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(54) **Title:** SURFACE PREPARATION AGENT AND SURFACE PREPARATION METHOD

(57) **Abstract:** An agent suitable for use in preparing metal surfaces, especially surfaces containing aluminum, is provided which contains at least one water-soluble vanadium compound, at least one titanium-containing or zirconium-containing water-soluble complex fluoride, and at least one resin. The agent is capable of forming a strongly rust preventive base coating that is highly adherent for top coats and bonded films.

Surface Preparation Agent and Surface Preparation Method

Field of the Invention

This invention relates to a surface preparation agent and a surface preparation method. More particularly, this invention relates to a chromium compound-free dry-in-place rust preventive surface preparation agent that can form an organic-inorganic composite coating on the aluminum sheet and aluminum alloy sheet used in the automotive sector and for household electrical appliances, construction materials, and food containers. This organic-inorganic composite coating can function as an underpaint base coating or as a base coating for bonded films and improves the antirusting performance and is highly adherent for top coats and films. The invention additionally relates to a rust preventive surface preparation method that uses said surface preparation agent.

Background of the Related Art

Chromate treatments that use a treatment agent containing chromic acid, dichromic acid, or a chromate salt are known as a rust preventive surface preparation method for the aluminum and aluminum alloy (also referred to hereinafter simply as aluminum alloy) sheet that is widely used, for example, for household electrical appliances, construction materials, and food containers. Chromate treatment is carried out in order to improve the rust preventive performance of aluminum alloy surfaces and in order to improve the adherence of aluminum alloy surfaces for top coats and bonded films. The chromate treatment of aluminum alloy surfaces is characterized by a high productivity and an excellent uniformity of surface treatment and has been widely practiced as a post-processing surface treatment method.

Chromate treatments can be broadly divided into the following 3 categories: reactive chromate treatments, dry-in-place chromate treatments, and electrolytic chromate treatments.

With respect to its features, dry-in-place chromate treatment wastes less treatment bath than the reactive and electrolytic varieties and, because it also does not require a post-treatment water rinse, it imposes a lighter load on wastewater treatment and affords a better productivity. In addition, the coating produced by dry-in-place chromate treatment contains hexavalent chromium, which acts on exposed regions of the substrate metal (treatment defect regions and damaged areas that are produced post-treatment) to form a passivating coating, i.e., dry-in-place coatings have a self-repairing activity. These features have led to the wide use of dry-in-place chromate treatments.

At the same time, however, the human-toxic hexavalent chromium present in the treatment bath is eluted by contact with water, and as a result dry-in-place chromate treatment suffers from problems with regard to environmental pollution and toxic effects for the human body.

In contrast, trivalent chromium is the main component of the coatings formed by reactive chromate and electrolytic chromate treatments. As a consequence, there is almost no chromium elution from metal sheet carrying these coatings and these technologies therefore enjoy an excellent position with regard to environmental pollution and human safety.

The coatings formed by reactive chromate or electrolytic chromate treatment do not, however, have the self-repairing function described above and may exhibit an inadequate corrosion resistance depending on the particular service. Moreover, in order to maintain the treatment bath in a condition suitable for the execution of surface treatment, it may be necessary in either technology to periodically renew the bath or to continually overflow prescribed amounts of the bath. These technologies also impose heavy wastewater treatment burdens since they cannot avoid the production of, for example, rinse water that contains hexavalent chromium.

Thus, there is a need for the development of a rust preventive surface preparation method that avoids the problems associated with the use of hexavalent-chromium containing treatment baths, that is, for the development of a dry-in-place treatment bath and method that are essentially free, or more preferably entirely free, of hexavalent chromium.

The conversion treatment bath disclosed in Japanese Laid Open (Kokai or Unexamined) Patent Application Number Sho 56-136978 (136,978/1981) is typical of nonchromate-type (chromium-free) surface treatment technologies. This bath characteristically comprises an aqueous solution containing a vanadium compound and at least one compound selected from the group consisting of titanium salts, zirconium salts, and zinc salts.

This treatment bath, however, cannot be considered a fully rationalized surface treatment for metal sheet because it is used in a treatment methodology that entails the immersion of aluminum alloy in the bath for 1 to 20 minutes and preferably 3 to 5 minutes.

