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(54) Process and composition for treating phosphated metal surfaces.

(57) Phosphated metal surfaces, particularly those which are iron-based or zinc-based, are treated, especially prior to cationic electrocoating, with an aqueous solution containing:

(a) at least 0.05 g/l (as ZrO_2) of water-soluble fluorozirconium compound; and

(b) at least 0.05 g/l of myo-inositol phosphate and/or water-soluble salt thereof;

the aqueous solution having a pH in the range 3 to 7, and the molar ratio of (a) to (b) being in the range 1:1 to 50:1.

EP 0 061 911 A1

PROCESS AND COMPOSITION FOR TREATING PHOSPHATED METAL SURFACES

An increasingly used commercial process for the application of siccative coatings to metal surfaces (e.g. iron-based or zinc-based surfaces) is the process of electrocoating, especially cationic electrocoating. Various pretreating processes are known, including the application of a phosphate coating to the metal surface followed by treatment of the phosphated surface with a solution which does not contain chromium, and which accordingly is pollution-free, to improve the corrosion resistance of the metal surface. For example, Japanese Patent Publication No. 5622/1978 uses an aqueous solution of phytic acid to treat the phosphated surface, and Japanese Patent Publication No. 21971/1977 uses an aqueous solution of zirconium compound for this purpose. Both techniques have disadvantages. In the former technique, unless the surface of the metal which has been subjected to phosphating and is suitable for cationic electrocoating is sufficiently washed with pure water in a final water washing process after such treatment, pitting occurs in the electrocoated film and the appearance of the film is markedly inferior. Also, zinc-based metal surfaces show inferior results compared to iron-based surfaces with respect to adhesion and corrosion resistance of the coating film produced by cationic electrocoating.

In the latter technique, the stability of the aqueous solution of zirconium compound is unsatisfactory, and, especially in the neutral zone, there is a strong tendency for the zirconium compound to be hydrolyzed, so that it is difficult to maintain the required concentration of this compound in the solution. In order to try to enhance the stability of the zirconium solution, the technique proposes the use of complexing agents such as gluconic acid and citric acid. However, in such instances there is a tendency for corrosive substances to remain on the treated metal surface, so that excessive water washing is required in the following final water washing step. Furthermore, here too, zinc-based surfaces so treated are inferior to iron-based surfaces so treated in adhesion and corrosion resistance of the coating film.

The present invention relates to an improved process for treating a metal surface, especially for subsequent cationic electrocoating. The process results in improved adhesion and corrosion resistance of the coating film deposited by cationic electrocoating.

Accordingly, the invention provides a process for treating a metal surface having a phosphate conversion coating, which process comprises treating said coated surface with an aqueous solution containing:

(a) at least 0.05 g/l (as ZrO_2) of water-soluble fluorozirconium compound; and

(b) at least 0.05 g/l of myo-inositol phosphate and/or water-soluble salt thereof;

the aqueous solution having a pH in the range 3 to 7, and the molar ratio of (a) to (b) being in the range 1:1 to 50:1.

The invention also provides a composition for treating a metal surface having a phosphate conversion coating, which composition is this aqueous solution.

When the metal surface is to be cationic electrocoated, the phosphate conversion coating is one suitable as a conversion coating for this purpose, and can be applied by an acidic aqueous phosphating solution which is already known in the art for this purpose. Such solutions include, for example, a solution containing from 0.4 to 1.5 g/l of zinc ion, from 5 to 40 g/l of phosphate ion, and a conversion coating accelerator. Examples of such known phosphating solutions are given in Japanese Patent Publications (unexamined) No. 107784/1980, 145180/1980 and 131177/1980.

Particularly effective is applying the phosphate conversion coating by dipping the metal surface into an acidic aqueous phosphating solution containing from 0.5 to 1.5 g/l, preferably from 0.7 to 1.2 g/l, of zinc ion,

from 5 to 30 g/l, preferably from 10 to 20 g/l, of phosphate ion, and a conversion coating accelerator. The accelerator can be at least one of the following: 0.01 to 0.2 g/l, preferably 0.04 to 0.15 g/l, of nitrite ion, 0.05 to 2 g/l, preferably 0.1 to 1.5 g/l, of m-nitrobenzene sulphonate ion, and 0.5 to 5 g/l, preferably 1 to 4 g/l, of hydrogen peroxide (as 100% H_2O_2). The phosphating solution may optionally also contain 1 to 10 g/l, preferably 2 to 8 g/l, of nitrate ion, and/or 0.05 to 2 g/l, preferably 0.2 to 1.5 g/l, of chlorate ion.

