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(54) **Aluminium wheel surface conditioner, method of coating therewith, and unpigmented aluminium wheel**

(57) This invention provides a surface conditioner for aluminum wheel comprising 0.01 to 10 mass % of a molybdic acid compound and 0.1 to 30 mass % of sulfuric acid and having a pH of less than 1 and a mass ratio of said molybdic acid compound to sulfuric acid within the range of 0.01 to 1 (former/latter), and further

provides a coating method of an aluminum wheel which comprises treating a degreased aluminum wheel with the surface conditioner as mentioned above, washing the treated wheel with water, chromating the same at a chromium coverage of 1 to 10 mg/m², washing the chromated wheel with water, drying the same and applying a clear coating.

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Description

FIELD OF THE INVENTION

[0001] This invention is related to a surface conditioner for aluminum wheel capable of producing a high rust-preventive effect even when the chromium coverage is so low as to cause no coloration, a coating method comprising a treatment with said surface conditioner, and 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. When, to avoid this disadvantage, the chromium coverage was reduced to the extent causing no coloration, there was a problem that the corrosion resistance was reduced. Furthermore, in consideration of the risk for environmental pollution, the amount of use of chromium is preferably as low as possible.

[0003] For example, in the invention disclosed in Japanese Kokai Publication Hei-7-18492, the surface of an aluminum wheel is machined to a R_{max} of 100 μm or less and a colorless chromate film is formed on the aluminum wheel by a cathodic electrolysis using an acidic solution containing not less than 2 g/l of hexavalent chromium ion and 20 to 2000 ppm of sulfate ion and having a pH of 0.6 to 1.7 at a current density of 0.5 to 15 A/dm².

[0004] 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, 0.0i to 0.5 g/l of Zr as fluorozirconate ion, 0.1 to 0.5 g/l of F as fluoride ion, and 0.01 to 0.1 g/l of Si as a water-soluble silicon compound.

SUMMARY OF THE INVENTION

[0005] In the above invention disclosed in Japanese Kokai Publication Hei-7-18492, the range of chromium coverage is as high as 50 to 250 mg/m². In the invention according to Japanese Kokai Publication Hei-11-6078, the amount of chromium deposition is acceptable, namely 13 to 15 mg/m², but from the standpoint of environmental protection, it is desirable that this amount be further reduced.

[0006] The present invention has for its object to provide a surface conditioner for aluminum wheel capable of producing a high rust-preventive effect even when the chromium coverage is so low as to cause no coloration, a coating method comprising a treatment with this surface conditioner, and a clear coated aluminum wheel.

[0007] The surface conditioner for aluminum wheel of the present invention is an aqueous solution comprising 0.01 to 10 mass % of a molybdic acid compound and 0.1 to 30 mass % of sulfuric acid and having a pH of less than 1 and a mass ratio of said molybdic acid compound to sulfuric acid within the range of 0.01 to 1 (former/latter).

[0008] The coating method of an aluminum wheel according to the present invention comprises treating a degreased aluminum wheel with said surface conditioner, washing the treated wheel with water, chromating the same at a chromium coverage of 1 to 10 mg/m², washing the chromated wheel with water, drying the same and applying a clear coating. The clear coated aluminum wheel of the present invention is a wheel fully retaining the original brightness of substrate aluminum as obtainable using the above coating method.

DETAILED DESCRIPTION OF THE INVENTION

[0009] The present invention is now described in detail.

[0010] The surface conditioner of the present invention contains 0.01 to 10 mass %, preferably 0.1 to 5 mass %, more preferably 0.1 to 2 mass %, of a molybdic acid compound. When the amount is less than 0.01 mass %, no sufficient resistance to filiform corrosion 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 anticorrosive effect 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, and should any other metal oxide such as tungstic acid and permanganic acid be substituted for said molybdic acid compound, no comparable effect could be obtained.

