

COMPOSITION AND METHOD FOR TREATMENT
OF CONVERSION-COATED METAL SURFACES

This invention relates to the treatment of metal surfaces prior to a finishing operation, such as the application of a siccative organic coating (also known as an "organic coating", "organic finish", or simply, "paint"). Specifically, this invention relates to the treatment of conversion-coated metal with an aqueous solution comprised of a selected organosilane and a selected Group IVA metal ion, namely titanium, hafnium, and mixtures thereof with other Group IVA metal ion. Treatment of conversion coated metal with such a solution improves paint adhesion and corrosion resistance.

The primary purposes of applying siccative coatings to metal substrates (e g , steel, aluminum, zinc and their alloys) are protection of the metal surface from corrosion and for aesthetic reasons. It is well-known, however, that many organic coatings adhere poorly to metals in their normal state. As a result, corrosion-resistance characteristics of the siccative coating are substantially diminished. It is therefore a typical procedure in the metal finishing industry to subject metals to a pretreatment process whereby a conversion coating is formed on the metal surface. This conversion coating acts as a protective layer, slowing the onset of the degradation of the base metal, owing to the conversion coating being less soluble in a corrosive environment than is the base metal. The conversion coating is also effective by serving as a recipient for a subsequent siccative coating. The conversion coating has a greater surface area than does the base metal and thus provides for a greater number of adhesion sites for the interaction between the conversion coating and the organic finish. Typical examples of such conversion coatings include, but are not limited to, iron phosphate coatings, zinc phosphate coatings, and chromate conversion coatings. These conversion coatings and others

are well-known in the art and will not be described in any further detail.

Normally, the application of an organic finish to a conversion-coated metal surface is not sufficient to provide the highest levels of paint adhesion and corrosion resistance. Painted metal surfaces are able to reach maximum performance levels when the conversion-coated metal surface is treated with a "final rinse", also referred to in the art as a "post-rinse" or a "seal rinse", prior to the painting operation. Final rinses are typically aqueous solutions containing organic or inorganic entities designed to improve paint adhesion and corrosion resistance. The purpose of any final rinse, regardless of its composition, is to form a system with the conversion coating in order to maximize paint adhesion and corrosion resistance. This may be accomplished by altering the electrochemical state of the conversion-coated substrate by rendering it more passive or it may be accomplished by forming a barrier film which prevents a corrosive medium from reaching the metal surface. The most effective final rinses in general use today are aqueous solutions containing chromic acid, partially reduced to render a solution comprised of a combination of hexavalent and trivalent chromium. Final rinses of this type have long been known to provide the highest levels of paint adhesion and corrosion resistance. Chromium-containing final rinses, however, have a serious drawback due to their inherent toxicity and hazardous nature. These concerns make chromium-containing final rinses less desirable from a practical standpoint, when one considers such issues as safe handling of chemicals and the environmental problems associated with the discharge of such solutions into municipal water streams. Thus, it has been a goal of the industry to find chromium-free alternatives which are less toxic and more environmentally benign than chromium-containing final rinses. It has also been desirable to develop chromium-free final rinses which are as effective as chromium-containing final rinses in

terms of paint adhesion and corrosion resistance properties.

Much work has already been done in the area of chromium-free final rinses. Some of these have utilized either Group IVA chemistry or organosilanes. US-A-3,695,942 describes a method of treating conversion-coated metal with an aqueous solution containing soluble zirconium compounds. US-A-4,650,526 describes a method of treating phosphated metal surfaces with an aqueous mixture of an aluminum zirconium complex, an organofunctional ligand and a zirconium oxyhalide. The treated metal could be optionally rinsed with deionized water prior to painting. US-A-4,457,790 describes a treatment composition utilizing titanium, zirconium and hafnium in aqueous solutions containing polymers with chain length from 1 to 5 carbon atoms. US-A-4,656,097 describes a method for treating phosphated metal surfaces with organic titanium chelates. The treated metal surface can optionally be rinsed with water prior to the application of a siccative organic coating. US-A-4,497,666 details a process for treating phosphated metal surfaces with solutions containing trivalent titanium and having a pH of 2 to 7. US-A-5,053,081 describes a final rinse composition comprising an aqueous solution containing 3-aminopropyltriethoxysilane and a titanium chelate. In EP-A-0153973 reactive organosilanes in combination with a titanium or zirconium-containing component are used to replace a chromate rinse after conversion coating. In all of the above examples, the treatment method described claimed to improve paint adhesion and corrosion resistance.