In this phosphating solution, when the amount of zinc ion is less than about 0.5 g/l, an even phosphate film is not formed on an iron-based surface, and a partially blue-coloured film is formed. On the other hand, when the amount is greater than about 1.5 g/l, then even though an even phosphate film is formed, the film tends to be a coarse, leaf-like crystalline film, which is unsuitable as an undercoating for cationic electrocoating. When the amount of phosphate ion is below about 5 g/l, the film tends to be uneven. On the other hand, when the amount exceeds about 30 g/l, no further improvement in the phosphate coating is realized, and it is therefore uneconomical to use such increased quantities of phosphate. When the amount of the specified conversion coating

accelerators is below about the lower limit given, the conversion coating on an iron-based surface is inadequate, and yellow rust, etc. are formed readily on the surface. On the other hand, when the amount is above about the upper limit given, a blue-coloured uneven film forms on an iron-based surface.

Recently in the automotive industry, steel components have been employed that are plated on one surface only with zinc or an alloy of zinc. When such metal components having both iron-based and zinc-based surfaces are employed, it is preferred that the phosphating solution discussed above also contain 0.6 to 3 g/l, preferably 0.8 to 2 g/l, of manganese ion, or 1 to 4, preferably 2 to 2.5 g/l, of nickel ion. It is even more preferred to include both manganese and nickel ions, and when both are included, the manganese ion is preferably employed in the range given above and the nickel ion is employed in the range of 0.1 to 4 g/l, preferably 0.3 to 2 g/l.

Alternatively, a spray process can be utilized to apply the phosphate coating to the metal surface. When a spray process is employed, the following solution is preferred: an acidic aqueous phosphating solution containing from 0.4 to 1 g/l, preferably 0.5 to 0.9 g/l, of zinc ion, 5 to 40 g/l, preferably 10 to 20 g/l, of phosphate ion, 2 to 5 g/l, preferably 2.5 to

4 g/l, of chlorate ion, and 0.01 to 0.2 g/l, preferably 0.04 to 0.15 g/l, of nitrite ion.

In the above treating solution for use in a spray process, when the amount of zinc ion is less than about 0.4 g/l, an even phosphate film is not formed on an iron-based surface, and a partially blue-coloured film is formed. On the other hand, when the amount is greater than about 1 g/l, then even though an even phosphate film is formed, it tends to be a coarse leaf-like crystalline film, which is unsuitable as an undercoating for cationic electrocoating. When the amount of phosphate ion is below about 5 g/l, the film tends to be uneven. On the other hand, when the amount is greater than about 40 g/l, no further improvement in the phosphate coating is realized, and it is therefore uneconomical to use such increased amounts of phosphate. When the amount of chlorate ion is below about 2 g/l, then even though an even film is formed, the film tends to be a coarse leaf-like crystalline film, which is unsuitable as an undercoating for cationic electrocoating. On the other hand, when the amount is greater than about 5 g/l, an uneven blue-coloured film is formed on an iron-based surface. When the amount of nitrite ion is below about 0.01 g/l, the conversion coating is inadequate, and an inferior film with yellow rust, etc. is formed on an iron-based surface. On the other hand,

when the amount is greater than about 0.2 g/l, it tends to form a blue-coloured uneven film on an iron-based surface.

As sources of the ions used in the acidic phosphating solutions discussed above, commonly known sources can be utilized, for example zinc oxide, zinc carbonate or zinc nitrate for zinc ions; phosphoric acid, sodium phosphate or zinc phosphate for phosphate ions; sodium nitrite or ammonium nitrite for nitrite ions; sodium m-nitrobenzene sulphonate for m-nitrobenzene sulphonate ions; hydrogen peroxide for hydrogen peroxide; chloric acid, sodium chlorate or ammonium chlorate for chlorate ions; manganese carbonate, manganese nitrate, manganese chloride or manganese phosphate for manganese ions; and nickel carbonate, nickel nitrate, nickel chloride or nickel phosphate for nickel ions.

Phosphating of the metal surfaces with the acidic aqueous solutions for phosphating discussed above can be carried out in accordance with conventional procedures. For example, the metal surfaces, which have been subjected, as needed, to degreasing and then to a known surface pretreatment (generally employed prior to a dipping treatment), where the dipping treatment is used for phosphating, can be treated at 40° to 70°C, preferably at 45° to 60°C, for 15 seconds or more (preferably for 30 to 120 seconds), and thus a desired phosphate

coating film of low film amount (1.5 to 3 g/m^2) is produced on iron-based surfaces. Also, a uniform phosphate film is formed thereby on zinc-based surfaces. In this dipping treatment, for application to articles of complicated configuration having many pockets etc., such as car bodies, it is advantageous to adopt the procedure disclosed in Japanese Patent Publication No. 107784/1980, of treating by dipping for 15 seconds or more (preferably for 30 to 90 seconds), followed by spraying for 2 seconds or more (preferably for 5 to 45 seconds). Where phosphating is carried out by a spray treatment, the phosphating solution can be sprayed onto the metal surfaces at the same temperature as is used for the dipping treatment discussed above for 40 seconds or more (preferably for 1 to 3 minutes), to produce a desired phosphate coating film of low film amount (1 to 1.8 g/m^2) on iron-based surfaces. Again, an even phosphate film is also formed on zinc-based surfaces.