[0011] Sulfuric acid is formulated in a proportion of 0.1 to 30 mass %, preferably 1 to 20 mass %, and the conditioner is adjusted with this amount of sulfuric acid to pH not over 1, preferably pH 0.3 to 0.8. In so doing, it is also necessary

to bring the mass ratio (molybdic acid compound/sulfuric acid) into the range of 0.01 to 1, preferably 0.05 to 0.5. When the pH of the conditioner is not less than 1, the aluminum oxide film-removing effect of sulfuric acid is insufficient. 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 sufficient resistance to filiform corrosion may be obtained. On the other hand, when the mass ratio is more than 1, the sulfuric acid concentration is relatively decreased to make it difficult to maintain the pH of the conditioner less than 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.

[0012] In addition to the above components, the 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 retarder, 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 used as corrosion inhibitors.

[0013] The coating method of an aluminum wheel according to the present invention is now described. The aluminum wheel is first treated with a degreasing agent for removing soils and oils from its surface. After degreasing, the degreasing agent is washed with water and, thereafter, the wheel is treated with the surface conditioner of the present invention. This treatment may be carried out in an immersion process or in a spray process. The bath temperature for the immersion 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 lower than 20 °C or the treating time is less than 10 seconds, the effect of treatment is decreased to thereby lose an acceptable resistance to filiform corrosion. The treatment at a temperature over 80 °C or exceeding 600 seconds is no more than a waste of energy.

[0014] After the above treatment with the surface conditioner, the wheel is washed with water and chromated at a chromium coverage of 1 to 10 mg/m². The chromate which can be used for this purpose may for example be the known CrO₃-hydrogen fluoride system, the chromate type system comprising the above system supplemented with K₃Fe(CN)₆, zirconium hydrofluoride (salt) or the like, or the chromium phosphate type system comprising CrO₃, hydrogen fluoride and phosphoric acid. The aluminum wheel treated by the above method is chromium-lean and retains the characteristic silvery gloss of the aluminum.

[0015] Then, the chromated aluminum wheel is washed thoroughly and dried and a clear coating is applied. The coating which can be used for this purpose is not particularly restricted and the coating method may also be any of spray coating, brush coating, electrostatic coating and electrodeposition. However, a clear powder coating is preferred because a sufficiently thick coat can be built up for enhanced chipping resistance. The clear coated aluminum wheel thus obtained retains the gloss of substrate aluminum and has good resistance to filiform corrosion, good resistance to hot water, and the additional advantage of a low chromium film content.

[0016] The surface conditioner for aluminum wheel of the present invention contains a molybdic acid compound and sulfuric acid in an amount and mass ratio within the specific range and has a pH of less than 1. Therefore, when the treatment process with this surface conditioner is applied to the general process (degreasing → chromating → coating) after degreasing, the aluminum wheel as obtained is excellent in the resistance to filiform corrosion and hot water.

[0017] As the result of the analysis of the aluminum surface after the above surface treatment, molybdenum is not detected, so the mechanism of said conditioner cannot be unraveled. However, molybdic acids may be considered to act as an oxidizing agent for removing the oxidized film from the aluminum surface to thereby enhance the etching by sulfuric acid, so it can be supposed that this action leads to an increased activity on the aluminum surface to thereby improve the effect of the resistance to filiform corrosion by chromating treatment. Furthermore, as mentioned hereinabove, other metal oxide such as tungstic acid and permanganic acid has no effects, therefore molybdic acids may have an action for leveling the etching in addition to the oxidizing force.

[0018] The above characteristics do not deteriorate even if the chromium coverage is decreased to 1 to 10 mg/m² in the chromating treatment, therefore a clear coated aluminum wheel excellent in gloss can be obtained.

BEST MODE FOR CARRYING OUT THE INVENTION

[0019] The following examples and comparative examples illustrate the present invention in further detail. It should be understood that all formulating quantities are by weight (mass %) unless otherwise specified.

Example 1

Surface conditioner

[0020] Ammonium molybdate and sulfuric acid were dissolved in deionized water at final concentrations of 2% and

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10%, respectively, to prepare an aqueous surface conditioner. The pH of this aqueous conditioner was 0.6 and the mass ratio of ammonium molybdate to sulfuric acid was 0.2.

