⑲ Europäisches Patentamt
European Patent Office
Office européen des brevets

⑪ Publication number: 0 276 371
A1

⑫ EUROPEAN PATENT APPLICATION

㉑ Application number: 87114670.0

㉒ Date of filing: 08.10.87

(51) Int. Cl.⁴: C23C 22/04 , C23C 22/03

㉚ Priority: 09.01.87 JP 1824/87

㊸ Date of publication of application:
03.08.88 Bulletin 88/31

(84) Designated Contracting States:
BE CH DE ES FR GB IT LI NL SE

(71) Applicant: Nippon Dacro Shamrock Co. Ltd.
49-5 Shimokochi Shimokurata-cho
Totsuka-ku
Yokohama, Kanagawa-ken(JP)

(72) Inventor: Nishikawa, Toshio
589-27, Iijima-cho Sakae-ku
Yokohama Kanagawa-ken(JP)
Inventor: Ayukawa, Nobuhiro
16-5, Shichirigahama-Higashi 4-chome
Kamakura Kanagawa-ken(JP)

(74) Representative: Strehl, Schübel-Hopf,
Groening, Schulz
Widenmayerstrasse 17 Postfach 22 03 45
D-8000 München 22(DE)

(54) Process for treating metal surface.

(57) An improved process for treating metal surface comprising a combination of the non-aqueous phosphating treatment and the non-aqueous chromic acid chemical conversion treatment is disclosed. The process is characterized in that the chromic acid chemical conversion treatment is carried out using a treatment solution in which chlorofluorinated hydrocarbon is used as the solvent and confers the metal surface with excellent adhesion property with regard to coating film or paint.

Process for treating metal surface

Field of the Invention

This invention relates to a process for treating metal surface, by which corrosion resistance of the metal and adhesion of coating thereto are improved.

Background of the Invention

It is known to phosphate a metal surface, and subject the thus formed phosphate film to chromic acid chemical conversion treatment (often called "chromium rinsing") in order to improve the corrosion resistance of the metal and adhesion of coating thereto.

In the early days, these two treatments were carried out using aqueous treating compositions. Such a process comprising phosphating and chromium rinsing requires a plurality of treating steps and a large space for the equipment, consumes a large amount of energy for evaporating water, and above all, is accompanied by problems of environmental pollution caused by aqueous waste. Therefore, recently, these treatments are mainly carried out using non-aqueous treating compositions. Such a typical process for this is disclosed in Japanese Patent Publication No. 42-3363 (1967). However, as the organic solvent for the compositions for the two treatments, only chlorinated hydrocarbon has been used.

The respective compositions per se have been improved, and there is known a phosphating treatment composition consisting of 100 parts by weight of a halogenated hydrocarbon solvent (carbon tetrachloride, chloroform, methylene chloride, 1,1,1-trichloroethane, trichloroethylene, perchloroethylene, trichlorotrifluoroethylene, perchloroethylene, trichlorotrifluoroethane, tetrachlorodifluoroethane, dichlorotetrafluoroethane, trifluoromonofluoromethane, etc. or a mixture thereof), 0.05-5 parts by weight of phosphoric acid compound such as orthophosphoric acid, pyrophosphoric acid, polyphosphoric acid such as triphosphoric acid, a salt thereof, an acidic metal salt of phosphoric acid, an acidic alkyl ester of phosphoric acid, or a mixture thereof), 1-75 parts by weight of an alcohol solubilizer having 1-10 carbon atoms such as methanol, ethanol, isopropyl alcohol, n-propanol, n-butanol, sec-butanol, t-butanol, etc. and 0.01-2 parts by weight of a nitrogen-containing organic compound reaction promoter, urea, pyridine, thiourea, dimethylisobutylenamine, ethylenediamine tetraacetate, dinitrotoluene, etc. This phosphating composition may contain a small amount of a quinone, an aromatic compound having a nitroso or azo functional group or a zinc compound such as zinc phosphate, zinc fluoride, zinc oxide, a fatty acid salt of zinc, etc. as a stabilizer for halogenated hydrocarbon solvent. The phosphating composition may further contain 0.5-15 parts by weight of aprotic polar organic compound such as N,N-dimethylformamide, dimethylsulfoxide, acetonitrile, acetone, nitromethane, nitrobenzene and tetramethylenesulfone. The phosphating composition may still further contain not less than 0.4 part by weight and not more than 5 parts by weight of water (in an amount that maintains a homogeneous phase). Water acts as a reaction promoter. (Japanese Patent Publication Nos. 57-49111, 56-31878, etc.)