The levels of paint adhesion and corrosion resistance afforded by the treatment solutions in the above examples do not reach the levels desired by the metal finishing industry, namely the performance characteristics of chromium-containing final rinses. I have found that aqueous solutions containing selected organosilane compounds and Group IVA metal ions, namely, zirconium,

titanium, hafnium, and mixtures thereof, provide paint adhesion and corrosion resistance characteristics comparable to those attained with chromium-containing final rinses. In many cases, the performance of conversion-coated metal surfaces treated with organosilane-Group IVA metal ion solutions in accelerated corrosion tests exceeds that of conversion-coated metal treated with chromium-containing solutions.

It is an object of this invention to provide a method and composition of an aqueous rinse which will impart an improved level of paint adhesion and corrosion resistance on painted, conversion-coated metal. The composition is comprised of an aqueous solution containing a selected organosilane and a selected Group IVA metal ion, namely, titanium, hafnium, and mixtures thereof with other group IVA metal ion, and provides levels of paint adhesion and corrosion resistance comparable to or exceeding those provided by chromium-containing final rinses.

It is a further object of the invention to provide a method and rinse composition which contains no chromium.

A first aspect of the invention includes a rinse solution for the treatment of conversion-coated metal substrates for improving the adhesion and corrosion resistance of siccative coatings, comprising an aqueous solution of a Group IVA metal ion selected from titanium, hafnium and mixtures thereof, and an organosilane selected from methyltrimethoxysilane, phenyltrimethoxysilane, and mixtures thereof, with the Group IVA metal ion concentration selected to provide a pH in the range of about 2.0 to about 9.0.

A second aspect of the invention provides a rinse solution for the treatment of conversion-coated metal substrate comprising an aqueous solution containing a Group IVA metal ion including hafnium and an organosilane selected from methyltrimethoxysilane, phenyltrimethoxysilane, 3-glycidoxypropyltrimethoxysilane and mixtures thereof, with the Group IVA metal ion

concentration selected to provide a pH in the range of from about 2.0 to about 9.0.

The invention also includes a method for treating such materials by applying the rinse solution to the substrate.

5 The rinse solution of the first aspect of the invention is an aqueous solution containing a selected organosilane compound and Group IVA metal ion, namely, titanium, hafnium, and mixtures thereof. In both aspects, mixtures with other Group IVA metal ions such as titanium
10 can also be used. It is intended that the rinse solution be applied to conversion-coated metal. The formation of conversion coatings on metal substrates is well-known within the metal finishing industry. In general, this process is usually described as a process requiring several
15 pretreatment stages. The actual number of stages is typically dependent on the final use of the painted metal article. The number of pretreatment steps normally varies anywhere from two to nine stages. A representative example
20 of a pretreatment process involves a five-stage operation where the metal to be ultimately painted goes through a cleaning stage, a water rinse, a conversion coating stage, a water rinse and a final rinse stage. Modifications to the pretreatment process can be made according to specific needs. As an example, surfactants can be incorporated into
25 some conversion coating baths so that cleaning and the formation of the conversion coating can be achieved simultaneously. In other cases it may be necessary to increase the number of pretreatment stages so as to accommodate more pretreatment steps.

30 Examples of the types of conversion coatings that can be formed on metal substrates are iron phosphates and zinc phosphates including mixed phosphates based on iron and/or zinc with other metal ions. Iron phosphating is usually accomplished in no more than five pretreatment stages,
35 while zinc phosphating usually requires a minimum of six pretreatment stages. The number of rinse stages between the actual pretreatment steps can be adjusted to insure

that rinsing is complete and effective and so that the chemical pretreatment from one stage is not carried on the metal surface to subsequent stages, thereby possibly contaminating them. It is typical to increase the number of rinse stages when the metal parts to be treated have unusual geometries or areas that are difficult for the rinse water to contact.

The method of application of the pretreatment operation can be either an immersion or a spray operation. In immersion operations, the metal articles are submersed in the various pretreatment baths for defined intervals before moving on to the next pretreatment stage. A spray operation is one where the pretreatment solutions and rinses are circulated by means of a pump through risers fashioned with spray nozzles. The metal articles to be treated normally proceed through the pretreatment operation by means of a continuous conveyor. Virtually all pretreatment processes can be modified to run in spray mode or immersion mode, and the choice is usually made based on the final requirements of the painted metal article. It is to be understood that the invention described here can be applied to any conversion-coated metal surface and can be applied either as a spray process or an immersion process.

