voltage by 5 V after treatment at the applying of the second voltage, and the voltage in the later treatment is lower by 5 V or more than the voltage in the immediately preceding treatment.

55 **[0016]** The above-described metal material surface treatment method according to the present invention further includes performing water repellent treatment on a surface of the cathode electrode after the applying of the first voltage and the applying of the second voltage.

[0017] A metal material according to the present invention is subjected to surface treatment by the metal material surface treatment method according to the above-described present invention.

Advantageous Effects of Invention

[0018] With the metal material surface treatment method and the metal material according to the present invention, a new function can be added to the surface of the metal material without requiring a lot of labor and high cost.

Brief Description of Drawings

[0019]

FIG. 1 is a flowchart illustrating the flow of surface treatment for a metal material according to a first embodiment of the present invention.

FIG. 2 is a schematic illustrating a configuration example of a device used in a surface treatment method of a metal material according to the first embodiment of the present invention.

FIG. 3 is a scanning electron microscope (SEM) photograph illustrating the surface of stainless steel SUS316 subjected to the surface treatment.

FIG. 4 is a photograph illustrating a state of distilled water added dropwise onto the surface of the test piece illustrated in FIG. 3, which is observed from the lateral direction.

FIG. 5 is a photograph illustrating a state of distilled water added dropwise onto the surface of the stainless steel illustrated in FIG. 3 that had been subjected to water repellent treatment, which is observed from the lateral direction.

FIG. 6 is a photograph illustrating a state of distilled water added dropwise onto the surface of stainless steel that is not subjected to the surface treatment and water repellent treatment, which is observed from the lateral direction.

FIG. 7 is a flowchart illustrating the flow of surface treatment for a metal material according to a second embodiment of the present invention.

FIG. 8 is a diagram illustrating a secondary electron image of the surface of stainless steel 316 treated at Step S12 in FIG. 7.

FIG. 9 is a diagram illustrating a secondary electron image of the surface of stainless steel 316 treated at Step S13 in FIG. 7.

FIG. 10 is a graph illustrating an example of absorbance spectra.

Description of Embodiments

[0020] The metal material surface treatment method according to the first and the second embodiments of the present invention will be described with reference to the accompanying drawings.

(First Embodiment)

[0021] FIG. 1 is a flowchart illustrating the flow of surface treatment for a metal material according to the first embodiment of the present invention. FIG. 2 is a schematic illustrating a configuration example of a device used in the metal material surface treatment method according to the first embodiment of the present invention. As illustrated in FIG. 1, in the surface treatment of a metal material according to the first embodiment of the present invention, first, a target material that is the metal material serving as a cathode electrode, and an anode electrode are immersed in an electrolyte solution, and a voltage A is applied between the cathode electrode and the anode electrode (Step S1). A voltage B different from the voltage A is applied between the cathode electrode and the anode electrode (Step S2). These two steps enable formation of a fine structure having a large specific surface area on the surface of the target material. More specifically, as illustrated in FIG. 2, an anode electrode 3 and a target material 4 are immersed in an electrolyte solution 2 in a container 1. The voltage A and the voltage B are applied to the anode electrode 3 and the target material 4 from a power source 6 through a conducting wire 5 such as a copper wire to form a fine structure on the surface of the target material 4. It is efficient to perform treatment at Step S1 and treatment at Step S2 in succession. However, the treatment at Step S2 may also be performed after a certain time from the treatment at Step S1 or after the device, the electrolyte solution, or the like is changed.

[0022] The electrolyte solution 2 is not particularly limited but is an electroconductive solution that is unlikely to excessively etch the surface of the target material 4, to adhere to or be deposited on the surfaces of the anode electrode 3 and the target material 4, and to form precipitates, during the surface treatment of the target material 4. Examples of an electrolyte of such an electrolyte solution 2 include potassium carbonate (K_2CO_3), sodium carbonate (Na_2CO_3), sodium hydrogencarbonate ($NaHCO_3$), ammonium carbonate ($(NH_4)_2CO_3$), lithium hydroxide (LiOH), sodium hydroxide (NaOH),

potassium hydroxide (KOH), ammonium hydroxide (NH₄OH), sodium chloride (NaCl), potassium chloride (KCl), ammonium chloride (NH₄Cl), sodium salts of sulfuric acid, potassium salts of sulfuric acid, ammonium salts of sulfuric acid, sodium salts of nitric acid, potassium salts of nitric acid, ammonium salts of nitric acid, sodium salts of citric acid such as sodium citrate (NaH₂(C₃H₅O(COO)₃)), potassium salts of citric acid, ammonium salts of citric acid, nitric acid, and hydrochloric acid.

[0023] The electrolyte solution 2 can have any pH and concentration so long as the electrolyte solution 2 can reform the surface of the target material 4. For example, when an aqueous solution of potassium carbonate is used as the electrolyte solution 2, its concentration is not particularly limited and may be 0.001 mol/L or higher and more preferably 0.005 mol/L or higher. This is because an excessively low concentration of the electrolyte solution 2 may make it difficult to maintain a favorable discharge state when voltage is applied between the anode electrode 3 and the target material 4. The upper limit of the concentration of the electrolyte solution 2 is not particularly set and may be, for example, 0.5 mol/L or lower. The pH of the electrolyte solution 2 can be any value unless the electrodes are excessively corroded or etched, and can be a pH of, for example, 10 to 12.

[0024] The anode electrode 3 is formed from a material thermally and chemically stable in electric discharge process. Examples of such an anode electrode 3 include Pt, Ir, and graphite.

[0025] The target material 4 is not particularly limited so long as it is a metal material. When the target material 4 is a steel material, a cold-rolled material, a hot-rolled material, a casting material, or a work thereof (including a welded material) can be employed. The type of the steel is not particularly limited, and plain carbon steel, low-alloy steel, stainless steel, or other steel is available. A plated steel sheet such as an electrogalvanized steel sheet is also available. The shape of the target material 4 is not particularly limited, and the target material 4 can have a form of a plate, a wire, a bar, or a pipe, or can employ a machined part. The target material 4 needs to be immersed in the electrolyte solution 2 and to be set at a place at least 1 mm lower than the liquid surface.