Japanese Laying-Open Patent Publication No. 61-34184 of the applicant of the present application discloses a metal-surface-treating solution consisting of 100 parts by weight of a chlorofluorinated hydrocarbon organic solvent (typically, trichlorotrifluoroethane, tetrachlorodifluoroethane, tetrachlorodifluoroethane, dichlorotetrafluoroethane, trichloromonofluoromethane, etc. or a mixture thereof), 0.01-10 part by weight of chromic acid anhydride, 0.001-0.1 part by weight of an organic acid having 1-20 carbon atoms (typically, formic acid, acetic acid, lactic acid, stearic acid, oxalic acid, fumaric acid, naleic acid, malic acid, etc.) and 1-20 parts by weight of an alcohol solubilizer having 3-20 carbon atoms (typically isopropyl alcohol, tert-butanol, tert-amyl alcohol, triphenyl carbinol, etc. or a mixture thereof). In this case, an organic acid reaction promoter can be dispensed with.

Up to today, however, in the combination of the phosphating treatment and the chromic acid chemical conversion treatment, there has been no case wherein a chromic acid chemical conversion treatment composition using a fluorochlorinated hydrocarbon as a solvent is used.

We have found that in the combination of the phosphating treatment and the chromic acid chemical conversion treatment, if at least the chromic acid chemical conversion treatment is carried out using a chromic acid chemical conversion treatment solution in which a fluorochlorinated hydrocarbon is used as the solvent, the treated metal surface exhibits excellent adhesion property to coatings (paints).

Disclosure of the Invention

This invention provides a process for treating metal surface comprising subjecting a metal surface to phosphating treatment and subjecting the phosphated surface to chromic acid chemical conversion treatment, said process being characterized in that the phosphating treatment is carried out using a non-aqueous phosphating treatment solution in which a chlorinated or chlorofluorinated hydrocarbon is used as the solvent and the chromic acid chemical conversion treatment is carried out using a non-aqueous chromic acid chemical conversion treatment solution in which a chlorofluorinated hydrocarbon is used as the solvent.

In the process of the present invention, the phosphating treatment composition per se is known as stated above.

In the process of the present invention, the chromic acid chemical conversion composition per se is also known as stated above.

The process of the present invention is applicable to all the metals to which the known phosphating treatment and chromic acid chemical conversion treatment are applicable, that is, iron and steel, zinc, aluminum, tin and alloys thereof.

Specific Description of the Invention

Now the invention will be described in detail by way of working examples and comparative examples. It should be understood that the invention is not limited to these working examples only.

Example 1

A phosphating treatment solution consisting of 100 parts by weight (hereinafter referred to simply as parts) trichlorotrifluoroethane, 22 parts methanol and 0.6 part orthophosphoric acid and 4 parts N,N-dimethylformamide was kept at the boiling temperature thereof. Test panels (70 x150 x 0.8 mm cold-rolled steel sheets) which had been degreased and cleansed beforehand were immersed in the boiling solution for 1 minute, were thereafter washed with the vapor in the vapor zone above the treating solution, and then were dried in the vapor-free space above the vapor zone. (Phosphating treatment)

Then, a chromic acid chemical conversion treatment solution consisting of 100 parts trichlorotrifluoroethane, 5 parts t-amyl alcohol, and 1 part chromic acid anhydride was kept at the boiling temperature thereof, and the test panels which had been phosphated as described above were immersed in the boiling treating solution for 15 seconds, and then were dried in the vapor-free space. (Chromic acid chemical conversion treatment)

The thus treated panels were coated with an epoxy resin powder paint ("Konac No. 3500" manufactured by Nippon Oil and Fats Company, Ltd.) or an acrylic resin powder paint ("Konac No. 4500" manufactured by Nippon Oil and Fats Company, Ltd.) by the electrostatic painting process, and the thus painted panels were baked at 180°C for 20 minutes.