The rinse solution of the invention is comprised of an aqueous solution of a selected organosilane and Group IVA metal ion. Specifically, the rinse solution is an aqueous solution containing titanium, or hafnium ions, and mixtures thereof, whose source can be hexafluorotitanic acid, hafnium oxychloride and mixtures thereof; and the organosilane(s) -

One specific titanium source, polyfunctional organic titanates (significant examples include the reaction products of tetraalkyltitanates with a beta-diketone and an alkanolamine), has been shown to perform poorly when combined with organofunctional silanes for use in final rinse solutions and is therefore preferably not included.

Where zirconium is also included in the solution, the source may be, for instance, hexafluorozirconic acid, zirconium basic sulfate, zirconium hydroxychloride, zirconium basic carbonate, zirconium oxychloride, zirconium acetate, zirconium fluoride, zirconium hydroxide, zirconium orthosulfate, zirconium oxide, zirconium potassium carbonate.

The rinse solution is prepared by making an aqueous solution containing the Group IVA metal ion, such that the pH of the resulting solution is in the range of about 2.0 to 9.0. The salts must be dissolved in 50% hydrofluoric acid in order to effect dissolution. The rinse solution of the invention typically contains Group IVA metal ions at a concentration of at least about 0.005% w/w, i.e. percent by weight. There is no significant upper limit to the titanium ion concentration or zirconium, if present. When hafnium is used in the rinse solution, its concentration should not exceed about 0.1% w/w. The pH of the rinse solution is measured; if the pH is outside the desired range, water or Group IVA metal salt is added to change the pH to fall within the desired range. Hence, the amount of Group IVA metal ion present in the finished solution is a function of the pH. The concentration is not likely to exceed about 1.0% w/w, and in the case of hafnium, should not exceed about 0.1% w/w. A selected organosilane in the concentration range of about 0.1 to 7.0% w/w is added to the solution containing the Group IVA metal ions described above. The solution is then mixed for at least 30 minutes to complete the hydrolysis of the selected organosilane, after which time the rinse solution is ready to be applied to conversion-coated metal. The addition of the silane does not affect the pH of the solution.

A preferred embodiment of the invention is an aqueous solution containing 0.005 to 0.5% w/w titanium ion and 0.25 to 1% w/w of phenyltrimethoxysilane. The resulting solution can be effectively operated at pH 2.0 to 5.0.

Another preferred embodiment of the invention is an aqueous solution containing 0.005 to 0.1% w/w hafnium ion and 0.25 to 2% w/w phenyltrimethoxysilane, with the resulting solution being effectively operated at pH 2.5 to 4.5.

Another especially preferred embodiment of the invention is an aqueous solution containing 0.005 to 0.6% w/w titanium ion and 0.5 to 7% w/w of methyltrimethoxysilane. The resulting solution can be effectively operated at pH 3.0 to 8.0.

Another especially preferred embodiment of the invention is an aqueous solution containing 0.005 to 0.09% w/w hafnium ion and 0.25 to 6% w/w methyltrimethoxysilane with the resulting solution being effectively operated at pH 3.0 to 5.0.

Another especially preferred embodiment of the invention is an aqueous solution containing 0.005 to 0.1% w/w hafnium ion and 0.25 to 1% w/w phenyltrimethoxysilane, with the resulting solution being effectively operated at pH 2.5 to 4.5.

Another especially preferred embodiment of the invention is an aqueous solution containing 0.005 to 0.1% w/w hafnium ion, 0.005 to 0.3% w/w zirconium ion, 0.005 to 0.5% w/w titanium ion and 0.1 to 2% w/w phenyltrimethoxysilane, with the resulting solution being effectively operated at pH 2.5 to 4.0.

Another especially preferred embodiment of the invention is an aqueous solution containing 0.005 to 0.1% w/w hafnium ion, 0.005 to 0.6% w/w zirconium ion, 0.005 to 0.4% w/w titanium ion and 0.5 to 6% w/w methyltrimethoxysilane, with the resulting solution being effectively operated at pH 2.5 to 6.0.

An especially preferred embodiment of the second aspect of the invention is an aqueous solution containing 0.005 to 0.1% w/w hafnium ion and 1 to 3% w/w 3-glycidoxypropyltrimethoxysilane, with the resulting solution being effectively operated at pH 2.5 to 4.0.

Another especially preferred embodiment of the second aspect of the invention is an aqueous solution containing 0.005 to 0.1% w/w hafnium ion, 0.005 to 0.4% w/w zirconium ion, 0.005 to 0.4% w/w titanium ion and 0.25 to 4% w/w 3-glycidoxypyrpyltrimethoxysilane, with the resulting solution being effectively operated at pH 2.5 to 5.0.