After the formation of the phosphate coating film, the metal so treated may be washed with water according to conventional methods, followed by an after-treatment in accordance with the present invention as described below.

The after-treatment involves treating the phosphated metal surface with an aqueous solution having a pH of 3 to 7, preferably 4 to 6, and containing:

(a) at least 0.05 g/l, preferably at least 0.1 g/l, (as ZrO_2) of water-soluble fluorozirconium compound; and

(b) at least 0.05 g/l of myo-inositol phosphate and/or water-soluble salt thereof;

wherein the molar ratio of (a) to (b) is in the range 1:1 to 50:1, preferably 2:1 to 40:1.

The preferred water-soluble zirconium compound is fluorozirconic acid or a salt thereof with a volatile base such as ammonia, a lower alkylamine or a hydroxy lower alkylamine (e.g. monoethanolamine, diethanolamine, triethanolamine, methylamine, ethylamine or dimethylamine). Alkali metal salts and alkaline earth metal salts of fluorozirconic acid exhibit a tendency to leave corrosive substances on the surface of the metal after the above-mentioned treatment step, and they are therefore not preferred. Neither zirconium carboxylates nor zirconium hydrocarboxylates exhibit as beneficial an effect of the present invention as do fluorozirconic acid and its salts with volatile bases. When the amount of the water-soluble zirconium compound is less than 0.05 g/l, neither the adhesion nor the corrosion-resistance of the coating film after cationic electrocoating is improved.

The myo-inositol phosphates and water-soluble salts thereof used in the above-mentioned aqueous solution are esters of myo-inositol having 1 to 6 phosphate groups.

Phytic acid is a commercially available product that can be employed herein. Other useful phosphates can be obtained by hydrolysis of phytic acid. As water-soluble salts of myo-inositol phosphates, salts of volatile bases are preferred, such as ammonia, a lower alkylamine, or a hydroxy-lower alkylamine (examples of these bases being specified above).

When the molar ratio of (a) to (b) is less than 1:1, a zirconium salt of myo-inositol phosphate is not formed on the phosphated metal surface, and it is this salt that improves the corrosion resistance of the metal surface. On the other hand, when the ratio exceeds 50:1, the stability of zirconium ion in the solution is diminished.

As stated above, the pH of the above-mentioned solution is in the range 3 to 7. When phytic acid is employed in the practice of the invention, the pH of the solution is strongly affected by its concentration. For example, the pH of a 0.1, 0.01, 0.001, and 0.0001, mole/l aqueous solution of phytic acid is respectively 0.9, 1.7, 2.68, and 3.61. When the pH of the present solution is lower than about 3, the phosphate film on the metal surface dissolves excessively and the benefits of the invention cannot be fully realized. On the other hand, when the pH exceeds about 7, a zirconium salt of for example phytic acid is not

formed readily on the metal surface, and the beneficial effects of the invention cannot be realized. Accordingly the pH must be adjusted, as necessary, to obtain a pH within the required range.

As pH increasing agents, volatile bases such as ammonia, a lower alkylamine or a hydroxy-lower alkylamine may be employed (and examples of these bases are specified above). Accordingly, a portion of the volatile base needed for pH control can be present as a salt of fluorozirconic acid and/or as a salt of the myo-inositol phosphate. In general, at least about 4 moles of volatile base is required per mole of myo-inositol phosphate. As a pH lowering agent, phosphoric acid may be employed.

The aqueous solution used to after-treat a phosphated metal surface preferably contains substantially no substance which will form a corrosive residue on the metal surface. Thus, the aqueous solution preferably contains substantially no alkali metal ions, alkaline earth metal ions, or any organic acid that will form a water-soluble chelate compound.

The treatment of the phosphated metal surface with the above-mentioned solution can be effected by any conventional contacting method such as by dipping or spraying. The treating temperature is preferably in the range of from room temperature to 90°C. The treatment time is at least long enough to wet the metal surface sufficiently with the solution, and is

usually in the range of from 5 seconds to 5 minutes. When contacting is by dipping, a cathodic electrolysis treatment may be utilized therefor.

