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(54) **Method of coating aluminum wheels and clear coated aluminium wheels**

(57) A method of coating an aluminum wheel comprising subjecting a degreased aluminum wheel to (1) treatment with a surface conditioner, (2) colorless rust prevention with a chromate-free rust preventing agent, and (3) application of a clear coating in succession

wherein said surface conditioner is an aqueous solution containing 0.01 to 20 mass % of a molybdic acid compound and 0.1 to 30 mass % of sulfuric acid, with its pH being less than 1 and the molybdic acid compound/sulfuric acid mass ratio of 0.01 to 1, and said rust inhibition being carried out without chromate and being not accompanied with pigmentation.

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**Description**

## FIELD OF THE INVENTION

**[0001]** The present invention relates to a chromium-free process for coating an aluminum wheel which provides for improved resistance to filiform corrosion and resistance to hot water and to a clear coated aluminum wheel.

## PRIOR ART

**[0002]** Since aluminum wheels require high corrosion resistance, chromates have been preferentially used in the chemical conversion treatment for surface preparation. However, in order that the bright finish of the substrate aluminum wheel may be fully preserved, yellow coloration due to chromating is a drawback. Therefore, attempts have been made to reduce the chromium coverage to the extent causing no coloration. However, hexavalent chromium is highly toxic and in consideration of the risk for environmental pollution by the waste water from the process and in the disposal of aluminum wheels, there is a demand for an anticorrosive agent which does not contain chromium at all.

**[0003]** Furthermore, in the invention described in Japanese Kokai Publication Hei-11-6078, an aluminum wheel is subjected to colorless chromate treatment with a chemical conversion reagent solution (pH 1.5 to 3.0) containing 0.1 to 0.5 g/L of hexavalent chromium ion, 0.01 to 0.5 g/L as Zr of fluorozirconate ion, 0.1 to 0.5 g/L as F of fluoride ion, and 0.01 to 0.1 g/L as Si of a water-soluble silicon compound. The amounts of deposition of chromium in the examples of the above invention are as satisfactory as 13 to 15 mg/m<sup>2</sup> but the fact that a chromate is used is still undeniable. The so-called chromium-free chemical conversion treatment so far proposed does not provide for enough corrosion resistance and has not been commercially implemented.

## SUMMARY OF THE INVENTION

**[0004]** The object of the present invention is to provide a method of coating an aluminum wheel which, despite being corrosion inhibition by a chromium-free chemical conversion treatment, is capable of providing for sufficient corrosion resistance, and a clear coated aluminum wheel.

**[0005]** The method of coating an aluminum wheel according to the present invention comprises subjecting a de-greased aluminum wheel to (1) treatment with a surface conditioner, (2) colorless rust prevention with a chromate-free rust preventing agent, and (3) application of a clear coating in succession,

wherein said surface conditioner is an aqueous solution containing 0.01 to 20 mass % of a molybdic acid compound and 0.1 to 30 mass % of sulfuric acid, with its pH being less than 1 and the molybdic acid compound/sulfuric acid mass ratio of 0.01 to 1, and said rust inhibition being carried out without chromate and being not accompanied with pigmentation.

**[0006]** The clear coated aluminum wheel according to the invention is obtainable by the above method.

## DETAILED DESCRIPTION OF THE INVENTION

**[0007]** The present invention is now described in detail.

**[0008]** The method of coating an aluminum wheel according to the present invention is characterized in that a de-greased aluminum wheel is treated with the under-defined surface conditioner. Thus, this surface conditioner contains 0.01 to 20 mass %, preferably 0.1 to 5 mass %, more preferably 0.1 to 2 mass %, of a molybdic acid compound. When the amount is below 0.01 mass %, no sufficient corrosion resistance can be imparted. When it exceeds 10 mass %, not only the risk of sludge formation is increased but a point of saturation is reached in the corrosion resistance to cause an economic disadvantage. The species of molybdic acid compound which can be used includes molybdic acid, ammonium molybdate, sodium molybdate, potassium molybdate, calcium molybdate, magnesium molybdate, and lithium molybdate, among others. The use of a molybdic acid compound is essential to the present invention. When any other metal oxide such as tungstic acid and permanganic acid is substituted for said molybdic acid compound, no comparable effect can be obtained.