Treatment and test coating

[0021] The aluminum test panel A1100 (manufactured by Japan Test Panel) was immersed in a degreasing bath of 3 mass % concentration (Surf Creaner 53, Nippon Paint) at 45 °C for 30 seconds and the degreased panel was rinsed with water. The rinsed panel was then immersed in a bath comprising said surface conditioner at 50 °C for 30 seconds to condition its surface. The panel was rinsed with water and immersed in a chemical conversion bath comprising a 0.1% solution of chromating reagent ("Alsurf 1000", Nippon Paint) at 40 °C for 1 minute. The treated panel was rinsed with water and dried at 80 °C for 10 minutes. The chromate-coating amount was about 5 mg/m². Then, a powder coating ("Powdax A400 Clear", Nippon Paint) was applied in a coat 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

[0022] The coated panel prepared above was evaluated as follows.

The results are shown in Table 1.

<Filiform corrosion resistance>

[0023] 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.

<Warm water resistance>

[0024] 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 11x11 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 5

[0025] Except that, in the surface conditioner recipe, the species and concentration of molybdic acid compound, the concentration of sulfuric acid and the ratio of molybdic acid compound to sulfuric acid were changed, the test panels were treated in otherwise the same manner as in Example 1 and the coated panels were evaluated also as in Example 1. The recipes used and the results of evaluation are shown in Table 1.

Comparative Examples 1 to 5

[0026] The surface conditioning treatment was omitted in Comparative Example 1; the molybdic acid compound was not used in Comparative Example 2; sulfuric acid was not used in Comparative Example 3; tungstic acid was used in lieu of molybdic acid compound in Comparative Example 4; and the concentration of molybdic acid compound was set at 0.005 mass % in Comparative Example 5. Otherwise the procedure of Example 1 was repeated to treat test panels and evaluate coated panels. The recipes 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	Species	NH ₃ salt	Anhydride	NH ₃ salt	Anhydride	NH ₃ salt
	Molybdc acid compound	2	20	0.01	5	0.1
	Sulfuric acid	10	30	0.1	5	10
	Ratio	0.2	0.67	0.1	1	0.01
	Treating conditions	30	30	30	30	30
	Temp. (°C)	50	50	50	50	50
	Filiform corrosion resistance (mm)	0.1	0.3	0.2	0.2	0.2
Warm water resistance		100/100	98/100	98/100	98/100	100/100

Table 2

Parameter		Compar. Ex. 1	Compar. Ex. 2	Compar. Ex. 3	Compar. Ex. 4	Compar. Ex. 5
Surface preparation	Molybdc acid compound	-	-	NH ₃ salt	-	NH ₃ salt
	Concentration (Mass %)	-	-	2	-	0.005
	Sulfuric acid	-	10	-	10	10
	Ratio	-	-	-	-	0.0005
	MO acid/H ₂ SO ₄	-	-	-	Tungstic acid	-
	Additives	-	-	-	-	-
	Level (mass %)	-	-	-	2	-
	Treating condition	-	30	30	30	30
	Temperature (°C)	-	50	50	50	50
	Filiform corrosion resistance (mm)	2.0	1.5	1.8	1.7	1.5
Warm water resistance		84/100	92/100	87/100	89/100	93/100

[0027] 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 warm water resistance for use as aluminum wheel.

Claims

1. A surface conditioner for aluminum wheel

5 which is an aqueous solution
 comprising 0.01 to 10 mass % of a molybdic acid compound and 0.1 to 30 mass % of sulfuric acid
 and having a pH of less than 1 and a mass ratio of said molybdic acid compound to sulfuric acid within the
 range of 0.01 to 1 (former/latter) .

10 **2.** A coating method of an aluminum wheel

 which comprises treating a degreased aluminum wheel with the surface conditioner according to Claim 1,
 washing the treated wheel with water, chromating the same at a chromium coverage of 1 to 10 mg/m², washing
 the chromated wheel with water, drying the same and applying a clear coating.

15 **3.** A clear coated aluminum wheel

 which is obtainable by the coating method according to Claim 2.

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