Japanese Laid Open (Kokai or Unexamined) Patent Application Number Hei 1-246370 discloses a conversion treatment method that employs degreasing with a particular degreasing agent followed by conversion treatment with a particular conversion treatment agent. The degreasing agent has a pH adjusted to 11 to 13 using alkali metal hydroxide and contains PO_4 ion, aluminum chelating agent, and surfactant. The conversion treatment agent has a pH adjusted to 1.5 to 4.0 and contains V ion, Zr ion, PO_4 ion, and effective F ion.

The advantages of this method are that it does not employ chromium and that it can carry out degreasing, rinsing, and conversion treatment at high speeds while maintaining the quality level. However, since this is a conversion treatment method, it requires a post-treatment water rinse, there are limitations on the weight of the obtained coating, and the corrosion resistance may be unsatisfactory depending on the particular application.

Japanese Laid Open (Kokai or Unexamined) Patent Application Number Hei 1-131281 (131,281/1989) discloses a highly corrosion-resistant rustproofing pigment that has both the oxidizer and deposition functions of the chromate ion. A chromium-free dry-in-place rust preventive treatment is made possible through the use of 0.1 to 50 parts of this pigment per 100 parts total paint solids. This is not, however, a technology contemplated for use for surface preparation prior to painting or film lamination, and its application within this sphere has been highly problematic.

The problems to be solved by this invention are therefore the problems associated with the prior art as described above. That is, this invention seeks to provide a technology that can form a strongly rust preventive base coating that is highly adherent for top coats and bonded films.

Summary of the Invention

As a result of intensive investigations into means that would remedy the foregoing problems, the inventors found that a composition containing a vanadium compound and a particular complex fluoride could impart an excellent rustproofing performance to aluminum alloy surfaces. The inventors also discovered that the admixture with, for example, waterborne polymer, made it possible to impart an excellent rustproofing performance of the dry-in-place type to aluminum alloy surfaces.

The inventors also discovered that the use of particular types of complex fluorides and waterborne polymers produced a dry-in-place rust preventive surface preparation agent capable of forming a base coating with an even better adherence for top coats and bonded films.

This invention was developed based on the preceding considerations. The problems described above are solved by a surface preparation agent that characteristically comprises

(A) at least one water-soluble vanadium compound,
(B) at least one titanium-containing or zirconium-containing water-soluble complex fluoride, and
(C) at least one resin.

Detailed Description of the Invention

Water is generally used as a solvent or carrier for the components of the surface preparation agent of the invention, although water-soluble or water-miscible organic solvents such as certain alcohols, ethers, glycol ethers, ketones, esters and the like could be present as co-solvents.

Inorganic and organic compounds containing vanadium with any available valence can be used as the water-soluble vanadium compound (A) employed by this invention. Compounds that form water-soluble V-containing ions in the presence of water are particularly preferred. Preferred examples of (A) are metavanadic acid and vanadic acid and salts thereof (for example, the sodium, potassium, and ammonium salts), vanadium oxides such as vanadium pentoxide, vanadium halides such as vanadium pentachloride and vanadium pentafluoride, vanadyl sulfate, vanadium sulfate, vanadium nitrate, vanadium phosphate, vanadium biphosphate, vanadium acetate, and organovanadium compounds such as vanadium acetylacetonate and vanadyl acetylacetonate. The vanadium compound can be introduced into the inventive surface preparation agent by using a reducing agent in combination with a vanadium compound as described above in order to introduce the partially or completely reduced vanadium compound. The reducing agent used to reduce the vanadium compound in such instances is not critical.

The titanium- or zirconium-containing water-soluble complex fluoride (B) used by this invention is particularly preferably a complex in which the number of bonded F atoms exceeds the valence of the titanium or zirconium. This compound should also be capable of releasing protons in the presence of water or should be capable of producing hydrofluoric acid in the presence of water. Fluozirconic acid, fluotitanic acid, and salts of these compounds are typical examples of component (B).

The resin (C) used by this invention is particularly preferably selected from the group consisting of polyacrylic acid resins (including copolymers of acrylic acid with other monomers), polyacrylamide resins (including copolymers of acrylamide with other monomers), polyamide resins, polyurethane resins, polyester resins, phenolic resins, or epoxy resins, and should be soluble or dispersible in water (waterborne). In addition, component (C) should be stable in the bath with (A) and (B) and preferably is capable of uniformly wetting the surface of the sheet, e.g., aluminum alloy, when applied thereto. More specifically, component (C) is preferably at least one water-soluble resin selected from polyacrylic acids, polyacrylamides, polyurethanes, polyesters, and phenolic resins. Preferably, the resin loses its water solubility upon evaporation of the water fraction or baking/drying.