[0026] The available range of the discharge condition is from a partial plasma state to a full plasma state in which the surface of the target material 4 has irregularities. However, the discharge needs to be performed in a voltage range lower than a voltage at which the target material 4 melts. Specifically, the range is from a state where emission of light observable by the unaided eye starts in a dark place while the discharge voltage is increased, to a state just before where the whole material glows, via a state where a spots of orange light are emitted. When the size of the target material 4 is 1 mm x 1 mm x 20 mm, the application voltage is preferably in a range from 70 to 200 V and more desirably in a range from 80 to 150 V. This voltage range is applicable to most of steel materials including alloy steel such as stainless steel. However, the voltage range varies depending on the type and the location of the target material 4. The voltage range may be thus determined by observing the surface of the target material 4 treated at different voltage conditions, with a scanning electron microscope (SEM).

[0027] A necessary condition for the discharge voltage is to be a voltage at which fine projections are formed on the surface of a steel material. No fine projection is formed on the surface at a voltage lower than the lower limit. Thus, the presence or absence of fine projections can be determined by examining it with an SEM. When the voltage exceeds the upper limit, the target surface is melted. The voltage at which the surface melts can thus be determined as the upper limit. When oxidization of the surface is not desirable, a voltage at which the surface is oxidized can be easily determined by examination with an SEM and an energy-dispersive X-ray spectrometer (EDS) included with the SEM. The surface can be determined to have been oxidized when oxygen is detected at an X-ray intensity nearly equal to that of the oxide of the target material 4. The X-ray intensity of oxygen normalized by the Fe-L line intensity of oxygen in the target material 4 needs to be equal to or less than one third the X-ray intensity of oxygen normalized by the Fe-L line intensity of the oxide (means the oxide of Fe in case of a cold-rolled steel sheet or low alloy steel, for example) of the target material 4. The above surface examination is performed in the following manner. The target material 4 is subjected to discharge for 30 minutes at a different voltage. The target material 4 is then taken out, washed with water, and dried. The resultant target material 4 is set in an SEM for observation.

[0028] The inventors of the present invention have found that, in a desirable voltage range, fine projections enlarge in accordance with the increase in the voltage. To increase a surface area, it is advantageous to provide finer irregularities onto large irregularities, and thus, the voltage B is desirably lower than the voltage A. The voltage difference between the voltage A and the voltage B is desirably 5 V or more because the size difference of formed projections was found when the voltage A was different from the voltage B by 5 V. Furthermore, a voltage close to the upper limit of the desirable voltage range may be selected as the voltage A because it is advantageous to form large irregularities in the treatment at Step S1.

[0029] The treatment at each of Step S1 and Step S2 requires a discharge treatment time of 3 seconds or more. Although a long discharge treatment time is possible such as 60 minutes, a treatment time of 30 minutes or more is not preferable because the target material 4 may be worn if the discharge treatment time is excessively long. It is also not preferable that the discharge treatment time be long in the treatment at Step S2. This is because when the discharge treatment time increases in the treatment at Step S2, fine projections formed on the surface depend on the voltage B. The discharge treatment time may thus be 5 minutes or less in the treatment at Step S2.

[0030] FIG. 3 is an example of a treated SUS 316 stainless steel sheet having a thickness of 0.8 mm. This SUS 316 stainless steel sheet was cut into a piece having a width of 2.5 mm and a length of 30 mm and was brought into conduction via a copper wire to serve as a cathode electrode. A Pt wire having a length of 50 cm that was bended in a form of a plane without making contact with each other was used as an anode electrode. A heat-resistant resin was thermally crimped to the connecting part of the SUS 316 stainless steel sheet and the copper wire. A 20-mm long portion of the electrode was immersed in an electrolyte solution to avoid the copper wire from coming in contact with the electrolyte solution. An aqueous solution with a concentration of 0.1 mol/L of K_2CO_3 was used as the electrolyte solution. Discharge (Step 1) was performed for 10 minutes while the voltage was set to 140 V, and then, discharge (Step 2) was performed for 3 minutes while the voltage was set to 110 V. The cathode electrode was then pulled out of the electrolyte solution and was washed with water immediately thereafter.

[0031] As a result, as illustrated in FIG. 3, it was confirmed that comparatively large projections were formed on the surface of the SUS 316 stainless steel sheet, and that fine projections having an average diameter of 1 μm or smaller were formed on the comparatively large projections. It was also confirmed from elementary analysis by an EDS that the surface of the SUS 316 stainless steel sheet was not oxidized. The front end of the SUS 316 stainless steel sheet was melted away at an application voltage exceeding 160 V. This determines the upper limit of the application voltage to be 160 V. It was also confirmed from the elementary analysis by an EDS that the surface of the SUS 316 stainless steel sheet was not oxidized at an application voltage of 140 V or less. This reveals that the upper limit of the application voltage at which the surface is not oxidized is 140 V in this experiment condition and with this test material. This also determines the lower limit of the application voltage to be 80 V in view of the presence or absence of a projection structure. Accordingly, the most preferable condition as the voltage A is determined to be 140 V.

[0032] Referring back to FIG. 1, a fine structure was formed on the surface of the target material 4 in a manner as described above, and then, the target material 4 was taken out of the electrolyte solution 2 and was washed as needed (Step S3). The surface having hydrophilicity is obtained in this state. The washing is performed to remove the electrolyte solution on the surface, and examples thereof include a pure water immersion and a pure water spray processing. Pure water is not a limiting example, and a weak acid or an alkaline solution may also be used unless it damages the fine structure on the surface. During the process, electrolysis can be performed thereon. After the washing, the target material 4 may be dried, or may be treated at the following step without being dried for water repellent treatment.

[0033] FIG. 4 is a photograph illustrating a state of distilled water added dropwise onto the surface of the test piece illustrated in FIG. 3, which is observed from the lateral direction. As illustrated in FIG. 4, the contact angle is very small, which reveals that a superhydrophilic surface is obtained. The contact angle was 52 degrees when the surface was subjected to 15-minute discharge set at 140 V, the same voltage as Step 1, while the contact angle was 70 degrees when the surface was subjected to 15-minute discharge set at 110 V, the same voltage as Step 2. This reveals that two-stage treatment of treatment at Step 1 and treatment at Step 2 is required in order to attain superhydrophilicity such that the contact angle of water is around 10 degrees as illustrated in FIG. 4.