When the solution used to treat the phosphated metal surface contains substantially no substance which will form a corrosive residue, as is preferred, the metal surfaces so treated may be dried without first washing with water. However, when the metal surface is to be dipped into an electrocoating bath for cationic electrocoating, it is desirable first to rinse the metal surface with pure water (which does not in any way diminish the beneficial effects produced by the present process).

Examples of metal surfaces that can be treated by the process of the invention include zinc-based surfaces such as zinc plated steel plate by hot dipping, alloyed zinc plated steel plate by hot dipping, zinc plated steel plate by electroplating or alloyed zinc plated steel plate by electroplating, and iron-based surfaces.

The invention is illustrated by the following Examples.

EXAMPLES

Five Examples using the process of the invention (referred to hereinafter as INVENTIVE EXAMPLE 1 to INVENTIVE EXAMPLE 5) were carried out together with nine Examples given for comparison purposes (referred to hereinafter as COMPARISON EXAMPLE 1 to COMPARISON EXAMPLE 9).

The treating techniques used, which are referred to in Table 1, are given in detail below. The aqueous phosphating compositions of each Example are set forth in Table 1, together with the treating solutions used thereafter on the phosphated surfaces, referred to in Table 1 as "After Treatment". The metal surfaces treated and the test results obtained at different stages of coating the metal surfaces are given in Table 2.

Samples of all four metal surfaces given in Table 2 were treated simultaneously according to the following procedure:

degreasing - washing with water - surface conditioning (used only where a dipping process is used for applying a conversion coating) - conversion coating - washing with water - after-treatment - washing with pure water - drying - coating.

A. Conditions for applying a conversion coating by the dipping process:

(a) degreasing, using an alkaline degreasing agent (Nippon Paint Co., "RIDOLINE SD200", 2% by weight) which was sprayed on the metal surfaces at 60°C for 1 minute, followed by dipping in the solution for 2 minutes;

(b) the metal surfaces were then washed with tap water at room temperature for 15 seconds;

(c) the metal surfaces were next dipped into a surface conditioner (Nippon Paint Co., "FIXODINE 5N-5, 0.1% by weight) at room temperature for 15 seconds;

(d) the metal surfaces were then dip treated with a phosphating solution given in Table 1 for dip treating at 52°C for 120 seconds to apply a conversion coating thereto; and

(e) the metal surfaces were washed with tap water at room temperature for 15 seconds.

B. Conditions for applying a conversion coating by the spray process:

(a) degreasing, using an alkaline degreasing agent (Nippon Paint Co., "RIDOLINE SD200", 2% by weight) which was sprayed on the metal surfaces at 60°C for 2 minutes;

(b) the metal surfaces were then washed with tap water at room temperature for 15 seconds;

(c) the metal surfaces were then spray treated with a phosphating solution given in Table 1 for spray treating at 50°C for 120 seconds; and

(d) the metal surfaces were washed with tap water at room temperature for 15 seconds.

C. Conditions for After-Treatment:

(a) after step A(e) or B(d), whichever is applicable, the metal surfaces without drying, were dip or spray treated with a Treating Solution given in Table 1 at 30°C for 10 to 30 seconds;

(b) the metal surfaces were then dip treated with deionized water at room temperature for 15 seconds; and

(c) the metal surfaces were dried in hot air at 100°C for 10 minutes. The appearance and film weight of the metal surfaces were determined and the results set forth in Table 2.

(d) a cationic electrocoating material (Nippon Paint Co., "Power Top U-30 Dark Gray") was coated to 20 μ thickness onto the treated metal surfaces (voltage 180V., treatment time 3 minutes), followed by baking at 180°C for 30 minutes. One sample of each electrocoated plate so obtained was subjected to the brine spray test;

(e) a second sample of each electrocoated plate so obtained was coated with an intermediate coating material (Nippon Paint Co., "ORGA T0778 Gray") to 30 μ thickness, followed by baking at 140°C for 20 minutes, and a top coating material (Nippon Paint Co., "ORGA T0626 Margaret White") in 40 μ thickness was then applied, followed by baking as above. Accordingly, coated plates with a total of 3 coatings and 3 bakings were obtained. All the thus coated plates were subjected to the adhesion test, and the thus coated cold rolled steel plate also to the spot rusting test.

The testing procedures referred to above are

described below:

(A) Brine spraying test (JIS-Z-2871):

Cross-cuts were made on an electrocoated plate; 5% brine was sprayed thereon for 500 hours (zinc plated steel plate) or 1000 hours (cold rolled steel plate).

(B) Adhesion test:

After dipping a coated plate in deionized water at 50°C for 10 days, grids (100 squares) were made at 1 mm intervals or at 2 mm intervals using a sharp cutter; an adhesive tape was attached to each surface; and the number of squares of coating film that remained on the plate after the removal of the adhesive tape were counted.