The proportions of the water-soluble vanadium compound (A), titanium-containing or zirconium-containing water-soluble complex fluoride (B), and resin (C) preferably provide the following weight ratios for the vanadium (V) in the vanadium compound (A), titanium (Ti) and/or zirconium (Zr) in the complex fluoride (B), and resin (C):

V : (Zr + Ti) = 1 : 5000 to 5000 : 1 (more preferred, 1:100 to 100:1)
{V + (Zr + Ti)} : (C) = 10 : 1 to 1 : 100 (more preferred, 10:1 to 1:10).

There is a tendency at V: (Zr + Ti) = (less than 1): 5000 (i.e., when there is less than 1 part by weight V per 5000 parts by weight total Zr + Ti) for the rustproofing performance of the ultimately obtained base coating to be unsatisfactory. The adherence of the ultimately obtained base coating for aluminum alloy surfaces has a tendency to deteriorate at V: (Zr + Ti) = 5000: (less than 1), i.e., when there is less than 1 part by weight total Zr + Ti per 5000 parts by weight V. At {V + (Zr + Ti)}: (C) = 10: (less than 1) there is a tendency for coating defects to occur when the surface preparation agent is applied and/or for the adherence of the ultimately obtained base coating for aluminum alloy surfaces to deteriorate. At {V + (Zr + Ti)}: (C) = (less than 1): 100 there is a tendency for the rustproofing performance of the ultimately obtained base coating to be unsatisfactory and/or for the adherence to top coats and bonded films to deteriorate.

The inventive surface preparation agent may as necessary or desired contain the various additives known in the art, e.g., leveling agents, defoamers, thickeners, and so forth.

The inventive surface preparation agent is used in particular as a rust preventive surface preparation agent for aluminum and aluminum alloys.

The mechanisms underlying the effects of the organic-inorganic composite coating formed by the inventive surface preparation agent are not entirely clear at the present stage, but the following (without wishing to be bound by theory) can be hypothesized.

With regard to the vanadium compound in the inventive surface preparation agent, it is thought that this component produces a water-soluble V-containing ion, such as the vanadyl ion, when the base coating is exposed to a corrosive environment in which water is present. This water-soluble V-containing ion is believed to exercise a corrosion inhibiting activity by oxidizing and stabilizing the substrate surface with the formation of nonconductive material.

With regard to the titanium-containing or zirconium-containing water-soluble complex fluoride, it is thought that in aqueous solution this component liberates small quantities of fluoride ion, which etches the surface of the aluminum alloy substrate and thereby secures adhesion between the substrate and the rust preventive base coating through an anchoring effect. In addition, upon treatment and drying, the complex fluoride is believed to precipitate metal salts on the aluminum surface, in addition to zirconium oxide or titanium oxide, and this phenomenon is thought to function as a rust preventive coating that inhibits aluminum corrosion.

The coating formed by the resin upon treatment and drying is thought to exercise a barrier effect against corrosive factors, such as oxygen and water, that can infiltrate from corrosive environments.

Treatment with an agent that contains the foregoing compounds in combination is thought to accrue the following effects. First, an organic-inorganic composite coating is formed from the inorganic solids (e.g., oxides and fluorides of Zr, Ti) and the waterborne organic polymer, and the presence of this composite coating improves the barrier performance of the coating against corrosive conditions. Second, with regard to coating defect regions and damaged regions produced after coating formation, the aluminum alloy substrate surface exposed in such regions is successively oxidized and stabilized, with the formation of nonconducting material, by the action of the water-soluble V-containing ion (e.g., vanadyl ion) produced by the vanadium compound. This again results in the manifestation of a corrosion inhibiting activity.

The problems identified above are also solved by a surface preparation method that characteristically comprises application and drying of the foregoing surface preparation agent on the substrate surface so as to give a total deposition of V plus Zr plus Ti of from 0.05 to 100 mg/m^2.