[0034] To provide a water repellent surface, the target surface of the washed target material 4 is subjected to water repellent treatment (Step S4). Examples of the available water repellent treatment method include a method of applying spray of a water repellent and a method of adsorbing an organic substance having water repellent function, such as a fluorine-based resin in a liquid phase or a vapor phase. In the present embodiment, the surface of the target material 4 was subjected to water repellent treatment by spraying Nanopro manufactured by Collonil (ingredients: a fluorocarbon resin and a silicone resin) on the surface of the target material 4 and drying it for 12 hours or longer.

[0035] FIG. 5 is a photograph illustrating a state of distilled water added dropwise onto the surface of the test piece illustrated in FIG. 3 that had been subjected to water repellent treatment, which is observed from the lateral direction. The contact angle of water was determined to be 170° through the observation, which indicates that super water repellency was achieved. The contact angle of water was 125° when a material on which no plasma discharge in solution had been performed was subjected to similar water repellent treatment. The contact angle of water was 77.2° (see FIG. 6) with a test piece to which no water repellent treatment was performed. Accordingly, it is recognized that both of the plasma discharge in solution having two stages of the treatment at Step 1 and the treatment at Step 2 and water repellent treatment are needed to provide a super water repellent surface.

[0036] The technique of the present invention to perform plasma discharge in solution in two different conditions is expandable to a technique in which plasma discharge treatment in solution is performed three or more times. Although performing treatment fewer times is advantageous in view of the time and cost required for the treatment, performing plasma discharge treatment in solution three or more times is applicable when a higher effect is required.

(Examples)

[0037] A commercially available SUS 316 stainless steel sheet having a thickness of 0.8 mm was cut into a piece having a width of 2.5 mm and a length of 50 mm and was immersed in a diluted hydrochloric acid to be degreased. The sheet was then brought into conduction via a copper wire to serve as a cathode electrode. The upper portion of the

electrode including the connecting part with the copper wire was coated with a heat-resistant resin, and the length of a target portion where the stainless steel was exposed was set to 20 mm. This electrode was immersed in an electrolyte solution. A 0.5 mm ϕ Pt wire having a length of 50 cm that was bended in a form of a plane without making contact with each other was used as an anode electrode. An aqueous solution with a concentration of 0.1 mol/L of K₂CO₃ was used as the electrolyte solution. The application voltage was set in a range from 110 to 140 V, and electric discharge was performed in each condition listed in Table 1. Immediately after the completion, the resultant stainless steel sheet was washed with pure water and dried. Subsequently, some of such test pieces were subjected to water repellent treatment by spraying Nanopro manufactured by Collonil onto the surfaces of the target materials, and drying the resultant target materials for 12 hours or more. Their water wettability was then examined. The water wettability was evaluated in the following manner. 1 μ m of distilled water was added dropwise onto the electrode surface at six points each at regular intervals using a micropipette. The side view of the dropped water was taken using a digital camera EOS Kiss X2 manufactured by Canon Inc., and the contact angle was measured from the obtained photograph. The contact angles at the six points were averaged. The used distilled water was distilled water 049-16787 manufactured by Wako Pure Chemical Industries, Ltd. Table 1 lists the test result.

[0038] The contact angle with the surface with no treatment (Comparative Example 1) was 77°, and even when water repellent treatment was performed thereon, the contact angle increased only to 125°. In contrast, the contact angles in the examples of the present invention were 8° to 42°, indicating high hydrophilicity. The example of the present invention subjected to water repellent treatment obtained super water repellency with a maximum of 172° (Example 2). Although in comparative examples in which a single voltage is applied, the hydrophilicity was improved and the water repellency was obtained by performing water repellent treatment (Comparative Examples 2 to 13), even the most excellent contact angles were merely 52° and 147°, respectively. This reveals that treatment at two different voltages is highly effective in imparting hydrophilicity and water repellency. However, no enhancing effects were found both in hydrophilicity and water repellency in Example 6 in which the treatment time at Step 2 was 15 minutes, which was long. It is thus more preferable that the treatment time at Step 2 be 5 minutes or less.

Table 1

| Test number | Step 1 | | Step 2 | | Contact angle (°) | | Remarks |
|-------------|-------------|------------|-------------|------------|------------------------------|--------------------------------|-------------|
| | Voltage (V) | Time (min) | Voltage (V) | Time (min) | No water repellent treatment | With water repellent treatment | |
| 1 | 140 | 5 | 120 | 5 | 10 | 170 | Example 1 |
| 2 | 140 | 15 | 120 | 5 | 8 | 172 | Example 2 |
| 3 | 120 | 15 | 140 | 5 | 18 | 159 | Example 3 |
| 4 | 135 | 10 | 125 | 2 | 13 | 163 | Example 4 |
| 5 | 140 | 10 | 110 | 2 | 15 | 165 | Example 5 |
| 6 | 140 | 15 | 120 | 15 | 42 | 154 | Example 6 |
| 7 | Not applied | | Not applied | | 77 | 125 | Comp. Ex. 1 |
| 8 | 110 | 2 | Not applied | | 75 | 130 | Comp. Ex. 2 |
| 9 | 110 | 15 | Not applied | | 70 | 138 | Comp. Ex. 3 |
| 10 | 125 | 2 | Not applied | | 72 | 135 | Comp. Ex. 4 |
| 11 | 125 | 15 | Not applied | | 63 | 143 | Comp. Ex. 5 |

(continued)

| Test number | Step 1 | | Step 2 | | Contact angle (°) | | Remarks |
|-------------|-------------|------------|-------------|------------|------------------------------|--------------------------------|--------------|
| | Voltage (V) | Time (min) | Voltage (V) | Time (min) | No water repellent treatment | With water repellent treatment | |
| 12 | 140 | 5 | Not applied | | 57 | 140 | Comp. Ex. 6 |
| 13 | 140 | 15 | Not applied | | 52 | 144 | Comp. Ex. 7 |
| 14 | 140 | 20 | Not applied | | 53 | 146 | Comp. Ex. 8 |
| 15 | 140 | 30 | Not applied | | 52 | 147 | Comp. Ex. 9 |
| 16 | 120 | 5 | Not applied | | 65 | 139 | Comp. Ex. 10 |
| 17 | 120 | 15 | Not applied | | 65 | 138 | Comp. Ex. 11 |
| 18 | 120 | 20 | Not applied | | 64 | 136 | Comp. Ex. 12 |
| 19 | 120 | 30 | Not applied | | 66 | 139 | Comp. Ex. 13 |

(Second Embodiment)

[0039] The inventors of the present invention have extensively studied to add a photocatalyst function to stainless steel materials by a simple method without using TiO_2 . As a result, they have found that a structure with fine irregularities is produced on the surface of a stainless steel material by subjecting the stainless steel material to plasma treatment in an electrolyte solution, thereby adding the photocatalyst function to the stainless steel material. The inventors of the present invention also have found that the photocatalyst function of a stainless steel material is significantly increased by subjecting the stainless steel material to plasma treatment twice at different voltages.