Another preferred embodiment of the second aspect of the invention is an aqueous solution containing 0.005 to 0.1% w/w hafnium ion and 0.25 to 6% w/w 3-glycidoxypyrpyltrimethoxysilane, with the resulting solution being effectively operated at pH 2.5 to 4.0.

The rinse solution of the invention can be applied by various means, so long as contact between the rinse solution and the conversion-coated substrate is effected. The preferred methods of application of the rinse solution of the invention are by immersion or by spray. In an immersion operation, the conversion-coated metal article is submersed in the rinse solution of the invention for a time interval from about 15 sec to 3 min, preferably 45 sec to 1 min. In a spray operation, the conversion-coated metal article comes in contact with the rinse solution of the invention by means of pumping the rinse solution through risers fashioned with spray nozzles. The application interval for the spray operation is about 15 sec to 3 min, preferably 45 sec to 1 min. The rinse solution of the invention can be applied at temperatures from about 5°C to 85°C, preferably 16°C to 32°C. The conversion-coated metal article treated with the rinse solution of the invention can be dried by various means, preferably oven drying at about 130°C for about 5 min. The conversion-coated metal article, now treated with the rinse solution of the invention, is ready for application of the siccative coating.

EXAMPLES

The following examples demonstrate the utility of the rinse solution of the invention. Comparative examples include conversion-coated metal substrates treated with a

chromium-containing rinse and conversion-coated metal substrates treated with an organosilane-organotitanate final rinse solution as described in US-A-5,053,081, specifically 3-glycidoxypyrpyltrimethoxysilane at 0.35% w/w. The TYZOR® CLA at 0.5% w/w. The TYZOR® CLA is used to promote adhesion. Throughout the examples, specific parameters for the pretreatment process, for the rinse solution of the invention, for the comparative rinses and the nature of the substrate and the type of siccative coating are described.

All treated and painted metal samples were subjected to accelerated corrosion testing. In general, the testing was performed according to the guidelines specified in ASTM B-117-85. Specifically, three identical specimens were prepared for each pretreatment system. The painted metal samples received a single, diagonal scribe which broke through the organic finish and penetrated to bare metal. All unpainted edges were covered with electrical tape. The specimens remained in the salt spray cabinet for an interval that was commensurate with the type of siccative coating that was being tested. Once removed from the salt spray cabinet, the metal samples were rinsed with tap water, dried by blotting with paper towels and evaluated. The evaluation was performed by scraping away the loose paint and corrosion products from the scribe area with the flat end of a spatula. The scraping was performed in such a manner so as only to remove loose paint and leave adhering paint intact. In the case of some organic finishes, like powder coating, removal of the loose paint and corrosion products from the scribe was accomplished by means of a tape pull as specified in ASTM B-117-85. Once the loose paint was removed, the scribe areas on the specimens were then measured to determine the amount of paint lost due to corrosion creepage. Each scribe line was measured at eight intervals, approximately 1 mm apart, measured across the entire width of the scribe area. The eight values were averaged for each specimen and the

averages of the three identical specimens were averaged to arrive at the final result. The creepage values reported in the following tables reflect these final results.

EXAMPLE 1

5 Cold-rolled steel test panels from Advanced Coating Technologies, Hillsdale, Michigan were processed through a five stage pretreatment operation. The panels were cleaned with Ardrox, Inc. Chem Clean 1303, a commercially available alkaline cleaning compound. Once rendered
10 water-break-free, the test panels were rinsed in tap water and phosphated with Ardrox, Inc. Chem Cote 3011, a commercially available iron phosphate. The phosphating bath was operated at about 6.2 points, 60°C, 3 min contact time, pH 4.8. After phosphating, the panels were rinsed in
15 tap water and treated with various final rinse solutions for 1 min. The comparative chromium-containing rinse was Ardrox, Inc. Chem Seal 3603, a commercially available product. This bath was run at 0.25% w/w. In accordance with normal practice in the metal finishing industry,
20 panels treated with the chromium-containing final rinse (1) were rinsed with deionized water prior to dry off. The comparative chromium-free final rinse (2) contained 0.35% w/w 3-glycidoxypentyltrimethoxysilane and 0.5% w/w TYZOR® CLA. All panels were then dried in an oven at 130°C for 5
25 min.

The conversion-coated test panels were painted with a melamine polyester organic finish. The various final rinses are summarized as follows.