The rustproofing performance of the ultimately obtained base coating will be unsatisfactory when the total deposition of V plus Zr plus Ti is less than 0.05 mg/m^2. A total deposition in excess of 100 mg/m^2 accrues no additional enhancements in rust prevention and for this reason is uneconomical. In addition, the adherence between the ultimately obtained base coating and the aluminum alloy surface — or the top coat or bonded film — begins to deteriorate at a total deposition in excess of 100 mg/m^2.

The method for producing a coating on an aluminum alloy surface from the inventive surface treatment agent is explained in the following.

The coating is formed by applying and drying the inventive surface preparation agent on the workpiece surface after the surface has been cleaned with a solvent-based cleaner or an alkaline or acidic water-based cleaner. Application of the inventive surface preparation agent to the workpiece surface can be carried out, for example, by spraying, dipping, roll coating, or shower coating. The treatment temperature and treatment time are not critical, but a treatment temperature of 10 to 40°C and a treatment time of 0.1 to several minutes will generally be used. The post-application drying temperature should be in a range including and above room temperature (normally at least 20°C) in which the water fraction can be evaporated and dried off, but is not otherwise critical. However, it is particularly preferred that drying be carried out at 150 to 250°C for the benefits this affords for the adherence by the base coating to the aluminum surface and top coat or bonded film and the rust prevention that are goals of this invention. While various top coats or laminated film layers may be provided on the surface-treated substrate carrying the inventive base coating, the type of top coat or laminate film layer is not critical. The top coat may be, for example, a hydrophilic coating layer, a lubricating organic coating layer, or an antimold/antibacterial coating. The laminated film can be, for example, a PET film, polyamide film, or polyethylene film. The top coat and laminated film can each be an organic coating, inorganic coating, or organic-inorganic composite coating without restriction. In addition, depending on the desired level of rustproofing, the surface-treated material carrying the inventive base coating can be put to final use without the provision of a top coat or laminated film layer.

The invention is explained more specifically by the working and comparative examples that follow, but this invention is not limited by these working examples.

Examples

Test materials

Two types of thin aluminum alloy sheets were used as the aluminum alloy materials. These were commercial products corresponding to JIS A1000 (for the top coating experiments) and JIS A3004A (for the bonded film experiments). The dimensions were thickness = 0.3 mm, width = 200 mm, and length = 300 mm.

Method for cleaning the test materials

A bath of a strongly alkaline degreaser (FINECLEANER 4377, registered trademark of Nihon Parkerizing Co., Ltd., reagent concentration in the bath = 20 g/L) was sprayed on the surface of the aluminum alloy sheet. The treatment temperature was 60°C and the treatment time was 7 seconds.

This cleaning operation removed oil and dust adhering on the surface. The alkaline material remaining on the surface was cleaned off by rinsing with tap water and the sheet was then dried at 80°C.

Composition of the rust preventive surface preparation agents

Table 1 reports the compositions of the rust preventive surface preparation agents used in the working and comparative examples. The solvent was water in all cases. The quantities of addition, which are reported in g/L, denote the weight (g) contained in one liter of treatment agent.

Table 1.

designation	vanadium compound (A)			complex fluoride (B)	
	source	addition in g/L		source and addition	as Zr + Ti
		source	as V	g/L	g/L
(a)	sodium metavanadate	24	10.0	fluozirconic acid : 20 fluotitanic acid : 0	8.8
(b)	ammonium metavanadate	0.02	0.009	fluozirconic acid : 50 fluotitanic acid : 50	37.0
(c)	vanadyl acetylacetonate	170	32.7	fluozirconic acid : 0 fluotitanic acid : 0.03	0.009
(d)	potassium vanadate	6	2.2	fluozirconic acid : 0 fluotitanic acid : 7	2.0
(e)	ammonium metavanadate	2.3	1.0	fluozirconic acid : 2.5 fluotitanic acid : 0	1.1
(f)	vanadyl acetylacetonate	5.2	1	fluozirconic acid : 45 fluotitanic acid : 0	19.8
(g)	sodium metavanadate	12	5.0	fluozirconic acid : 6 fluotitanic acid : 6	4.4
(h)	potassium metavanadate	6	2.2	fluozirconic acid : 0 fluotitanic acid : 11	3.2
(i)	—	—	0	fluozirconic acid : 0 fluotitanic acid : 35	10.2
(j)	ammonium metavanadate	23	10.0	—	0
(k)	sodium metavanadate	24	10.0	fluozirconic acid : 20 fluotitanic acid : 0	8.8

(Table 1 is continued on the next page)