The adhesion of the paint was tested by scoring some of the painted panels in a grid pattern at intervals of 1 mm reaching the substrate, forming 100 small squares by means of a knife edge, applying a cellophane adhesive tape 20 mm in width (manufactured by Nichiban Co.) onto the scored surface and peeling off the tape quickly at an angle of 45°. The number of the remaining squares of the coating (paint) was counted and the adhesion of the coating film before the corrosion test (named primary adhesion) was evaluated.

Other coated (painted) panels were scored in an X pattern (called cross cutting), and the panels were subjected to the salt spray test to investigate the corrosion resistance performance of the coating.

Occurrence of blisters at the cross-cutting was observed (the width of blisters formed along the cutting (score) was measured), and the adhesion of the coating film after the corrosion test (called "secondary adhesion") was measured by the cellophane adhesive tape test. (Width of the peeled-off zone of the coating was measured and the number of the remaining squares was counted.)

The results are indicated in Table 1 together with the results of Example 1a, Comparative Example 1 and Comparative Example 1a described hereinafter.

Example 1a

Example 1 was repeated using the same chromic acid chemical conversion treatment composition which had been continuously used for 12 months.

Comparative Example 1

The procedure of Example 1 was repeated using a conventional chromic acid chemical conversion treatment composition in which methylene chloride (chlorinated hydrocarbon) was used as the solvent instead of the composition in which the fluorochlorinated hydrocarbon solvent was used.

Comparative Example 1a

The procedure of Example 1 was repeated using the same chromic acid chemical conversion treatment composition as used in Comparative Example 1 (using the chlorinated hydrocarbon) which had been continuously used for one week.

Table 1

Example No.	Paint	Primary Adhesion grid scoring*2	Corrosion Test*1		
			Width of blistered region at cross-cutting	Secondary Adhesion	
				Grid scoring	Width of Peeled-off coating at cross-cutting
Example 1	Epoxy	100/100	0 mm	100/100	0 mm
	Acrylic	"	"	"	"
" 1a	Epoxy	"	"	"	"
	Acrylic	"	"	"	"
Comparative Example 1	Epoxy	"	"	"	"
	Acrylic	"	Each side 1 mm	"	Each side 1 mm
" 1a	Epoxy	"	" 4 mm	92/100	" 11 mm
	Acrylic	"	" 10 mm	88/100	" 20 mm

*1 Measurement after 1000 hr. salt spray

*2 100/100 means no peel-off; 0/100 means 100 % peel-off.

Example 2

Test panels of the same kind as used in Example 1 were phosphated in the same manner as in Example 1. Then the thus phosphated panels were immersed in a fresh chromic acid chemical conversion treatment solution consisting of 100 parts trichlorotrifluoroethane, 5 parts t-amyl alcohol, and 0.05 part chromic acid anhydride, which was kept at the boiling temperature thereof, for 30 seconds, and then dried in the vapor-free space above the solution.

The thus treated panels were coated with the same epoxy and acrylic resin powder paints as used in Example 1 and the primary adhesion and the secondary adhesion were respectively measured.

The results are indicated in Table 2 together with the results of Comparative Example 2.

Comparative Example 2

The procedure of Example 2 was repeated with the exception that trichloroethane was used as the solvent in the chromic acid chemical conversion treatment solution.

Table 2

Example No.	Paint	Primary Adhesion grid scoring *2	Corrosion Test *1		
			Width of blistered region at cross-cutting	Secondary Adhesion	
				Grid scoring	Width of Peeled-off coating at cross-cutting
Example 2	Epoxy	100/100	0 mm	100/100	0 mm
	Acrylic	100/100	Each side 0.5 mm	100/100	Each side 0.5 mm
Comparative Example 2	Epoxy	100/100	" 2 mm	98/100	" 3 mm
	Acrylic	100/100	" 8 mm	85/100	" 15 mm

*1 Measurement after 1000 hr. salt spray

*2 100/100 means no peel-off; 0/100 means 100 % peel-off.