- 30 1. Chem Seal 3603, chromium-containing final rinse.
2. Comparative chromium-free final rinse.
3. phenyltrimethoxysilane, 0.25% w/w, pH 2.88, Ti concentration, 0.026% w/w.
4. phenyltrimethoxysilane, 0.5% w/w, pH 4.32, Ti
35 concentration, 0.014% w/w
5. phenyltrimethoxysilane, 1.0% w/w, pH 3.20, Ti concentration, 0.046% w/w.

The salt spray results are described in Table 1. The values represent total creepage about the scribe area in mm. The numbers in parentheses represent the exposure interval for that particular organic finish.

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TABLE I

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Final Rinse No.	Melamine-Polyester (336 hr)
1	2.6
2	37.1
3	5.1
4	2
5	4.4

EXAMPLE 2

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Another set of cold-rolled steel test panels was prepared using the parameters described in Example 1. The conversion-coated test panels were painted with the melamine polyester organic finish that was used in Example 1. The various final rinses are summarized as follows.

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1. Chem Seal 3603, chromium-containing final rinse.
2. Comparative chromium-free final rinse.
6. methyltrimethoxysilane, 0.5% w/w, pH 4.15, Ti concentration, 0.035% w/w.
- 25 7. methyltrimethoxysilane, 1.0% w/w, pH 8.00, Ti concentration, 0.042% w/w.
8. methyltrimethoxysilane, 2.0% w/w, pH 4.81, Ti concentration, 0.030% w/w.
9. methyltrimethoxysilane, 6.0% w/w, pH 3.06, Ti concentration, 0.053% w/w.
- 30 10. methyltrimethoxysilane, 7.0% w/w, pH 4.76, Ti concentration, 0.026% w/w.

The salt spray results are described in Table II. The values represent total creepage about the scribe area in mm. The numbers in parentheses represent the exposure interval for that particular organic finish.

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TABLE II

Final Rinse No.	Melamine-Polyester (336 hr)
1	2.6
2	37.1
6	1.1
7	2.5
8	2.8
9	2.5
10	2.3

EXAMPLE 3

Another set of cold-rolled steel test panels was prepared using the parameters described in Example 1. The conversion-coated test panels were painted with the melamine polyester organic finish that was used in Example 1, a high solids polyester (designated as High-Solids Polyester), and a baking enamel. The various final rinses are summarized as follows.

1. Chem Seal 3603, chromium-containing final rinse.
11. phenyltrimethoxysilane, 0.25% w/w, pH 3.72, Hf concentration, 0.055% w/w.
12. phenyltrimethoxysilane, 0.5% w/w, pH 4.22, Hf concentration, 0.10% w/w.
13. phenyltrimethoxysilane, 1.0% w/w, pH 2.56, Hf concentration, 0.082% w/w.
14. phenyltrimethoxysilane, 2.0% w/w, pH 3.97, Hf concentration, 0.051% w/w.

The salt spray results are described in Table III. The values represent total creepage about the scribe area in mm. The numbers in parentheses represent the exposure interval for that particular organic finish.

TABLE III

Final Rinse No.	Melamine-Polyester (240 hr)	High-Solids Polyester (168 hr)	Baking Enamel (240 hr)
1	9.1	4.3	4.2
11	6	3.4	9.5
12	4.7	4.3	9.9
13	2	5	12.9
14	11.8	5.1	9.3

10 EXAMPLE 4

Another set of cold-rolled steel test panels was prepared using the parameters described in Example 1. The conversion-coated test panels were painted with the three organic finishes used in Example 3. The various final
15 rinses are summarized as follows.

1. Chem Seal 3603, chromium-containing final rinse.

15. methyltrimethoxysilane, 0.25% w/w, pH 3.53, Hf concentration, 0.034% w/w.

20 16. methyltrimethoxysilane, 0.5% w/w, pH 4.05, Hf concentration, 0.066% w/w.

17. methyltrimethoxysilane, 1.0% w/w, pH 4.44, Hf concentration, 0.017% w/w.

18. methyltrimethoxysilane, 2.0% w/w, pH 3.91, Hf concentration, 0.071% w/w.

25 19. methyltrimethoxysilane, 4.0% w/w, pH 3.41, Hf concentration, 0.058% w/w.

20. methyltrimethoxysilane, 6.0% w/w, pH 4.53, Hf concentration, 0.087% w/w.

The salt spray results are described in Table IV. The
30 values represent total creepage about the scribe area in mm. The numbers in parentheses represent the exposure interval for that particular organic finish.