[0040] FIG. 7 is a flowchart illustrating the flow of surface treatment for a metal material according to the second embodiment of the present invention. A treatment device used in the metal material surface treatment method of the second embodiment of the present invention has the same configuration as that of the treatment device illustrated in FIG. 2. As illustrated in FIG. 7, in the surface treatment of a metal material according to the second embodiment of the present invention, first, a target material that is made of a stainless steel material and has a target surface, which serves as a cathode electrode, and an anode electrode are immersed in an electrolyte solution (Step S11). The voltage A that is 60 V or more and in a voltage range in which the cathode electrode does not melt is applied between the cathode electrode and the anode electrode to form a fine structure on the surface of the target material (Step S12). Specifically, as illustrated in FIG. 2, the anode electrode 3 and the target material 4 are immersed in the electrolyte solution 2 in the container 1. The voltage is applied to the anode electrode 3 and the target material 4 from the power source 6 through the conducting wire 5 such as a Cu wire and a Pt wire to form a fine structure on the surface of the target material 4. FIG. 8 is a diagram illustrating a secondary electron image of the surface of the stainless steel 316 treated at Step S12. As illustrated in FIG. 8, fine irregularities are formed on the surface of the stainless steel 316 treated at Step S12.

[0041] The electrolyte solution 2 is not particularly limited but is an electroconductive solution that is unlikely to excessively etch the surface of the target material 4, to adhere to or be deposited on the surfaces of the anode electrode 3 and the target material 4, and to form precipitates, during the surface treatment of the target material 4. Examples of an electrolyte of such an electrolyte solution 2 include potassium carbonate (K_2CO_3), sodium carbonate (Na_2CO_3), sodium hydrogencarbonate (NaHCO_3), ammonium carbonate ($(\text{NH}_4)_2\text{CO}_3$), lithium hydroxide (LiOH), sodium hydroxide (NaOH), potassium hydroxide (KOH), ammonium hydroxide (NH_4OH), sodium chloride (NaCl), potassium chloride (KCl), ammonium chloride (NH_4Cl), sodium salts of sulfuric acid, potassium salts of sulfuric acid, ammonium salts of sulfuric acid, sodium salts of nitric acid, potassium salts of nitric acid, ammonium salts of nitric acid, sodium salts of citric acid such as sodium citrate ($\text{NaH}_2(\text{C}_3\text{H}_5\text{O}(\text{COO})_3)$), potassium salts of citric acid, ammonium salts of citric acid, nitric acid, and hydrochloric acid.

[0042] The electrolyte solution 2 can have any pH and concentration so long as the electrolyte solution 2 can reform the surface of the target material 4. For example, when an aqueous solution of potassium carbonate is used as the electrolyte solution 2, its concentration is not particularly limited and may be 0.001 mol/L or higher and more preferably 0.005 mol/L or higher. This is because an excessively low concentration of the electrolyte solution 2 makes it difficult to maintain a favorable discharge state when voltage is applied between the anode electrode 3 and the target material 4. The upper limit of the concentration of the electrolyte solution 2 is not particularly set and may be, for example, 0.5 mol/L or lower. The pH of the electrolyte solution 2 can be any value unless it excessively corrodes or etches the electrodes, and can be a pH of, for example, 10 to 12.

[0043] The anode electrode 3 is formed from a material that is thermally and chemically stable for electric discharge. Examples of such an anode electrode 3 include Pt, Ir, and graphite.

[0044] The target material 4 is a stainless steel material containing 12% by weight or more of Cr and may be any of ferritic, austenitic, and dual-phase stainless steels. Any surface finishes can be used. The shape of the target material 4 is not particularly limited, and the target material 4 can have a form of foil, a plate, a wire, a bar, or a pipe, or can employ a machined part or an assembled part. The target material 4 needs to be immersed in the electrolyte solution 2 and to be set at a place at least 1 mm lower than the liquid surface.

[0045] In the discharge condition, the available voltage range is from equal to or more than a voltage at which a partial plasma state is exhibited in which irregularities are formed on the surface of the target material 4, to a voltage at which the target material 4 does not melt. The partial plasma state indicates a state in a range from a voltage at which emission of light observable by the unaided eye starts in a dark place while the discharge voltage is increased, to a voltage before reaching a full plasma state at which spots of orange light are emitted. Specifically, the voltage range can be determined by performing electric discharge and confirming the formation of a fine structure on the surface using a SEM or other devices. The general application voltage is preferably in a range from 90 to 150 V, and is adjusted to be in this voltage range for the treatment. The applicable application time is 5 seconds to 30 minutes. The fine structure means a rough structure having projection and holes, which do not exist before the treatment.

[0046] A necessary condition for the discharge voltage is to be a voltage at which the fine structure can be formed on the surface of the target material 4. No fine structure is formed on the surface of the target material 4 at discharge voltages lower than the lower limit. The presence or absence of the fine structure can be determined by examining it with an SEM. The upper limit of the discharge voltage is determined proportional to the treatment time. In other words, in high discharge voltages, although the irregularities on the surface increase, a favorable fine structure is unlikely to be formed because melting occurs. Thus, the upper limit of the discharge voltage may be determined by predetermining a time t for the treatment and performing electric discharge for the time t while the voltage is changed, thereby confirming the formation of the fine structure using a SEM. This revealed that the photocatalyst function increases in accordance with the increase in the discharge voltage in the preferable voltage range. Accordingly, the most preferable discharge voltage is obtained by selecting a discharge voltage in the preferable voltage range close to the upper limit.

[0047] The voltage B different from the voltage A is applied between the anode electrode 3 and the target material 4 (Step S13). The treatment at these two Steps S12 and S13 (Step 1 and Step 2) enables formation of a fine structure having a large specific surface area on the surface of the target material 4. The condition of the electrolyte solution and other conditions may be changed from those at Step S12. The inventors of the present invention have found that in a desirable voltage range, a fine structure enlarges in accordance with the increase in the discharge voltage. To increase a surface area, it is advantageous to provide finer irregularities onto large irregularities. Thus, the voltage B is desirably lower than the voltage A. The voltage difference between the voltage A and the voltage B is desirably 5 V or more because size difference of formed projections has been found when the voltage A differs from the voltage B by 5 V. Furthermore, a voltage close to the upper limit of the desirable voltage range may be selected as the voltage A because it is advantageous to form large irregularities in the treatment at Step S12.