Example 3

A phosphating treatment solution consisting of 100 parts methylene chloride, 36 parts methanol, 0.5 part orthophosphoric acid and 6 parts N,N-dimethyl formamide was kept at the boiling temperature thereof. Test panels of the same kind as used in Example 1 which had been degreased and cleansed beforehand were immersed in this boiling solution for 1 minute, thereafter they were dried in the vapor-free zone in the treating vessel. (Phosphating treatment)

Then, a chromic acid chemical conversion treatment solution consisting of 100 parts trichlorotrifluoroethane, 5 parts t-amyl alcohol and 0.5 part chromic acid anhydride was kept at the boiling temperature thereof, and the test panels which had been phosphated as described above were immersed in this boiling solution for 20 seconds, and then were dried in the vapor-free space. (Chromic acid chemical conversion treatment)

The thus treated panels were coated with a room-temperature-dryable acrylic resin paint ("Acrite No. 500" manufactured by Nippon Oil and Fats Co.) by air-spraying and dried at 80°C for 30 minutes. The primary adhesion and the corrosion resistance were tested and the results are indicated in Table 3.

Comparative Example 3

The procedure of Example 3 was repeated with the exception that trichloroethylene was used as the solvent and 0.007 part zinc fluoride was added to the chromic acid chemical conversion treatment solution as a stabilizer. The results are indicated in Table 3 together with the results of Example 3. There was marked occurrence of blisters at the cross cutting, and the width of the peeled-off zone of the coating caused by the cellophane tape was broader.

Example 4

The procedure of Example 3 was repeated with the exception that the panels were coated with a phthalic acid resin paint ("Glastone No. 1000" manufactured by Nippon Oil and Fats Co.) by spraying and were forcedly dried at 80°C for 30 minutes. The results are indicated in Table 4.

Comparative Example 4

The procedure of Comparative Example 3 was repeated with the exception that the panels were coated with the phthalic acid resin paint used in Example 4 and was forcedly dried at 80°C for 30 minutes. The results are indicated in Table 4 together with the results of Example 4. The coating around the cross cutting was markedly damaged.

Table 3

Example No.	Primary Adhesion	Corrosion Test[*1] Width of blisters at cross-cutting	Width of peeled-off coating at cross-cutting
Ex. 3	100/100	Each side 0.5 mm	Each side 0.5 mm
Comp. Ex. 3	100/100	Each side 8 mm	Each side 10 mm

[*1] After 96 hr. salt spray

Table 4

Example No.	Primary Adhesion	Corrosion Test[*1] Width of blisters at cross-cutting	Width of peeled-off coating at cross-cutting
Ex. 4	100/100	Each side 1 mm	Each side 1 mm
Comp. Ex. 4	100/100	Each side 14 mm	Each side 18 mm

[*1] After 168 hr. salt spray

Example 5

The procedure of Example 3 was repeated with the exception that the panels were coated with a melamine alkyd resin paint ("Melamine No. 1" manufactured by Nippon Oil and Fats Co.) by spraying and baked at 150°C for 20 minutes, and the panels were tested in the same manner as in Example 3. The results are indicated in Table 5.

Comparative Example 5

The procedure of Example 3 was repeated with the exception that the panels were coated with the melamine alkyd resin paint used in Example 5 by spraying and baked at 150°C for 20 minutes and the panels were tested in the same manner. The results are indicated in Table 5.

Example 6

A phosphating solution consisting of 100 parts trichlorotrifluoroethane, 22 parts methanol, 0.6 part orthophosphoric acid and 4 parts N,N-dimethylformamide was kept at the boiling temperature thereof. Test panels (70 x 150 x 0.8 mm galvanized steel sheets) which had been degreased and cleansed beforehand were immersed in the boiling solution for 1 minute, were thereafter washed with the vapor in the vapor zone above the treating solution and then dried in the vapor-free space. (Phosphating treatment).