(C) Spot rusting test:

A coated plate was set at a 15 degree angle to the horizontal plane, and an arrow with a cone shaped head with a 90 degree vertical angle, made of alloyed steel (material quality, JIS-G-4404, hardness Hv 700 or higher), weighing 1.00 g and 14.0 mm in total length was dropped repeatedly from a distance of 150 cm, until 25 scratches were made on the coated surface. Subsequently, the coated plate was subjected to 4 cycles of testing, each cycle consisting of first the brine spray test (JIS-Z-2871, 24 hours), second, a moisture test (temperature of 40°C, relative humidity 85%, 120 hours), and third, standing at room temperature (24 hours). After testing,

the average value (mm) of the largest diameter of rust spots and blisters was obtained, with the results shown in Table 2.

TABLE 1

			Inventive Example 1	Inventive Example 2	Comparison Example 1	Comparison Example 2	Comparison Example 3
Conversion Coating Treatment	Phosphating Solution	Zn (g/l)	0.8	0.6	0.3	0.6	0.6
		PO_4 (g/l)	14.0	14.3	10.3	14.3	14.3
		Mn (g/l)	—	—	—	—	—
		Ni (g/l)	0.5	0.53	—	0.53	0.53
		NO_2 (g/l)	0.06	0.08	0.1	0.08	0.08
		H_2O_2 (g/l)	—	—	—	—	—
		NO_3 (g/l)	4.0	4.2	—	4.2	4.2
		ClO_3 (g/l)	0.7	3.0	0.16	3.0	3.0
		Total Acidity (points)	17	16	11	16	16
		Free Acidity (points)	0.9	0.6	0.3	0.6	0.6
	Treatment Method		dipping	spray	spray	spray	spray
After Treatment	Treating Solution	Phytic Acid (g/l)	0.64	0.64	0.64	1.00	—
		$(NH_4)_2ZrF_6$ (as ZrO_2) (g/l)	0.54	0.54	0.54	0.68	0.3*
		$(NH_4)_2ZrF_6$/Phytic Acid (molar ratio)	4.53/1	4.53/1	4.53/1	3.63/1	—
		Base for adjusting pH	NH_3	NH_3	NH_3	NaOH	—
		pH	5.0	5.0	5.0	3.0	4.9
		Base/Phytic Acid (molar ratio)	7.6/1	7.6/1	7.6/1	2.6/1	—
	Treatment Time (second)		20	30	30	30	30
	Treatment Method		dipping	spray	spray	spray	spray

*Ammonium Zirconium Glycolate used (calculated as ZrO_2)

TABLE 1 (Continued)

				Comparison Example 4	Comparison Example 5	Inventive Example 3	Inventive Example 4
Conversion Coating Treatment	Phosphating Solution	Zn	(g/l)	0.6	1.0	1.0	1.0
		PO_4	(g/l)	14.3	14.0	14.0	14.0
		Mn	(g/l)	—	—	0.8	0.8
		Ni	(g/l)	0.53	0.5	0.3	0.3
		NO_2	(g/l)	0.08	0.06	0.06	0.06
		H_2O_2	(g/l)	—	—	—	—
		NO_3	(g/l)	4.2	4.0	4.0	4.0
		ClO_3	(g/l)	3.0	0.7	0.7	0.7
		Total Acidity (points)		16	17	18	18
		Free Acidity (points)		0.6	0.9	0.9	0.9
	Treatment Method			spray	dipping	dipping	dipping
After Treatment	Treating Solution	Phytic Acid	(g/l)	0.5		0.64	0.32
		$(NH_4)_2ZrF_6$ (as ZrO_2)	(g/l)	—		0.54	0.27
		$(NH_4)_2ZrF_6$/Phytic Acid	(molar ratio)	—		4.53/1	4.53/1
		Base for adjusting pH		NaOH		NH_3	NH_3
		pH		3.0		5.0	6.0
		Base/Phytic Acid	(molar ratio)	—		7.6/1	8.7/1
	Treatment Time (second)			30		10	10
	Treatment Method			spray		dipping	dipping

TABLE 1 (Continued)