Table 1. (Continued from the previous page)

designation	organic polymer (C)		component ratios	
	source (see definitions below)	addition g/L	V : (Zr + Ti)	(V + Zr + Ti) : (C)
(a)	acrylic (1)	3	10 : 8.8	18.8 : 3
(b)	acrylic (2)	10	0.009 : 37	37.009 : 10
(c)	acrylamide	100	32.7 : 0.009	32.709 : 100
(d)	polyurethane	350	2.2 : 2	4.2 : 350
(e)	polyester	190	1 : 1.1	2.1 : 190
(f)	phenol	20	1 : 19.8	20.8 : 20
(g)	amide	50	5 : 4.4	9.4 : 50
(h)	epoxy	7	2.2 : 3.2	5.4 : 7
(i)	acrylic (1)	50	0 : 10.2	10.2 : 50
(j)	acrylamide	20	10 : 0	10 : 20
(k)	—	0	10 : 8.8	18.8 : 0

definition of the resin sources:

acrylic (1) = acrylic acid homopolymer with a number-average molecular weight of 20,000

acrylic (2) = acrylic acid homopolymer with a number-average molecular weight of 200,000

acrylamide = acrylamide homopolymer with a number-average molecular weight of 70,000

polyurethane= UCOAT UWS-145, registered trademark of Sanyo Chemical Industries, Ltd., 35 weight% solids

polyester = VYLONAL MD1100, registered trademark of Toyobo Co., Ltd., 30 weight% solids

phenol = HITANOL 7102, registered trademark of Hitachi Chemical Co., Ltd., 43 weight% solids

amide = block polymer of adipic acid, aminoethylpiperazine, and ε-caprolactam, number-average molecular weight = 10,000

epoxy = EPOMICK WR942030, registered trademark of Mitsui Chemicals, Inc., 28 weight% solids

Rust preventive surface preparation methods

The following treatments were carried out using the treatment agents reported in Table 1.

Example 1

Treatment agent (a) was air-spray coated so as to provide a one-side total deposition of V + Zr + Ti of 50 mg/m^2. This was followed by drying at 200°C for 0.5 minute using an electric oven.

Example 2

Treatment agent (b) was roll coated so as to provide a one-side total deposition of V + Zr + Ti of 100 mg/m^2. This was followed by drying at 180°C for 0.2 minute using an electric oven.

Example 3

Treatment agent (c) was bar coated so as to provide a one-side total deposition of V + Zr + Ti of 0.05 mg/m^2. This was followed by drying at 200°C for 0.2 minute using an electric oven.

Example 4

Treatment agent (d) was dip coated so as to provide a one-side total deposition of V + Zr + Ti of 10 mg/m^2. This was followed by drying at 200°C for 0.5 minute using an electric oven.

Example 5

Treatment agent (e) was roll coated so as to provide a one-side total deposition of V + Zr + Ti of 60 mg/m^2. This was followed by drying at 200°C for 0.3 minute using an electric oven.

Example 6

Treatment agent (f) was roll coated so as to provide a one-side total deposition of V + Zr + Ti of 10 mg/m^2. This was followed by drying at 150°C for 0.5 minute using an electric oven.

Example 7

Treatment agent (g) was roll coated so as to provide a one-side total deposition of V + Zr + Ti of 5 mg/m^2. This was followed by drying at room temperature for 120 minutes using an electric oven.

Example 8

Treatment agent (h) was roll coated so as to provide a one-side total deposition of V + Zr + Ti of 40 mg/m^2. This was followed by drying at 250°C for 0.1 minute using an electric oven.

Comparative Example 1

Treatment agent (i) was roll coated so as to provide a one-side total deposition of V + Zr + Ti of 50 mg/m^2. This was followed by drying at 200°C for 0.3 minute using an electric oven.

Comparative Example 2

Treatment agent (j) was roll coated so as to provide a one-side total deposition of V + Zr + Ti of 50 mg/m^2. This was followed by drying at 200°C for 0.2 minute using an electric oven.

Comparative Example 3

Treatment agent (k) was roll coated so as to provide a one-side total deposition of V + Zr + Ti of 5 mg/m^2. This was followed by drying at 200°C for 0.5 minute using an electric oven.