Then, a chromic acid chemical conversion treatment solution consisting of 100 parts trichlorotrifluoroethane, 5 parts t-amyl alcohol and 1 part chromic acid anhydride was kept at the boiling temperature thereof. The test panels which had been phosphated as described above were immersed in this boiling solution for 15 seconds and dried in the vapor-free space. (Chromic acid chemical conversion treatment)

The thus treated panels were coated with an acrylic resin cationic electrodeposition paint ("Aqua No. 8000" manufactured by Nippon Oil and Fats Co.) by the conventional electrodeposition process, and baked at 170°C for 25 minutes.

The thus prepared painted panels were tested for the primary adhesion and then scored in the grid pattern and subjected to the corrosion test. The results are indicated in Table 6.

Comparative Example 6

The procedure of Example 6 was repeated with the exception that methylene chloride was used as the solvent in the chromic acid chemical conversion treatment solution. The test results are indicated in Table 6 together with the results of Example 6.

Table 5

Example No.	Primary Adhesion	Corrosion Test*1	
		Width of blisters at cross-cutting	Width of peeled-off coating at cross-cutting
Ex. 5	100/100	Each side 0.5 mm	Each side 0.5 mm
Comp. Ex. 5	100/100	Each side 7 mm	Each side 9 mm

*1 After 240 hr. salt spray

Table 6

Example No.	Primary Adhesion	Corrosion Test*1	
		Width of blisters at cross-cutting	Width of peeled-off coating at cross-cutting
Ex. 6	100/100	Each side 0.5 mm	Each side 0.8 mm
Comp. Ex. 6	100/100	Each side 4 mm	Each side 6 mm

*1 After 240 hr. salt spray

Claims

1. A process for treating metal surface comprising subjecting a metal surface to phosphating treatment and subjecting the phosphated surface to chromic acid chemical conversion treatment, said process being characterized in that the phosphating treatment is carried out using a non-aqueous phosphating treatment solution in which a chlorinated or chlorofluorinated hydrocarbon is used as the solvent and the chromic acid chemical conversion treatment is carried out using a non-aqueous chromic acid chemical conversion treatment solution in which a chlorofluorinated hydrocarbon is used as the solvent.

2. The process for treating metal surface as set forth in Claim 1, wherein the non-aqueous phosphating treatment solution comprises 100 parts by weight of a chlorinated or chlorofluorinated hydrocarbon, 0.05-5 parts by weight of a phosphoric acid compound, 1-75 parts by weight of an alcohol solubilizer having 1-20 carbon atoms, 0-2 parts by weight of nitrogen-containing organic compound reaction promoter and 0-15 parts by weight of aprotic polar compound; and the non-aqueous chromic acid chemical conversion treatment solution comprises 100 parts by weight of a chlorofluorinated hydrocarbon, 0.01-10 parts by weight of chromic acid anhydride, 0-0.1 parts by weight of an organic acid having 1-20 carbon atoms and 1-20 parts by weight of an alcohol solubilizer having 3-20 carbon atoms.

3. The process for treating metal surface as set forth in Claim 1, wherein in the phosphating treatment solution, the chlorinated or chlorofluorinated hydrocarbon is selected from a group consisting of carbon tetrachloride, chloroform, methylene chloride, 1,1,1-trichloroethane, trichloroethylene, perchloroethylene, trichlorotrifluoroethane, tetrachlorodifluoroethane, dichlorotetrafluoroethane, trichloromonofluoromethane, and mixtures of one or more thereof; the phosphoric acid compound is selected from a group consisting of orthophosphoric acid, pyrophosphoric acid, polyphosphoric acid, salts thereof, an acidic metal salt of phosphoric acid, an acidic alkyl ester of phosphoric acid, and mixtures thereof; the alcohol solubilizer is selected from a group consisting of methanol, ethanol, isopropyl alcohol, n-propanol, n-butanol, isobutanol and t-butanol; the nitrogen-containing organic compound is selected from a group consisting of urea, pyridine, thiourea, dimethyl isobutyleneamine, ethylenediamine tetraacetate and dinitrotoluene and aprotic polar compound is selected from a group consisting of N,N-dimethylformamide, dimethylsulfoxide, acetonitrile, acetone, nitromethane, nitrobenzene and tetramethylenesulfone; and in the chromic acid chemical conversion treatment solution, the chlorofluorinated compound is selected from a group consisting of trichlorotrifluoroethane, tetrachlorodifluoroethane, dichlorotetrafluoroethane and trichloromonofluoromethane; the organic acid is selected from a group consisting of formic acid, acetic acid, lactic acid, stearic acid, oxalic acid, fumaric acid, maleic acid and malic acid; and the alcohol solubilizer is selected from a group consisting of isopropyl alcohol, n-propanol, tert-butanol, tert-amyl alcohol, triphenyl carbinol and mixtures of one or more thereof.