[0048] The treatment at each of Step S12 and Step S13 requires a discharge treatment time of 3 seconds or more. Although a long discharge treatment time is possible such as 60 minutes, a treatment time of 30 minutes or more is not preferable because the target material 4 may be worn if the discharge treatment time is excessively long. It is also not preferable that the discharge treatment time be long in the treatment at Step S13. This is because when the discharge treatment time increases in the treatment at Step S13, a fine structure formed on the surface depends only on the voltage B, which loses the effect of treatment at two stages. The discharge treatment time may thus be 5 minutes or less in the treatment at Step S13.

[0049] FIG. 9 is a diagram illustrating a secondary electron image of the surface of the stainless steel 316 treated at Step S13. In the example illustrated in FIG. 9, Pt was used for the anode electrode 3. Electric discharge was performed for 10 minutes in an aqueous solution of 0.1 mol/L of K_2CO_3 while the voltage A was set to 140 V, and then, electric discharge was performed for 3 minutes while the voltage B was set to 110 V. The stainless steel 316 as the target material 4 was then pulled out of the aqueous solution of K_2CO_3 and was washed with water immediately thereafter. As illustrated in FIG. 9, it is confirmed that a comparatively large projection structure is formed on the surface of the stainless steel 316, and fine projections having an average diameter of 1 μm or smaller are formed on the comparatively large

projections.

[0050] A decolorization test of methylene blue was performed on the stainless steel 316 illustrated in FIGS. 8 and 9 to confirm their photocatalysis performance. This also confirmed that the stainless steel 316 illustrated in FIG. 9 had higher photocatalysis performance. This reveals that higher photocatalysis performance is obtained by performing plasma treatment twice in the electrolyte solution. This technique is expandable to a technique in which plasma discharge treatment in an electrolyte solution is performed in three or more stages. Although performing plasma treatment fewer times is advantageous in view of the time and cost required for the treatment, performing plasma discharge treatment in an electrolyte solution in three or more stages can be selected when higher photocatalysis performance is required.

(Examples)

[0051] A commercially available SUS 316 stainless steel sheet having a thickness of 0.8 mm was cut into a piece having a width of 2.5 mm and a length of 30 mm and was immersed in a diluted hydrochloric acid to be degreased. The sheet was then brought into conduction via a copper wire to serve as a cathode electrode. The upper portion of the electrode including the connecting part with the copper wire was coated with a heat-resistant resin so that the copper wire would not come in contact with an electrolyte solution, and the length of a target portion where the stainless steel was exposed was set to 20 mm. This electrode was immersed in the electrolyte solution. A 0.5 mm ϕ Pt wire having a length of 50 cm that was bended in a form of a plane without making contact with each other was used as an anode electrode. An aqueous solution with a concentration of 0.1 mol/L of K_2CO_3 was used as the electrolyte solution. The application voltage was set in a range from 90 to 140 V, and electric discharge was performed in each condition listed in Table 2. Immediately after the completion, the resultant stainless steel sheet was washed with pure water and dried. As a comparative example, an untreated stainless steel sheet used as a base material was used (on which degreasing was performed by being immersed in a diluted hydrochloric acid). A decolorization test of methylene blue was performed on each of such test pieces to examine their photocatalysis performance.

[0052] The following describes the decolorization test of methylene blue. Before the decolorization test of methylene blue, an aqueous solution with a concentration of 0.1% by mass of methylene blue was singly charged into a cell. The absorbance of the aqueous solution of methylene blue was measured by an absorptiometer, type: V630 manufactured by JASCO Corporation, in which the measurement starts at a wavelength of 720 nm and ends at a wavelength of 500 nm. An absorbance peak at about 660 nm that was relatively large absorbance was determined as an absorbance A_{XS} at a wavelength (X) corresponding to the maximum absorbance, and was employed as a reference.

[0053] In the decolorization test of methylene blue, 4 ml of an aqueous solution with a concentration of 0.1% by mass of methylene blue was charged into a cell, and a test piece (such as a stainless steel sheet subjected to discharge treatment) having a size of 2.5 mm x 20 mm x 0.8 mm (sheet thickness) was immersed therein. The cell containing the aqueous solution was irradiated with ultraviolet rays (having a wavelength of 365 nm). Aluminum foil was set around the cell so that the whole cell could be irradiated with the ultraviolet rays. After the ultraviolet rays were radiated for 24 hours, the test piece was taken out of the cell. The absorbance of the remaining aqueous solution was measured in the aforementioned manner, whereby the absorbance A_{XP} at the wavelength (X) was obtained. A_{XP}/A_{XS} was determined as a change in the absorbance of the aqueous solution of methylene blue to evaluate the degree of decolorization of methylene blue. Decolorization proceeds in accordance with the decrease in the value of A_{XP}/A_{XS} , and the test piece has higher photocatalysis performance, accordingly. FIG. 10 illustrates and Table 2 lists an example of the obtained absorbance spectra and the evaluation result.

[0054] Examples 1 to 3 indicate high decolorization rates as compared with untreated stainless steel sheets (Comparative Examples 1 to 5). It is also confirmed that the performance is greatly improved with discharge performed twice at different voltages.

Table 2

| Test number | Step 1 | | Step 2 | | Absorbance* | Remarks |
|-------------|-------------|------------|-------------|------------|-------------|-------------|
| | Voltage (V) | Time (min) | Voltage (V) | Time (min) | | |
| 21 | - | - | - | - | 0.92 | Comp. Ex. 1 |
| 22 | 90 | 15 | - | - | 0.85 | Comp. Ex. 2 |
| 23 | 120 | 15 | - | - | 0.80 | Comp. Ex. 3 |
| 24 | 140 | 15 | - | - | 0.80 | Comp. Ex. 4 |
| 25 | 140 | 30 | - | - | 0.74 | Comp. Ex. 5 |
| 26 | 140 | 15 | 110 | 5 | 0.27 | Example 1 |

(continued)

| Test number | Step 1 | | Step 2 | | Absorbance* | Remarks |
|-----------------------------------------------------------------------------------------------------------------------------------------------------|-------------|------------|-------------|------------|-------------|-----------|
| | Voltage (V) | Time (min) | Voltage (V) | Time (min) | | |
| 27 | 140 | 15 | 120 | 5 | 0.32 | Example 2 |
| 28 | 140 | 15 | 135 | 5 | 0.41 | Example 3 |
| *) The absorbance of the aqueous solution of methylene blue after the test when the absorbance of the aqueous solution before the test was set to 1 | | | | | | |

Industrial Applicability

[0055] The present invention provides a metal material surface treatment method that can add new function to the surface of the metal material without requiring a lot of labor and high cost, and a metal material subjected to surface treatment by the surface treatment method.