**[0009]** Sulfuric acid is formulated in a proportion of 0.1 to 30 mass %, preferably 1 to 20 mass %, and the surface conditioner is brought to less than pH 1 by using said amount of sulfuric acid. In so doing, it is also necessary to bring the molybdic acid compound/sulfuric acid mass ratio into the range of 0.01 to 1, preferably 0.05 to 0.5. When the pH of the conditioner is over 1, the removal of aluminum oxide film cannot satisfactorily be carried out using sulfuric acid. When the mass ratio is less than 0.01, the concentration of the molybdic acid compound is too low to insure a sufficient etching action on the aluminum surface so that no adequate corrosion resistance may be realized. On the other hand,

when the mass ratio is over 1, the sulfuric acid concentration is relatively decreased to make it difficult to maintain the conditioner below pH 1. Incidentally, the use of phosphoric acid in lieu of sulfuric acid is not acceptable because the treated aluminum surface is contaminated with residues of molybdenum to detract from corrosion resistance.

**[0010]** The above surface conditioner may contain a variety of additives. As examples, there can be mentioned an inorganic acid, such as nitric acid, which is expected to double as a corrosion inhibitor for stainless steel vessels and an etching aid, acetic acid as a sludge inhibitor, an organic acid such as polyacrylic acid, an oxidizing agent such as hydrogen peroxide which is added for oxidizing the Mo (IV) formed on bath aging to Mo (VI), and metal ions, such as cerium, manganese and other ions, which are corrosion-resistant adjuvants.

**[0011]** The method of coating an aluminum wheel according to the present invention includes a first step which comprises treating a degreased aluminum wheel with said surface conditioner. Prior to this treatment, the degreasing agent is preferably rinsed off with water. This treatment may be carried out by whichever of the dip process and the spray process. The bath temperature for the dip process and the solution temperature for the spray process may both be 20 to 80 °C, preferably 50 to 70 °C, while the immersion or spraying time may be 10 to 600 seconds, preferably 30 to 300 seconds. When the temperature is less than 20 °C or the treating time is less than 10 seconds, the effect of treatment is not sufficient, failing to provide an adequate corrosion resistance. The treatment at a temperature over 80 °C or exceeding 600 seconds is no more than a waste of energy.

**[0012]** As a second step after the first step, the method further comprises treating the above surface-conditioned wheel with a chromium-free chemical conversion reagent for rust prevention. Here, the substrate is first rinsed with water and, then, the rust inhibition treatment is carried out. As the chemical conversion reagent, any hitherto-known colorless reagent not containing chromium can be applied. For example, a zirconium salt, titanium salt, a silicon salt or a boron salt; a fluoride thereof; or a chromium-free chemical conversion reagent comprising any of these salts and phosphoric acid, sulfuric acid, nitric acid or manganic acid. The aluminum wheel treated by the above method retains the characteristic silvery gloss of aluminum because, unlike chromates, the chromium-free chemical conversion reagent has no color of its own.

**[0013]** As a third step, the method further comprises optionally cleaning and drying the aluminum wheel which has undergone the above chromium-free chemical conversion treatment, followed by coating it with a clear coating. The coating which can be used is not particularly restricted but a clear powder coating is preferably used because it can be coated thickly for improving chipping resistance. As examples of said clear coating, there may be mentioned coatings containing, as the film-forming component, thermosetting resins which are solid at room temperature, such as polyester resin, acrylic resin-modified polyester resin, epoxy resin-modified polyester resin, epoxy resin and fluororesin. These are generally used in combination with a curing agent. The curing agent, when used, is preferably a blocked isocyanate. The film-forming component is preferably used in a proportion of 45 to 95 mass parts per 100 mass parts of the powder coating from the standpoints of hiding power, bend processability, film flatness and physical properties of the coating film.

**[0014]** Regarding the coating technique, electrostatic coating, spray coating, brush coating, electrodeposition, etc. can be selectively employed. However, when a clear powder coating is used, electrostatic coating is preferred. The clear coated aluminum wheel thus obtained in accordance with the present invention retains the gloss of the substrate aluminum wheel and has good white rust resistance and pitting resistance.

**[0015]** Since the method of coating an aluminum coating of the invention comprises treating the substrate with a surface conditioner which contains a defined concentration of a molybdic acid compound in a defined mass ratio with sulfuric acid, with its pH being less than 1, the method provides an aluminum wheel excellent in corrosion resistance using chromate-free chemical conversion reagents and coating without any chromate type chemical conversion reagent. Further, choosing a colorless type chromium-free chemical conversion reagent, the product aluminum wheel having the characteristic silvery gloss itself can be obtained without polluting environment.

## EXAMPLES

**[0016]** The following working and comparative examples illustrate the present invention in further detail. It should be understood that all formulating amounts are mass % unless otherwise specified.