			Inventive Example 5	Comparison Example 6	Comparison Example 7	Comparison Example 8	Comparison Example 9
Conversion Coating Treatment	Phosphating Solution	Zn (g/l)	1.0	3.0	1.0	1.0	1.0
		PO_4 (g/l)	14.0	20.0	14.0	14.0	14.0
		Mn (g/l)	0.8	0.8	0.8	0.8	0.8
		Ni (g/l)	0.3	0.3	0.3	0.3	0.3
		NO_2 (g/l)	—	0.06	0.06	0.06	0.06
		H_2O_2 (g/l)	1.0	—	—	—	—
		NO_3 (g/l)	4.0	4.0	4.0	4.0	4.0
		ClO_3 (g/l)	0.7	0.7	0.7	0.7	0.7
		Total Acidity (points)	18	26	18	18	18
		Free Acidity (points)	0.9	1.0	0.9	0.9	0.9
	Treatment Method		dipping	dipping	dipping	dipping	dipping
After Treatment	Treating Solution	Phytic Acid (g/l)	0.32	0.64	—	0.5	
		$(NH_4)_2ZrF_6$ (as ZrO_2) (g/l)	0.27	0.54	0.3	—	
		$(NH_4)_2ZrF_6$/Phytic Acid (molar ratio)	4.53/1	4.53/1	—	—	
		Base for adjusting pH	NH_3	NH_3	—	NaOH	
		pH	5.0	5.0	4.9	3.0	
		Base/Phytic Acid (molar ratio)	7.6/1	7.6/1	—	—	
		Treatment Time (second)	10	10	30	30	
		Treatment Method	dipping	dipping	spray	spray	

TABLE 2

Metal	Test Item	Inventive Example 1	Inventive Example 2	Comparison Example 1
Hot Dipped Zinc Alloy Plated on Steel Plate	Film Appearance	Good Evenness	Good Evenness	Good Evenness
	Film Weight (g/m^2)	4.5	4.0	4.3
	Brine Spray (average in mm)	2.5	2.5	4.5
	Adhesivity 2 mm cuts	100/100	100/100	35/100
	Adhesivity 1 mm cuts	100/100	100/100	0/100
Electro-Plated Zinc on Steel Plate	Film Appearance	Good Evenness	Good Evenness	Good Evenness
	Film Weight (g/m^2)	3.5	3.2	3.3
	Brine Spray (average in mm)	3.0	3.5	8.0
	Adhesivity 2 mm cuts	100/100	95/100	0/100
	Adhesivity 1 mm cuts	90/100	85/100	0/100
Electro-Plated Zinc Alloy on Steel Plate	Film Appearance	Good Evenness	Good Evenness	Good Evenness
	Film Weight (g/m^2)	4.0	3.6	3.9
	Brine Spray (average in mm)	2.0	2.5	4.0
	Adhesivity 2 mm cuts	100/100	100/100	30/100
	Adhesivity 1 mm cuts	95/100	90/100	0/100
Cold Rolled Steel Plate	Film Appearance	Good Evenness and Denseness	Good Evenness and Denseness	Good Evenness and Denseness
	Film Weight (g/m^2)	3.1	1.4	1.6
	Brine Spray (average in mm)	1.0 >	1.0 >	1.5
	Adhesivity 2 mm cuts	100/100	100/100	50/100
	Adhesivity 1 mm cuts	100/100	100/100	0/100
	Spot Rusting (average in mm)	0.86	0.88	1.80

TABLE 2 (Continued)

Metal	Test Item	Comparison Example 2	Comparison Example 3	Comparison Example 4
Hot Dipped Zinc Alloy Plated on Steel Plate	Film Appearance	Good Evenness	Good Evenness	Good Evenness
	Film Weight (g/m^2)	4.0	4.0	4.0
	Brine Spray (Average in mm)	6.0	5.5	7.0
	Adhesivity 2 mm cuts	0/100	55/100	20/100
	Adhesivity 1 mm cuts	0/100	0/100	0/100
Electro-Plated Zinc on Steel Plate	Film Appearance	Good Evenness	Good Evenness	Good Evenness
	Film Weight (g/m^2)	3.2	3.2	3.2
	Brine Spray (average in mm)	6.5	8.5	6.0
	Adhesivity 2 mm cuts	0/100	20/100	0/100
	Adhesivity 1 mm cuts	0/100	0/100	0/100
Electro-Plated Zinc Alloy on Steel Plate	Film Appearance	Good Evenness	Good Evenness	Good Evenness
	Film Weight (g/m^2)	3.6	3.6	3.6
	Brine Spray (average in mm)	5.5	5.0	6.5
	Adhesivity 2 mm cuts	0/100	60/100	15/100
	Adhesivity 1 mm cuts	0/100	0/100	0/100
Cold Rolled Steel Plate	Film Appearance	Good Evenness and Denseness	Good Evenness and Denseness	Good Evenness and Denseness
	Film Weight (g/m^2)	1.4	1.4	1.4
	Brine Spray (average in mm)	3.5	3.0	3.0
	Adhesivity 2 mm cuts	60/100	80/100	45/100
	Adhesivity 1 mm cuts	15/100	30/100	10/100
	Spot Rusting (average in mm)	2.45	1.21	2.66