TABLE IV

Final Rinse No.	Melamine-Polyester (240 hr)	High-Solids Polyester (168 hr)	Baking Enamel (240 hr)
1	9.1	4.3	4.2
15	4.2	1.4	4.3
16	1.3	0.8	1.6
17	0.7	0.9	1.3
18	0.5	0.5	1.1
19	0.5	0.7	0.9
20	0.5	0.5	1.1

EXAMPLE 5

Another set of cold-rolled steel test panels was prepared using the parameters described in Example 1. The conversion-coated test panels were painted with the three organic finishes used in Example 3. The various final rinses are summarized as follows.

1. Chem Seal 3603, chromium-containing final rinse.
2. Comparative chromium-free final rinse.
21. 3-glycidoxypropyltrimethoxysilane, 0.25% w/w, pH 3.23, Zr concentration, 0.35% w/w, Hf concentration, 0.080% w/w.
22. (comparative) 3-glycidoxypropyltrimethoxysilane, 0.5% w/w, pH 3.72, Zr concentration, 0.48% w/w.
23. 3-glycidoxypropyltrimethoxysilane, 1.0% w/w, pH 3.25, Zr concentration, 0.18% w/w, Ti concentration, 0.39% w/w, Hf concentration, 0.050% w/w.
24. 3-glycidoxypropyltrimethoxysilane, 2.0% w/w, pH 4.02, Ti concentration, 0.02% w/w, Hf concentration, 0.090% w/w.

The salt spray results are described in Table V. The values represent total creepage about the scribe area in mm. The numbers in parentheses represent the exposure interval for that particular organic finish.

TABLE V

Final Rinse No.	Melamine-Polyester (240 hr)	High-Solids Polyester (168 hr)	Baking Enamel (240 hr)
1	6.9	4.3	4.2
2	32	26.3	28.3
21	4.4	1.9	5.7
22	8	2.5	5.3
23	12.5	3.2	6.3
24	6.7	2.8	2

EXAMPLE 6

Another set of cold-rolled steel test panels was prepared using the parameters described in Example 1. The conversion-coated test panels were painted with the three organic finishes used in Example 3. The various final rinses are summarized as follows.

1. Chem Seal 3603, chromium-containing final rinse.

2. Comparative chromium-free final rinse.

25. phenyltrimethoxysilane, 0.1% w/w, pH 2.98, Zr concentration, 0.23% w/w, Hf concentration, 0.060% w/w.

26. phenyltrimethoxysilane, 0.5% w/w, pH 3.54, Ti concentration, 0.46% w/w.

27. phenyltrimethoxysilane, 1.0% w/w, pH 3.98, Zr concentration, 0.09% w/w, Ti concentration, 0.47% w/w.

The salt spray results are described in Table VI. The values represent total creepage about the scribe area in mm. The numbers in parentheses represent the exposure interval for that particular organic finish.

TABLE VI

Final Rinse No.	Melamine-Polyester (240 hr)	High-Solids Polyester (168 hr)	Baking Enamel (240 hr)
1	6.9	4.3	4.2
2	32	26.3	28.3
25	3.2	1.5	3.4
26	5.3	2.7	11.7
27	3.2	1.6	9

10 EXAMPLE 7

Another set of cold-rolled steel test panels was prepared using the parameters described in Example 1. The conversion-coated test panels were painted with the three organic finishes used in Example 3. The various final
15 rinses are summarized as follows.

1. Chem Seal 3603, chromium-containing final rinse.

2. Comparative chromium-free final rinse.

28. methyltrimethoxysilane, 0.5% w/w, pH 3.47, Zr
concentration, 0.53% w/w, Ti concentration, 0.18% w/w, Hf
20 concentration, 0.030% w/w.

29. methyltrimethoxysilane, 1.0% w/w, pH 4.46, Zr
concentration, 0.17% w/w, Ti concentration, 0.14% w/w, Hf
concentration, 0.080% w/w.

30. methyltrimethoxysilane, 3.0% w/w, pH 3.54, Hf
25 concentration, 0.070% w/w.

31. methyltrimethoxysilane, 6.0% w/w, pH 4.86, Zr
concentration, 0.09% w/w, Ti concentration, 0.31% w/w, Hf
concentration, 0.040% w/w.

The salt spray results are described in Table VII.
30 The values represent total creepage about the scribe area
in mm. The numbers in parentheses represent the exposure
interval for that particular organic finish.