Top coat application and film bonding

(1) Top coat application

A waterborne paint (PALENE 5013 from Nihon Parkerizing Co., Ltd.) was applied with a roll coater on the rust preventive base-coated sample so as to provide a dry coating weight of 0.8 g/m^2. The sample was then dried by heating to a maximum attained sheet temperature of 200°C.

(2) Film bonding

Polyester resin film (thickness = 20 μ, 12 mole% polyethylene isophthalate, 88 mole% polyethylene terephthalate) was melt-bonded at 250°C/100 kgf/cm^2 on the rust preventive base-coated sample. This was followed by immersion in water and drying at room temperature.

Performance evaluation test methods

The following tests were run with evaluation according to the scales provided hereinbelow.

(1) Evaluation of the top coated sheet

(A) Corrosion resistance

The proportion of white rust production on the surface of the specimen was inspected based on appearance after salt-spray testing (JIS Z 2371) for 240 hours.

— Evaluation scale —

++ : rust production less than 1%
\+ : proportion of white rust production is at least 1% but less than 5%
Δ : proportion of white rust production is at least 5% but less than 10%
× : proportion of white rust production is at least 10%

(B) Adherence

A small amount of deionized water was placed on the surface of the specimen and rubbed strongly 20 times with gauze. The condition of the surface was then inspected based on its appearance.

— Evaluation scale —

++ : less than 1% substrate exposure in tested region
\+ : less than 5% but at least 1% substrate exposure in tested region

Δ : less than 50% but at least 5% substrate exposure in tested region

× : at least 50% substrate exposure in tested region

(2) Evaluation of the bonded-film sheet

(A) Corrosion resistance

Orthogonal 20-mm cuts were executed on the surface of the specimen using a sharp cutter. The specimen was then immersed for 3 days at 70°C in an aqueous solution containing 1 weight% citric acid and 0.5 weight% salt (model juice). The maximum blister width of the film was measured and the corrosion resistance at the cut was evaluated using the following scale.

— Evaluation scale —

++ : maximum blister width from the cut is less than 0.1 mm

\+ : maximum blister width from the cut is at least 0.1 mm but less than 0.5 mm

Δ : maximum blister width from the cut is at least 0.5 mm but less than 1.0 mm

× : maximum blister width from the cut is at least 1.0 mm

(B) Adherence

A cut was made on the back side of the specimen using a sharp cutter and the specimen was thereafter held for 30 minutes in an autoclave at 125°C and 0.8 MPa. The specimen was then sheared at the cut. The width of film protrusion from the sheared location on the side under evaluation was measured and the adherence was evaluated using the following scale.

— Evaluation scale —

++ : the maximum width of protrusion using the sheared location as reference point is less than 0.1 mm

+ : the maximum width of protrusion using the sheared location as reference point is at least 0.1 mm but less than 0.2 mm

Δ : the maximum width of protrusion using the sheared location as reference point is at least 0.2 mm but less than 0.5 mm

× : the maximum width of protrusion using the sheared location as reference point is at least 0.5 mm

Table 2 reports the results of the evaluations carried out according to the foregoing test procedures.

Table 2.

type of rust preventive surface preparation	top coat		bonded film	
	corrosion resistance	adherence	corrosion resistance	adherence
Example 1	+ +	+ +	+ +	+ +
Example 2	+ +	+ +	+ +	+ +
Example 3	+ +	+ +	+ +	+ +
Example 4	+ +	+ +	+ +	+ +
Example 5	+ +	+ +	+ +	+ +
Example 6	+ +	+ +	+ +	+ +
Example 7	+ +	+ +	+ +	+ +
Example 8	+ +	+ +	+ +	+ +
Comparative Example 1	Δ	+ +	×	Δ
Comparative Example 2	+ +	Δ	Δ	×
Comparative Example 3	+	×	Δ	×

The results in Table 2 confirm that Examples 1 through 8, which employed surface preparation agents in accordance with the present invention, gave an excellent corrosion resistance and adherence in both the top coat and bonded film experiments.

In contrast to this, the omission of the vanadium compound specified for this invention resulted in a reduced corrosion adherence and in the case of the bonded film experiment resulted in a decline in adherence in association with the corrosion (see Comparative Example 1).

Comparative Example 2 concerned omission of the complex fluoride specified for this invention. In the top coat experiments, the activity of the vanadium compound did result in a good corrosion resistance in Comparative Example 2, but the adherence was poor. In the bonded film experiments, a substantial deterioration in adherence was noted and the corrosion resistance also deteriorated accompanying the decline in adherence.