TABLE 2 (Continued)

Metal	Test Item	Comparison Example 5	Inventive Example 3	Inventive Example 4
Hot Dipped Zinc Alloy Plated on Steel Plate	Film Appearance	Good Evenness	Good Evenness and Denseness	Good Evenness and Denseness
	Film Weight (g/m^2)	4.5	3.0	3.0
	Brine Spray (average in mm)	3.5	1.0	1.5
	Adhesivity 2 mm cuts	58/100	100/100	100/100
	Adhesivity 1 mm cuts	0/100	100/100	100/100
Electro-Plated Zinc on Steel Plate	Film Appearance	Good Evenness	Good Evenness and Denseness	Good Evenness and Denseness
	Film Weight (g/m^2)	3.5	2.2	2.2
	Brine Spray (average in mm)	6.5	1.5	1.5
	Adhesivity 2 mm cuts	24/100	100/100	100/100
	Adhesivity 1 mm cuts	0/100	100/100	100/100
Electro-Plated Zinc Alloy on Steel Plate	Film Appearance	Good Evenness	Good Evenness and Denseness	Good Evenness and Denseness
	Film Weight (g/m^2)	4.0	3.1	3.1
	Brine Spray (average in mm)	3.0	1.0	1.5
	Adhesivity 2 mm cuts	64/100	100/100	100/100
	Adhesivity 1 mm cuts	8/100	100/100	100/100
Cold Rolled Steel Plate	Film Appearance	Good Evenness and Denseness	Good Evenness and Denseness	Good Evenness and Denseness
	Film Weight (g/m^2)	3.1	2.3	2.3
	Brine Spray (average in mm)	1.5	1.0 >	1.0 >
	Adhesivity 2 mm cuts	100/100	100/100	100/100
	Adhesivity 1 mm cuts	100/100	100/100	100/100
	Spot Rusting (average in mm)	1.10	0.70	0.76

TABLE 2 (Continued)

Metal	Test Item	Inventive Example 5	Comparison Example 6
Hot Dipped Zinc Alloy Plated on Steel Plate	Film Appearance	Good Evenness and Denseness	Good Evenness
	Film Weight (g/m^2)	3.0	4.6
	Brine Spray (average in mm)	1.5	3.5
	Adhesivity 2 mm cuts	100/100	30/100
	Adhesivity 1 mm cuts	100/100	0/100
Electro-Plated Zinc on Steel Plate	Film Appearance	Good Evenness and Denseness	Good Evenness
	Film Weight (g/m^2)	2.2	3.8
	Brine Spray (average in mm)	1.5	6.0
	Adhesivity 2 mm cuts	100/100	0/100
	Adhesivity 1 mm cuts	100/100	0/100
Electro-Plated Zinc Alloy on Steel Plate	Film Appearance	Good Evenness and Denseness	Good Evenness
	Film Weight (g/m^2)	3.1	4.5
	Brine Spray (average in mm)	1.0	3.0
	Adhesivity 2 mm cuts	100/100	45/100
	Adhesivity 1 mm cuts	100/100	0/100
Cold Rolled Steel Plate	Film Appearance	Good Evenness and Denseness	Good Evenness
	Film Weight (g/m^2)	2.3	3.4
	Brine Spray (average in mm)	1.0	2.5
	Adhesivity 2 mm cuts	100/100	60/100
	Adhesivity 1 mm cuts	100/100	0/100
	Spot Rusting (average in mm)	0.72	1.96

TABLE 2 (Continued)

Metal	Test Item	Comparison Example 7	Comparison Example 8	Comparison Example 9
Hot Dipped Zinc Alloy Plated on Steel Plate	Film Appearance	Good Evenness and Denseness	Good Evenness and Denseness	Good Evenness and Denseness
	Film Weight (g/m^2)	3.0	3.0	3.0
	Brine Spray (average in mm)	1.5	2.0	1.5
	Adhesivity 2 mm cuts	100/100	100/100	100/100
	Adhesivity 1 mm cuts	100/100	95/100	100/100
Electro-Plated Zinc on Steel Plate	Film Appearance	Good Evenness and Denseness	Good Evenness and Denseness	Good Evenness and Denseness
	Film Weight (g/m^2)	2.2	2.2	2.2
	Brine Spray (average in mm)	2.5	3.5	2.5
	Adhesivity 2 mm cuts	100/100	95/100	100/100
	Adhesivity 1 mm cuts	93/100	90/100	95/1000
Electro-Plated Zinc Alloy on Steel Plate	Film Appearance	Good Evenness and Denseness	Good Evenness and Denseness	Good Evenness and Denseness
	Film Weight (g/m^2)	3.1	3.1	3.1
	Brine Spray (average in mm)	1.5	2.5	2.0
	Adhesivity 2 mm cuts	100/100	100/100	100/100
	Adhesivity 1 mm cuts	100/100	97/100	100/100
Cold Rolled Steel Plate	Film Appearance	Good Evenness and Denseness	Good Evenness and Denseness	Good Evenness and Denseness
	Film Weight (g/m^2)	2.3	2.3	2.3
	Brine Spray (average in mm)	1	1.5	1
	Adhesivity 2 mm cuts	100/100	100/100	100/100
	Adhesivity 1 mm cuts	100/100	100/100	100/100
	Spot Rusting (average in mm)	0.94	0.98	0.98