4. The process for treating metal surface as set forth in Claim 2 or 3, wherein the phosphating treatment solution contains a small amount of a stabilizer for the chlorinated hydrocarbon solvent selected from a group consisting of a quinone, an aromatic compound having a nitroso or azo functional group and a zinc compound.

5. The process for treating metal surface as set forth in Claim 4, wherein in the phosphating treatment solution, the chlorofluorinated compound is selected from methylene chloride and trichlorotrifluoroethane; the acid compound is selected from a group consisting of orthophosphoric acid, pyrophosphoric acid and polyphosphoric acid; the alcohol solubilizer is selected from a group consisting of methanol, ethanol, isopropyl; alcohol and t-butanol; the nitrogen-containing organic compound is selected from a group consisting of dinitrotoluene, thiourea and dimethylisobutylenamine; and in the chromic acid chemical conversion the chlorofluorinated hydrocarbon solvent is selected from a group consisting of trichlorotrifluoroethane, tetrachlorodifluoroethane and trichloromonofluoromethane; the organic acid is selected from a group consisting of formic acid, fumaric acid, oxalic acid, acetic acid and lactic acid; the alcohol solubilizer is selected from a group consisting of t-butanol, t-amyl alcohol and isopropyl alcohol.

6. The process for treating metal surface as set forth in Claim 5, wherein the phosphating treatment solution consists of 100 parts by weight of methylene chloride or trichlorotrifluoroethane; 0.1-3.0 parts by weight of orthophosphoric acid or pyrophosphoric acid; 10-40 parts by weight of methanol, ethanol or t-butanol; 0.1-1 parts by weight of dinitrotoluene or thiourea; and 1-10 parts by weight of N,N-dimethylformamide or dimethylsulfoxide; and the chromic acid chemical conversion treatment solutions contains 100 parts by weight of trichlorofluoroethane or tetrachlorodifluoroethane; 0.07-2 parts by weight of chromic acid anhydride, 0.01-0.05 part by weight of formic acid, fumaric acid or oxalic acid.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 87 11 4670

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
Y	US-A-3 285 788 (R.E. SVADLENAK) * Column 3, line 73 - column 4, line 19 * ---	1-6	C 23 C 22/04 C 23 C 22/03
D,Y	EP-A-0 170 988 (NIPPON DACRO SHAMROCK CO., LTD) * Claims 1-7 * & JP-A-61 034 184 ---	1-6	
D,A	FR-A-2 304 685 (DIAMOND SHAMROCK CORP.) * Page 18, lines 1-17; claims 6,9,12-15,17,22,23,27 * & JP-B-57 049 111 ---	1-3,5,6	
A	EP-A-0 089 456 (CHEMISCHE WERKE HÜLS) * Page 5, line 31 - page 7, line 12 * ---	3	
D,A	FR-A-2 304 684 (DIAMOND SHAMROCK CORP.) & JP-B-56 031 878 ---		**TECHNICAL FIELDS SEARCHED (Int. Cl.4)**
D,A	US-A-3 437 531 (R.E. SVADLENAK) & JP-B-42 003 363 ---		C 23 C 22/00
A	US-A-2 927 046 (D.S. ANDRADE) -----		

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	15-04-1988	TORFS F.M.G.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document