Reference Signs List

[0056]

- 1 container
- 2 electrolyte solution
- 3 anode electrode
- 4 target material (cathode electrode)
- 5 conducting wire
- 6 power source
- 7 thermometer

Claims**1.** A metal material surface treatment method, comprising:

immersing, in an electrolyte solution, a target material as a cathode electrode that is made of the metal material and that has a target surface, and an anode electrode;
 applying a first voltage between the cathode electrode and the anode electrode; and
 applying a second voltage different from the first voltage between the cathode electrode and the anode electrode.

2. The metal material surface treatment method according to claim 1, wherein
 the first voltage is 70 V or more and in a voltage range in which the cathode electrode is not oxidized or does not melt, and
 the second voltage is in the voltage range and differs from the first voltage by 5 V or more.

3. The metal material surface treatment method according to claim 1, wherein
 the metal material is a stainless steel material,
 the first voltage is 60 V or more and in a voltage range in which the cathode electrode does not melt, and the second voltage is in the voltage range and differs from the first voltage by 5 V or more.

4. The metal material surface treatment method according to claim 2 or 3, wherein the second voltage is lower than the first voltage.

5. The metal material surface treatment method according to claim 2 or 4, further comprising
 performing one or more times of treatment at a voltage lower than the second voltage by 5 V after treatment at the applying of the second voltage, and
 wherein the voltage in the later treatment is lower by 5 V or more than the voltage in the immediately preceding treatment.

6. The metal material surface treatment method according to claim 2, 4, or 5, further comprising:

performing water repellent treatment on a surface of the cathode electrode after the applying of the first voltage and the applying of the second voltage.

7. A metal material obtained by being subjected to surface treatment by the metal material surface treatment method according to any one of claims 1 to 6.