CLAIMS

1. A process for treating a metal surface having a phosphate conversion coating characterised by treating said coated surface with an aqueous solution containing:

(a) at least 0.05 g/l (as ZrO_2) of water-soluble fluorozirconium compound; and

(b) at least 0.05 g/l of myo-inositol phosphate and/or water-soluble salt thereof;

the aqueous solution having a pH in the range 3 to 7, and the molar ratio of (a) to (b) being in the range 1:1 to 50:1.

2. A process according to claim 1 characterised by employing as (a) at least 0.1 g/l (as ZrO_2) of water-soluble fluorozirconium compound.

3. A process according to claim 1 or 2 characterised in that the myo-inositol phosphate or water-soluble salt thereof is one or both of phytic acid and a salt thereof with a volatile base.

4. A process according to any one of the preceding claims characterised in that the molar ratio of (a) to (b) is from 2:1 to 40:1.

5. A process according to any one of the preceding claims characterised in that the water-soluble fluorozirconium compound is one or both of fluorozirconic acid and a salt thereof with a volatile base.

6. A process according to claim 5 characterised in that the salt with a volatile base is the ammonium salt.

7. A process according to any one of the preceding claims characterised in that the pH of the aqueous solution is adjusted into said range by the addition of a volatile base thereto.

8. A process according to any one of the preceding claims characterised in that the metal surface is iron-based or zinc-based.

9. A process according to claim 8 characterised by treating an article which has an iron-based surface and a zinc-based surface.

10. A process according to any one of the preceding claims characterised in that the phosphate conversion coating is applied by dipping the metal surface into an acidic aqueous phosphating solution containing from 0.5 to 1.5 g/l of zinc ion, from 5 to 30 g/l of phosphate ion, and a conversion coating accelerator.

11. A process according to claim 10 characterised in that the conversion coating accelerator is at least one selected from the group consisting of 0.01 to 0.2 g/l of nitrite ion, 0.05 to 2 g/l of m-nitrobenzene sulphonate ion, and 0.5 to 5 g/l of hydrogen peroxide.

12. A process according to claim 10 or 11 characterised in that the phosphating solution also contains

(i) 1 to 10 g/l of nitrate ion; and/or

(ii) 0.05 to 2 g/l of chlorate ion.

13. A process according to any one of claims 1-9 characterised in that the phosphate conversion coating is applied by spraying the metal surface with an acidic aqueous phosphating solution containing 0.4 to 1 g/l of zinc ion, 5 to 40 g/l of phosphate ion, 2 to 5 g/l of chlorate ion, and 0.01 to 0.02 g/l of nitrite ion.

14. A process according to any one of claims 10, 11 and 13 characterised in that the phosphating solution also contains 0.1 to 4 g/l of nickel ion.

15. A process according to any one of the preceding claims characterised in that the metal surface is subsequently cationic electrocoated.

16. A composition for treating a metal surface having a phosphate conversion coating, characterised in that the composition is an aqueous solution defined in any one of claims 1-7.

European Patent Office

EUROPEAN SEARCH REPORT

0061911

Application number

EP 82301602.7

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
X	US - A - 3 076 734 (K.E. SCHIMKUS) * Claims *	1,2,4, 8,9,16
Y	US - A - 4 110 129 (Y. MATSUSHIMA et al.) * Table 1; claims *	1,3,8, 16
Y	US - A - 4 148 670 (T.L. KELLY) * Tables 1,3,5,6; claims *	1,2,5, 16
Y	US - A - 4 187 127 (K. YASHIRO et al.) * Claims *	1,3,16

CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)

C 23 F 7/10
C 23 F 7/12
C 25 D 5/34
C 25 D 5/36

TECHNICAL FIELDS SEARCHED (Int.Cl. 3)

C 23 F
C 25 D

CATEGORY OF CITED DOCUMENTS

X: particularly relevant if taken alone
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A: technological background
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D: document cited in the application
L: document cited for other reasons

&: member of the same patent family, corresponding document

X The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	02-06-1982	SLAMA

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