TABLE VII

Final Rinse No.	Melamine-Polyester (240 hr)	High-Solids Polyester (168 hr)	Baking Enamel (240 hr)
1	6.9	4.3	4.2
2	32	26.3	28.3
28	2.8	1.7	2.4
29	1.3	1	1
30	1.2	0.4	1.1
31	2.2	0.9	1.9

EXAMPLE 8

Another set cold-rolled steel panels was prepared using the parameters described in Example 1. The conversion-coated test panels were painted with the melamine-polyester organic finish that was used in Example 1, and the high solids polyester and baking enamel used in Example 3. The various final rinses are summarised as follows:

1. Chem Seal 3603, chromium-containing final rinse.
32. 3-glycidoxypropyltrimethoxysilane, 0.25% w/w, pH 2.83, Hf concentration, 0.088% w/w.
33. 3-glycidoxypropyltrimethoxysilane, 1.0% w/w, pH 3.84, Hf concentration, 0.098% w/w.
34. 3-glycidoxypropyltrimethoxysilane, 2.0% w/w, pH 2.69, Hf concentration, 0.069% w/w.
35. 3-glycidoxypropyltrimethoxysilane, 3.0% w/w, pH 3.25, Hf concentration, 0.040% w/w.
36. 3-glycidoxypropyltrimethoxysilane, 6.0% w/w, pH 2.90, Hf concentration, 0.034% w/w.

TABLE VIII

Final Rinse No.	Melamine-Polyester (240 hr)	High-Solids Polyester (168 hr)	Baking Enamel (240 hr)
1	9.1	4.3	4.2
32	13.2	4.6	11.3
33	5.9	2.3	3.0
34	4.3	1.9	2.9
35	6.9	3.8	6.1
36	5.5	4.6	6.1

CONCLUSIONS

The results from accelerated corrosion testing demonstrated in Examples 1 to 8 show that rinse solutions containing a selected organosilane and the selected Group IVA metal ion(s) provided substantially better performance than the comparative chromium-free rinse. The results demonstrated in Examples 1 to 8 also show that rinse solutions containing a selected organosilane and Group IVA metal ion, namely titanium, hafnium and mixtures thereof with each other and with zirconium, provided, in many cases, corrosion resistance comparable to that of a chromium-containing rinse, such as Final Rinse No. 1. In several instances, the rinse solutions provided significantly higher levels of corrosion resistance than that achieved with a chromium-containing rinse.

CLAIMS

1. A rinse solution comprising an aqueous solution of Group IVA metal ion including titanium, hafnium, or a mixture thereof, and an organosilane in a concentration in the range 0.1 to 7.0% w/w and selected from methyltrimethoxysilane and phenyltrimethoxysilane, and mixtures thereof, with the Group IVA metal ion concentration selected to provide a pH for the entire solution in the range 2.0 to 9.0.
2. A rinse solution according to claim 1 wherein the Group IVA metal ion is from a Group IVA metal ion source selected from hexafluorotitanic acid, hafnium oxychloride and mixtures thereof.
3. A rinse solution comprising an aqueous solution of Group IVA metal ion including hafnium and an organosilane in a concentration in the range 0.1 to 7.0% w/w and selected from methyltrimethoxysilane, 3-glycidoxypropyltrimethoxysilane and phenyltrimethoxysilane, and mixtures thereof, with the Group IVA metal ion concentration selected to provide a pH for the entire solution in the range 2.0 to 9.0.
4. A rinse solution according to claim 3 in which the group IVA metal ion source includes hafnium oxychloride.
5. A solution according to any preceding claim which also includes zirconium.
6. A rinse solution according to any preceding claim wherein the Group IVA metal ion concentration is at least 0.005% w/w.
7. A rinse solution according to claim 1 or claim 2 wherein the titanium ion concentration in the rinse solution is at least 0.005% w/w and the organosilane comprises 0.25 to 1.0% w/w phenyltrimethoxysilane, with a pH in the range 2.0 to 5.0.
8. A rinse solution according to claim 1 or claim 2 wherein the titanium ion concentration in the rinse solution is at least about 0.005% w/w and the organosilane



comprises 0.5 to 7.0% w/w methyltrimethoxysilane, with a pH in the range 3.0 to 8.0.

9. A rinse solution according to any of claims 1 to 6 wherein the hafnium ion concentration in the rinse solution is at least 0.005% w/w and the organosilane comprises 0.25 to 2.0% w/w (preferably 0.25 to 1.0%) phenyltrimethoxysilane, with a pH in the range 2.5 to 4.5.

10. A rinse solution according to any of claims 1 to 6 wherein the hafnium ion concentration in the rinse solution is at least 0.005% w/w and the organosilane comprises 0.25 to 6.0% w/w methyltrimethoxysilane, with a pH in the range 3.0 to 5.0.