FIG.1

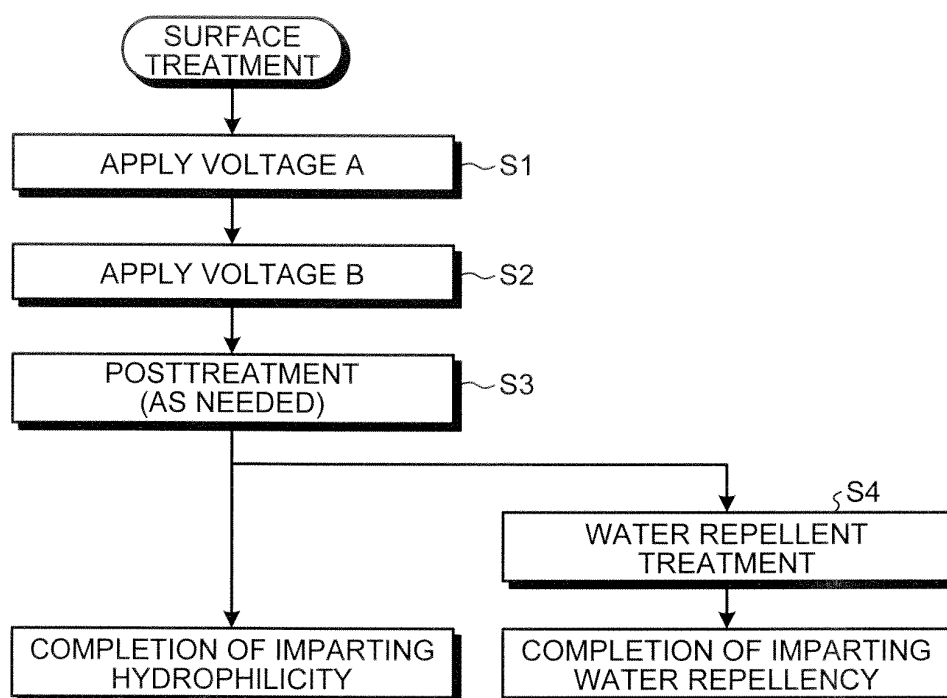


FIG.2

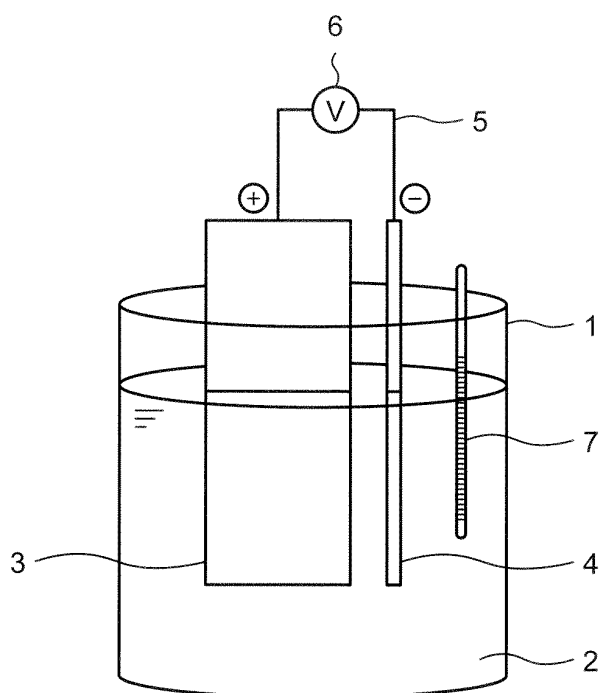


FIG.3

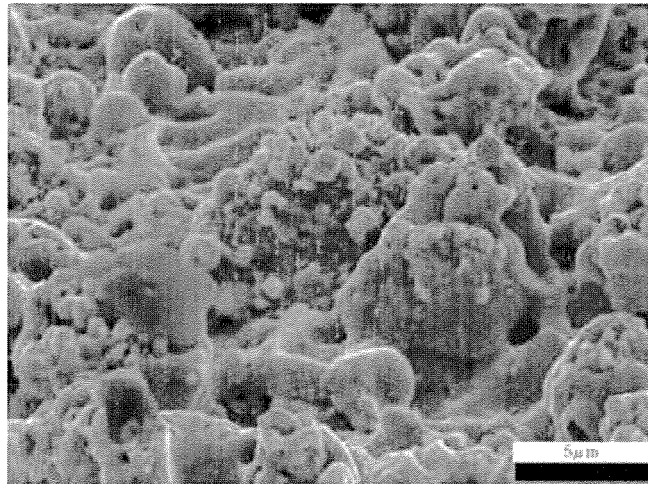


FIG.4

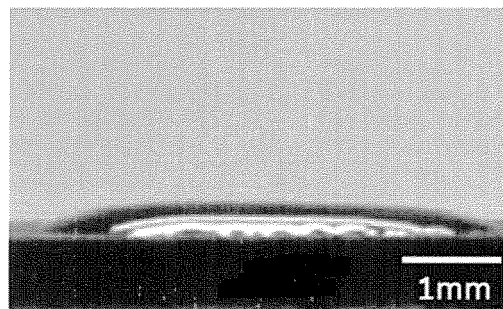


FIG.5

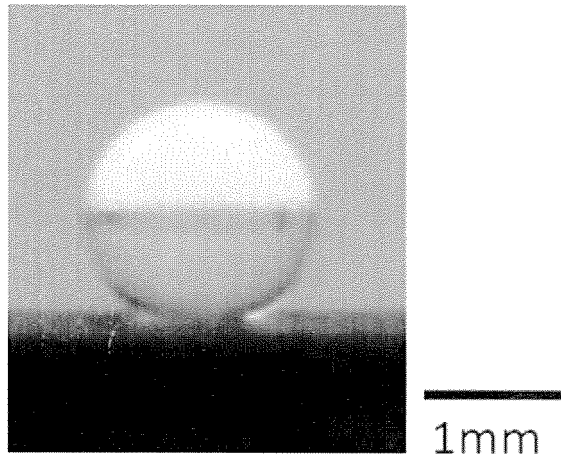


FIG.6

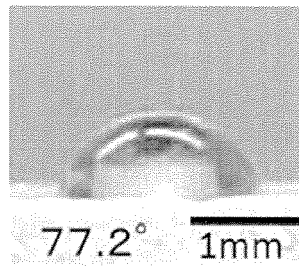


FIG.7

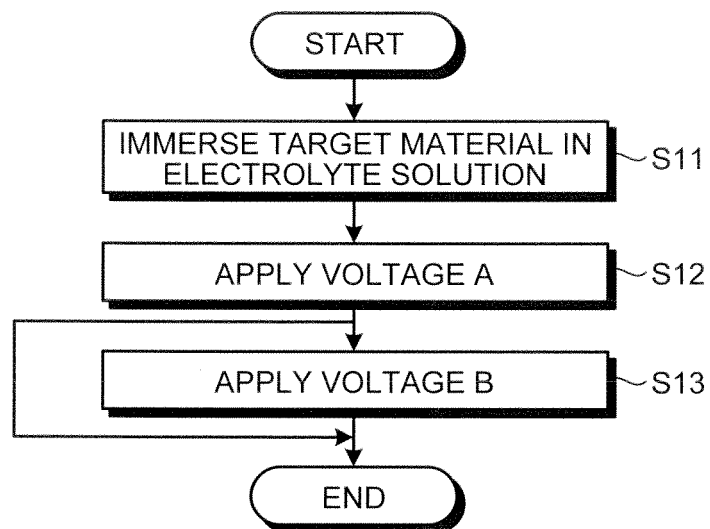


FIG.8

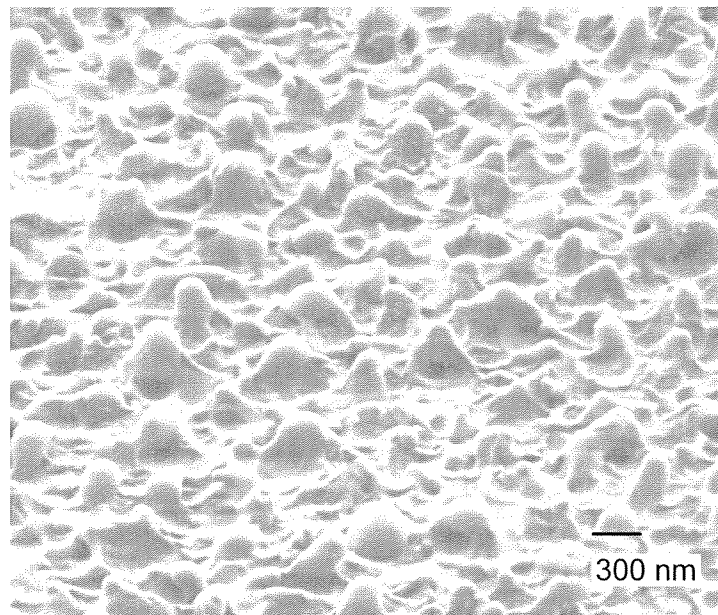


FIG.9

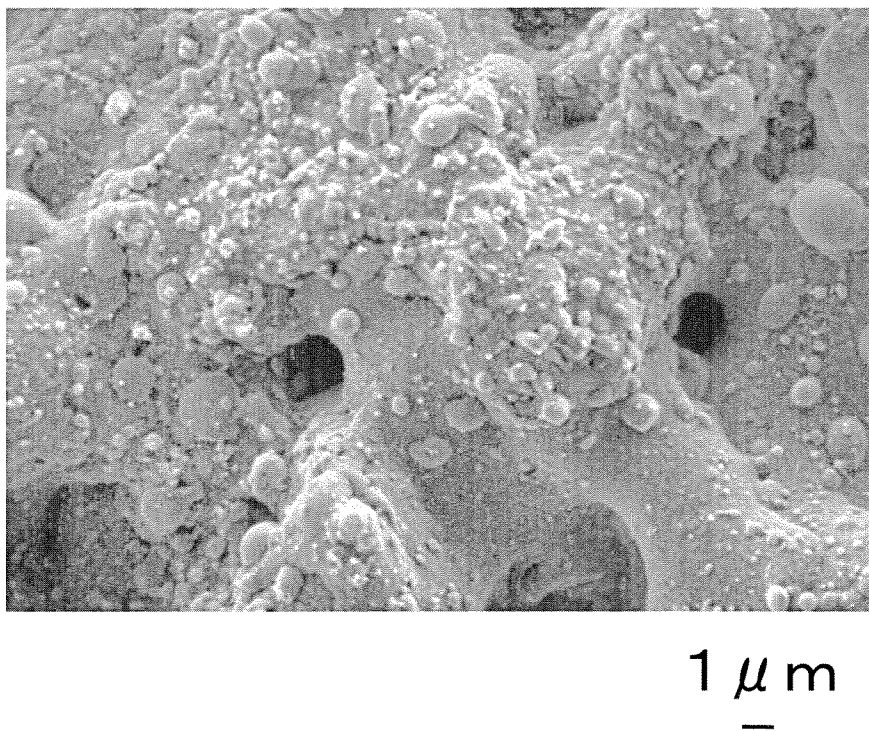
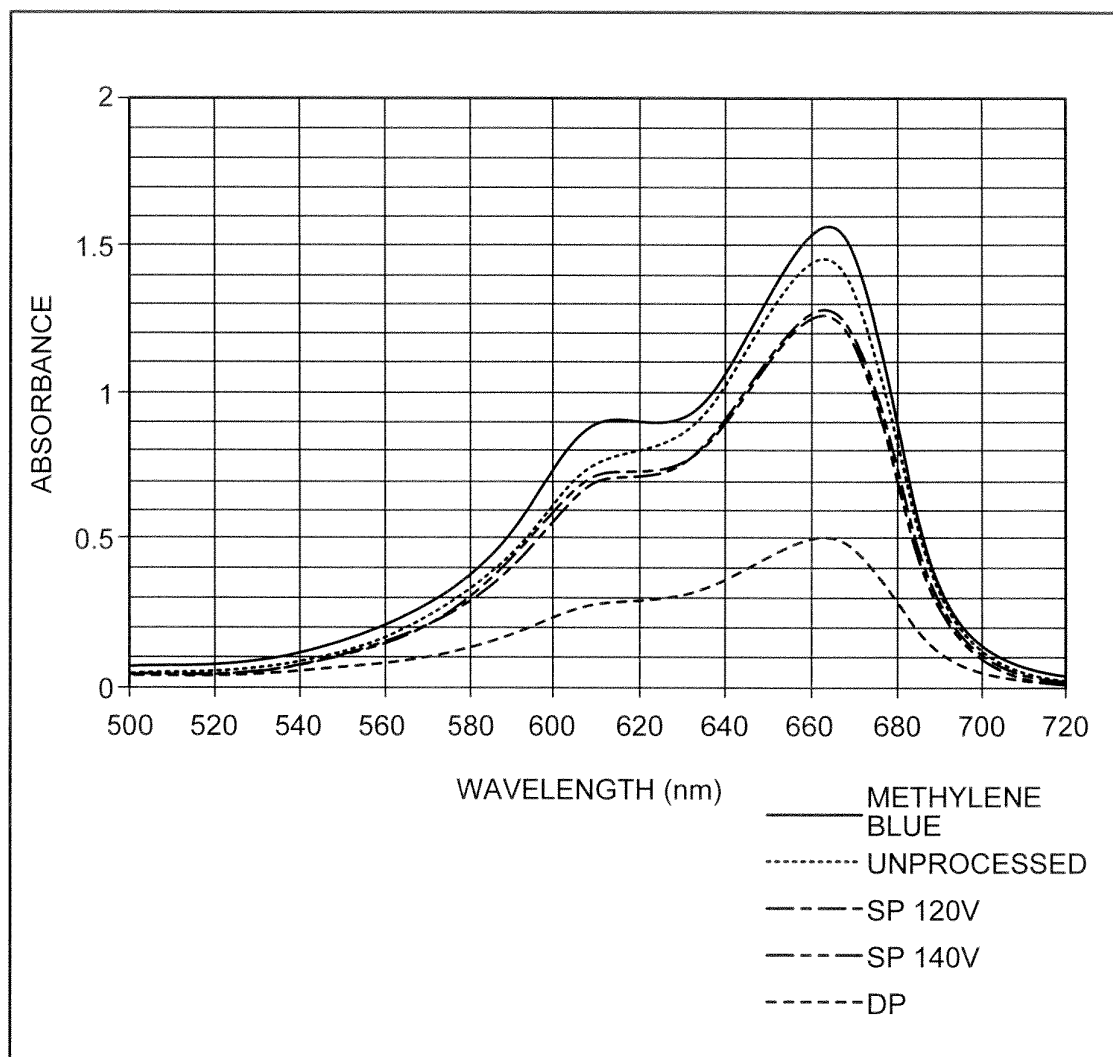


FIG.10



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2013/054412

A. CLASSIFICATION OF SUBJECT MATTER

C23C26/00 (2006.01) i, B23H1/00 (2006.01) i, C25D5/26 (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)

C23C26/00, B23H1/00, C25D5/26

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 1996-2013

Kokai Jitsuyo Shinan Koho 1971-2013 Toroku Jitsuyo Shinan Koho 1994-2013

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 | JP 4-136198 A (Yugen Kaisha Nau Chemical), 11 May 1992 (11.05.1992), entire text (Family: none) | 1-7 |
| A | JP 42-18043 B1 (Kubota Tekko Kabushiki Kaisha), 19 September 1967 (19.09.1967), entire text (Family: none) | 1-7 |
| A | JP 2004-512430 A (Chak Man Thomas Chang), 22 April 2004 (22.04.2004), entire text & US 2003/0052011 A1 & EP 1348041 A & WO 2002/038827 A1 & AU 1479702 A & CN 1473206 A | 1-7 |

☐ 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

"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

11 March, 2013 (11.03.13)

Date of mailing of the international search report

19 March, 2013 (19.03.13)

Name and mailing address of the ISA/
Japanese Patent Office

Authorized officer

Facsimile No.

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

- JP 5179419 A [0006]
- JP 2002053977 A [0006]
- JP 1068477 A [0006]
- JP 9020983 A [0006]
- JP 2008075064 A [0006]
- JP 2000014755 A [0006]
- JP 2001131768 A [0006]
- JP 2007268761 A [0006]
- JP 2002053978 A [0006]

Non-patent literature cited in the description

- **CHANG-SOOLEE et al.** *Thin Solid Films*, 2010, vol. 518, 4757-4761 [0007]