### Example 1

#### Preparation of surface conditioner

**[0017]** Ammonium molybdate and sulfuric acid were dissolved in deionized water at final concentrations of 2% and 10%, respectively, to prepare an aqueous surface conditioner. The pH of the conditioner was 0.6 and the mass ratio of ammonium molybdate to sulfuric acid was 0.2.

Treatment and coating

**[0018]** An aluminum alloy test panel ("A3003", Japan Test Panel Co.) was immersed in a degreasing bath of 3 mass % concentration ("Surf Cleaner 53", Nippon Paint) at 40 °C for 30 seconds and, then, rinsed with water. The rinsed panel was dipped in a bath comprising said surface conditioner at 50 °C for 30 seconds for surface preparation. The panel was rinsed with water and treated with a chromate-free rust preventing agent ("Alsurf 301", Nippon Paint) at 40 °C for 60 seconds and dried at 160 °C for 20 minutes.

**[0019]** Then, a powder coating ("Powdax A400 Clear", Nippon Paint) was applied in a film thickness of 100 μm by the corona electrostatic coating technique and baked at 160 °C for 20 minutes to prepare a coated panel.

Method of Evaluation

**[0020]** The coated panel prepared above was evaluated as follows . The results are shown in Table 1.

## &lt;Filiform corrosion resistance&gt;

**[0021]** Using a sharp-edged cutter knife, the coated surface of the panel was cross-cut and subjected to a 24-hour salt spray test in accordance with JIS Z 2371. The panel was then allowed to sit for 1000 hours in a humid atmosphere at 40 °C and 70 to 75% R.H. The maximum width of corrosion (on one side of the cutting line) was measured. The panel was regarded as acceptable when the maximum width of corrosion was not over 0.5 mm.

## &lt;Warm water resistance&gt;

**[0022]** The coated panel was immersed in deionized water at 50 °C for 120 hours and, then, left sitting to dry for 24 hours. Thereafter, using a cutter knife, the coated surface was scored at a pitch of 2 mm in a crisscross pattern of 11×11 lines to make 100 squares. A transparent adhesive tape ("Cellophane tape", Nichiban) was affixed to the surface to cover all the squares and, then, peeled off in a perpendicular direction, and the intact squares were counted. When at least 97 of the 100 squares remained unpeeled, the panel was regarded as being acceptable.

Examples 2 to 10

**[0023]** Except that the surface conditioner compositions (species and concentration of molybdic acid compound, concentration of sulfuric acid, the ratio of molybdic acid compound to sulfuric acid, presence or absence of an additive) and conditions of surface preparation used were varied, the testpieces were prepared in the same way as in Example 1 and evaluated by the same method as above. The compositions used and the results of evaluation are shown in Table 1.

Comparative Examples 1 to 5

**[0024]** With regard to the surface preparation step, this step was omitted in Comparative Example 1; a surface conditioner with a molybdic acid compound/sulfuric acid ratio of 5 which is outside the range of the invention was used in Comparative Example 2, surface preparation treatments represently not using molybdic acid compound and sulfuric acid were carried out in Comparative Examples 3 and 4; and tungstic acid instead of molybdic acid was used in Comparative Example 5. Otherwise the testpieces were prepared in the same way as in Example 1 and evaluated by the same method as above. The compositions used and the results of evaluation are shown in Table 2.

Table 1

| Parameter           |                                             |                                        | Ex. 1                | Ex. 2                | Ex. 3     | Ex. 4                | Ex. 5                |
|---------------------|---------------------------------------------|----------------------------------------|----------------------|----------------------|-----------|----------------------|----------------------|
| Surface preparation | Molybdic acid compound                      | Species                                | NH <sub>3</sub> salt | NH <sub>3</sub> salt | Anhydride | NH <sub>3</sub> salt | NH <sub>3</sub> salt |
|                     |                                             | Conc. (mass %)                         | 2                    | 0.01                 | 20        | 0.1                  | 5                    |
|                     | H <sub>2</sub> SO <sub>4</sub>              | Conc. (mass %)                         | 10                   | 0.1                  | 30        | 10                   | 5                    |
|                     | Ratio                                       | Mo acid/H <sub>2</sub> SO <sub>4</sub> | 0.2                  | 0.1                  | 0.66      | 0.01                 | 1                    |
|                     | Treating condition                          | Time (sec)                             | 30                   | 30                   | 30        | 30                   | 30                   |
|                     |                                             | Temp. (°C)                             | 50                   | 50                   | 50        | 50                   | 50                   |
| Evaluation          | Filiform corrosion resistance after coating |                                        | 0.1 mm               | 0.3 mm               | 0.4 mm    | 0.1 mm               | 0.5 mm               |
|                     | Warm water resistance after coating         |                                        | 100/100              | 97/100               | 97/100    | 99/100               | 97/100               |