Comparative Example 3 concerned omission of the resin specified for this invention, and in this case the adherence was impaired.

The inventive surface preparation agent accrues substantial practical benefits because it enables the very productive manufacture of highly corrosion-resistant sheet that is strongly adherent for top coats and bonded films. In addition, the inventive surface preparation agent does not employ chromium at all and so does not produce chromium-containing spent bath or wastewater and is therefore highly efficacious with regard to environmental protection and reducing the costs of wastewater treatment.

What is claimed is:

1. A surface preparation agent comprising:
   (A) at least one water-soluble vanadium compound;
   (B) at least one water-soluble complex fluoride selected from the group consisting of titanium-containing water-soluble complex fluorides and zirconium-containing water-soluble complex fluorides; and
   (C) at least one resin.
2. The surface preparation agent of claim 1 wherein at least one water-soluble vanadium compound is a compound that generates water-soluble vanadium-containing ions in the presence of water.
3. The surface preparation agent of claim 1 or 2, wherein at least one water-soluble vanadium compound is selected from the group consisting of metavanadic acid, salts of metavanadic acid, vanadium halides, vanadyl sulfate, vanadium nitrate, vanadium phosphate, vanadium biphosphate, vanadium acetate and organovanadium compounds.
4. The surface preparation agent of claim 1, 2 or 3 wherein at least one water-soluble complex fluoride is a compound capable of releasing protons in the presence of water.
5. The surface preparation agent of claim 1, 2, 3 or 4 wherein at least one water-soluble complex fluoride is a compound capable of generating hydrofluoric acid in the presence of water.
6. The surface preparation agent of claim 1, 2, 3, 4 or 5 wherein at least one water-soluble complex fluoride is selected from the group consisting of fluozironic acid, salts of fluozirconic acid, fluotitanic acid, and salts of fluotitanic acid.
7. The surface preparation agent of claim 1, 2, 3, 4, 5, or 6 having a V: (Zr + Ti) weight ratio in a range of from 1:5000 to 5000:1.
8. The surface preparation agent of claim 1, 2, 3, 4, 5, 6, or 7 having a {V + (Zr + Ti)}: resin weight ratio in a range of 10:1 to 1:100.
9. The surface preparation agent of claim 1, 2, 3, 4, 5, 6, 7 or 8 wherein at least one resin is soluble or dispersible in water.
10. The surface preparation agent of claim 1, 2, 3, 4, 5, 6, 7 or 8 wherein at least one resin is a resin which is soluble in water but loses water solubility when said surface preparation agent is dried.
11. The surface preparation agent of claim 1, 2, 3, 4, 5, 6, 7, 8, 9 or 10 wherein at least one resin is selected from the group consisting of

polyacrylic acids, polyacrylamides, polyamides, polyurethanes, polyesters, phenolic resins and epoxy resins.

12. A metal sheet having on at least one surface a coating comprised of the surface preparation agent of claim 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 or 11.

13. The metal sheet of claim 12 wherein said metal sheet is comprised of aluminum.

14. The metal sheet of claim 12 wherein the total amount of V + Zr + Ti in said coating is from 0.05 to 100 mg/m^2.

15. A method of preparing a metal surface, said method comprising applying the surface preparation agent of claim 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 or 11 to said metal surface to form a coating.

16. The method of claim 15 wherein the total amount of V + Zr + Ti in said coating is from 0.05 to 100 mg/m^2.

17. The method of claim 15 wherein said surface preparation agent additionally comprises water and said method comprises an additional step of drying the coating.

18. The method of claim 17 wherein said drying is carried out at a temperature of 150°C to 250°C.

19. The method of claim 15 or 16 wherein said metal surface is comprised of aluminum.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US01/26114

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) :C08K 3/00, 3/10
US CL : 252/389.54; 524/408, 413
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)

U.S. : 252/389.54; 524/408, 413

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
none

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
WEST
search terms: vanadium, vanadate, fluotitanic, fluozirconic

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 6,193,815 A (WADA et al) 27 February 2001, abstract and claims.	1-19
Y	US 5,449,415 A (DOLAN) 12 September 1995, abstract and claims.	1-19
Y	US 5,885,373 A (SIENKOWSKI) 23 March 1999, claims.	1-19

☐ 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 document 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

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