11. A rinse solution according to any of claims 1 to 6 wherein the zirconium ion concentration in the rinse solution is at least 0.005% w/w, the hafnium ion concentration in the rinse solution is at least about 0.005% w/w, the titanium ion concentration in the rinse solution is at least 0.005% w/w, and the organosilane comprises 0.1 to 2.0% w/w phenyltrimethoxysilane, with a pH in the range 2.5 to 4.0.

12. A rinse solution according to any of claims 1 to 6 wherein the zirconium ion concentration in the rinse solution is at least 0.005% w/w, the hafnium ion concentration in the rinse solution is at least 0.005% w/w, the titanium ion concentration in the rinse solution is at least 0.005% w/w, and the organosilane comprises 0.25 to 6.0% w/w methyltrimethoxysilane, with a pH in the range 2.5 to 6.0.

13. A rinse solution according to claim 3 or claim 4 wherein the hafnium ion concentration in the rinse solution is at least about 0.005% w/w and the organosilane comprises 0.25 to 6.0% w/w (preferably 1.0 to 3.0% w/w) 3-glycidoxypropyltrimethoxysilane, with a pH in the range 2.5 to 4.0.

14. A rinse solution according to claim 3 or claim 4 wherein the zirconium ion concentration in the rinse solution is at least 0.005% w/w, the hafnium ion



concentration in the rinse solution is at least 0.005% w/w, the titanium ion concentration in the rinse solution is at least 0.005% w/w, and the organosilane comprises 0.1 to 4.0% w/w 3-glycidoxypropyltrimethoxysilane, with a pH in the range 2.5 to 5.0.

15. A process for treating conversion-coated metal substrates applying to the conversion-coated substrate an aqueous solution of a Group IVA metal ion, including titanium, hafnium, or a mixture thereof, and an organosilane in a concentration in the range 0.1 to 7.0% w/w and selected from methyltrimethoxysilane and phenyltrimethoxysilane, and mixtures thereof having a pH in the range 2.0 to 9.0.

16. A process for treating conversion-coated metal substrates applying to the conversion-coated substrate an aqueous solution of a Group IVA metal ion, including hafnium or a mixture thereof, and an organosilane in a concentration in the range 0.1 to 7.0% w/w and selected from methyltrimethoxysilane, 3-glycidoxypropyltrimethoxysilane and phenyltrimethoxysilane, and mixtures thereof having a pH in the range 2.0 to 9.0.

17. A process according to claim 10 in which the rinse solution is a solution according to any of claims 2 and 4 to 14.

18. A process according to any of claims 15 to 17 including the preliminary step of conversion coating the metal substrate, preferably phosphate coating the substrate.

19. A process according to claim 18 in which the conversion coated metal product is rinsed with water before being contacted with the rinse solution.

20. A process according to any of claims 15 to 19 in which the substrate is dried by heating, preferably at a temperature of about 130°C.

21. A process according to any of claims 15 to 20 in which the treated substrate is subsequently coated with a siccative coating.



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(21) International Application Number: PCT/GB95/02805 ✓ (22) International Filing Date: 30 November 1995 (30.11.95) ✓ (30) Priority Data: 08/348,044 1 December 1994 (01/12.94) US ✓ (71) Applicant: BRENT INTERNATIONAL PLC [GB/GB]; Ridge-way, Iver, Buckinghamshire SL0 9JJ (GB). ✓ (72) Inventor: GORECKI, George, John; 7134 Wright Terrace, Niles, IL 60648 (US). ✓ (74) Agent: GILL JENNINGS & EVERY; Broadgate House, 7 Eldon Street, London EC2M 7LH (GB).		(81) Designated States: AU, BR, CA, CN, JP, KR, MX, SG European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: COMPOSITION AND METHOD FOR TREATMENT OF CONVERSION-COATED METAL SURFACES (57) Abstract A rinse solution for the treatment of conversion-coated metal substrates for approving the adhesion and corrosion resistance of siccative coatings comprising an aqueous solution of a group IVA metal ion selected from titanium, hafnium and mixtures thereof, optionally with other groups IVA metal ions, and an organosilane selected from the group consisting of methyltrimethoxysilane, phenyl trimethoxysilane and, for hafnium-containing compositions, 3-glycidoxypentyltrimethoxysilane. The group IVA metal ion concentration is selected to provide a pH in the range from 2.0 to 9.0. The solution is applied to a conversion-coated substrate.		