| Parameter           |                                             |                                        | Ex. 6                | Ex. 7                | Ex. 8                              | Ex. 9                  | Ex. 10               |
|---------------------|---------------------------------------------|----------------------------------------|----------------------|----------------------|------------------------------------|------------------------|----------------------|
| Surface preparation | Molybdic acid compound                      | Species                                | NH <sub>3</sub> salt | NH <sub>3</sub> salt | NH <sub>3</sub> salt               | NH <sub>3</sub> salt   | NH <sub>3</sub> salt |
|                     |                                             | Conc. (mass %)                         | 2                    | 2                    | 2                                  | 2                      | 2                    |
|                     | H <sub>2</sub> SO <sub>4</sub>              | Conc. (mass %)                         | 10                   | 10                   | 10                                 | 10                     | 10                   |
|                     | Ratio                                       | Mo acid/H <sub>2</sub> SO <sub>4</sub> | 0.2                  | 0.2                  | 0.2                                | 0.2                    | 0.2                  |
|                     | Additives                                   |                                        | -                    | -                    | H <sub>2</sub> O <sub>2</sub> , 1% | Polyacrylic acid, 0.2% | Nitric acid, 1%      |
|                     | Treating condition                          | Time (sec)                             | 30                   | 180                  | 30                                 | 30                     | 30                   |
|                     |                                             | Temp. (°C)                             | 70                   | 20                   | 50                                 | 50                     | 50                   |
| Evaluation          | Filiform corrosion resistance after coating |                                        | 0.1 mm               | 0.1 mm               | 0.1 mm                             | 0.1 mm                 | 0.1 mm               |
|                     | Warm water resistance after coating         |                                        | 100/100              | 100/100              | 100/100                            | 100/100                | 100/100              |

Table 2

| Parameter           |                                             |                                        | Compar<br>. Ex. 1 | Compar<br>. Ex. 2    | Compar<br>. Ex. 3 | Compar<br>. Ex. 4    | Compar<br>. Ex. 5 |
|---------------------|---------------------------------------------|----------------------------------------|-------------------|----------------------|-------------------|----------------------|-------------------|
| Surface preparation | Molybdic acid compound                      | Species                                | -                 | NH <sub>3</sub> salt | -                 | NH <sub>3</sub> salt | -                 |
|                     |                                             | Conc. (mass %)                         | -                 | 5                    | -                 | 1                    | -                 |
|                     | H <sub>2</sub> SO <sub>4</sub>              | Conc. (mass %)                         | -                 | 1                    | 10                | -                    | 10                |
|                     | Ratio                                       | Mo acid/H <sub>2</sub> SO <sub>4</sub> | -                 | 5                    | -                 | -                    | -                 |
|                     | Additives                                   |                                        | -                 | -                    | -                 | -                    | Tungstic acid     |
|                     | Treating condition                          | Time (sec)                             | -                 | 30                   | 30                | 30                   | 30                |
|                     |                                             | Temp. (°C)                             | -                 | 50                   | 50                | 50                   | 50                |
| Evaluation          | Filiform corrosion resistance after coating |                                        | 2.8 mm            | 1.9 mm               | 1.7 mm            | 2.2 mm               | 1.8 mm            |
|                     | Warm water resistance after coating         |                                        | 77/<br>100        | 85/<br>100           | 89/<br>100        | 83/<br>100           | 87/<br>100        |

[0025] It will be apparent from Tables 1 and 2 that the panels treated with the surface conditioners according to the above Examples have sufficient filiform corrosion resistance and pitting resistance for use as aluminum wheels.

## Claims

### 1. A method of coating an aluminum wheel

comprising subjecting a degreased aluminum wheel to (1) treatment with a surface conditioner, (2) colorless rust prevention with a chromate-free rust preventing agent, and (3) application of a clear coating in succession wherein said surface conditioner is an aqueous solution containing 0.01 to 20 mass % of a molybdic acid compound and 0.1 to 30 mass % of sulfuric acid, with its pH being less than 1 and the molybdic acid compound/sulfuric acid mass ratio of 0.01 to 1, and said rust inhibition being carried out without chromate and being not accompanied with pigmentation.

### 2. A clear coated aluminum wheel

which is obtainable by the method according to Claim 1.