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(71) Applicant: **Nippon Paint Company, Ltd, 2-1-2, Oyodokita Oyodo-ku, Osaka-shi Osaka-fu (JP)**

(72) Inventor: **Mino, Yasutake, c/o Nippon Paint Co. Ltd. 19-17 Ikedanaka-machi, Neyagawa-shi Osaka-fu (JP)**
Inventor: **Murakami, Ryoichi, c/o Nippon Paint Co. Ltd. 19-17 Ikedanaka-machi, Neyagawa-shi Osaka-fu (JP)**
Inventor: **Saito, Koichi, c/o Nippon Paint Co. Ltd. 19-17 Ikedanaka-machi, Neyagawa-shi Osaka-fu (JP)**

(74) Representative: **Sanderson, Laurence Andrew et al, Sanderson & Co. 97 High Street, Colchester Essex C01 1TH (GB)**

(54) Phosphating metal surfaces.

(57) Surfaces of iron-based metals or zinc-based metals are phosphated by contacting the metal surfaces with an acidic aqueous solution containing from 0.1 to 2.0 g/l of zinc ion, from 5 to 30 g/l of phosphate ion, from 0.2 to 3 g/l of manganese ion, and a conversion coating accelerator. The phosphated metal surfaces are then suitable for electrocoating.

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PHOSPHATING METAL SURFACES

This invention relates to phosphating metal surfaces.

Japanese Patent Publications (unexamined) No. 107784/1980 and No. 152183/1980 (both in the name Nippon Paint Co. Ltd.) disclose phosphating methods for treating iron-based metal surfaces which are particularly suitable for treating manufactured products having complicated surfaces, such as automobile bodies. The phosphating methods are in use commercially in the automotive industry for pre-treating automobile bodies prior to cationic electrocoating, which is a coating process now used extensively in this industry. The phosphating method of Japanese Patent Publication No. 107784/1980 is carried out by first subjecting the metal surface to a dipping treatment with an acidic aqueous solution containing 0.5 to 1.5 g/l of zinc ion, 5 to 30 g/l of phosphate ion, and 0.01 to 0.2 g/l of nitrite ion and/or 0.05 to 2 g/l of m-nitrobenzene-sulfonate ion at a bath temperature of 40° to 70°C for 15 seconds or more, followed by spraying with the above-mentioned solution for 2 seconds or more. The method of Japanese Patent Publication No. 152183/1980 comprises spraying onto the metal surface an acidic aqueous solution containing 0.4 to 1.0 g/l of zinc ion, 5 to 40 g/l of phosphate ion, 0.01 to 0.2 g/l of nitrite ion and 2.0 to 5.0 g/l of chlorate ion at 40° to 70°C for 40 seconds or more.

Recently, in the automotive industry, with the aim of further improving corrosion-resistance after the application of a siccative coating, steel components which are plated on one surface only with zinc or a zinc alloy have come to be used as materials for automobile bodies. When the processes of these Japanese Patent Publications are applied to such materials (i.e. to metal components having both iron-based metal surfaces and zinc-based metal surfaces), the iron-based surfaces are provided with a phosphate coating film having a low film thickness with uniform and dense cubic or plate-like crystals, as well as excellent adhesion and corrosion-resistance. Such a phosphate coating on the iron-based surface is suitable as a substrate for cationic electrocoating. However, in the case of the phosphate coating film formed on the zinc-based surfaces, the resistance to salt water spraying after the application of a cationic electrocoating thereto is insufficient, and secondary adhesion (tested by immersion of the surface bearing the film with cross-hatched scratches in warm water) after the sequence cationic electrocoating - intermediate coating - top coating is greatly inferior to that on the iron--based surfaces.

In addition to these Japanese Patent Publications, the following references disclose phosphating compositions for metal surfaces:

U.S. Patent 3,338,755 (Jenkins et al) discloses a process for phosphating metal surfaces with a phosphating solution containing zinc, manganese, phosphate, nitrate, and nitrite, as essential ingredients, in stated proportions.

German Patent 29 31 693 (Fosfa-Col) discloses a phosphating process using a solution containing zinc, manganese, phosphate, nitrate, and chlorate ions in stated gram-atom relationships.

However, none of the above proposed phosphating methods has succeeded in giving satisfactory results, especially with the above-mentioned combination of substrate materials.

Japanese Patent J50139-039 (JA 197511) discloses a conversion coating solution containing manganese ions for the treatment of zinc surfaces. However, this prior art solution contains from 3 to 20 g/l of zinc ions, which results in a conversion coating having leaf-like crystals on iron-based surfaces. Such leaf-like crystals are unsuitable as a substrate for cationic electrocoating. Hence, the solutions of this patent are unsuitable for treating both zinc-based and iron-based surfaces.

The present inventors have suprisingly found that by the inclusion of defined quantities of manganese ion in certain acidic aqueous phosphating solutions, very satisfactory results can be attained, and that the resulting solutions can be applied by dipping, spraying, or a combination thereof. The inventors have further found that while chlorate ion can also be present, it is not an essential component of the treating solution especially for spray applications, provided the defined amounts of manganese ion are present, and that even when chlorate ion is added, as is preferred, the amounts of chlorate ion can be markedly lower than those of known compositions.

Accordingly, the present invention provides an improved phosphating method for metal surfaces, which is particularly suitable for treating metal surfaces, such as those of car bodies, which have both iron-based surfaces and zinc-based surfaces. The invention also provides the aqueous treating compositions involved, concentrates useful in their preparation, and the phosphate coating films resulting from their use. The method is especially advantageous for forming phosphate coating films suitable for electrocoating, particularly cationic electrocoating.

Accordingly, the invention provides a process for phosphating an iron- or zinc-based metal surface comprising contacting the metal surface with an acidic aqueous solution containing:

(a) from about 0.1 to about 2.0 g/l, preferably about 0.5 to about 1.5 g/l, and more preferably about 0.7 to about 1.2 g/l, of zinc ion;

(b) from about 5 to about 30 g/l, preferably about 10 to about 20 g/l, of phosphate ion;

(c) from about 0.2 to about 3 g/l, preferably about 0.6 to about 3 g/l, and more preferably about 0.8 to about 2 g/l, of manganese ion; and

(d) a conversion coating accelerator which is preferably at least one of the following:

  (i) from about 0.01 to about 0.2 g/l, preferably about 0.04 to about 0.15 g/l, of nitrite ion;

  (ii) from about 0.05 to about 2 g/l, preferably about 0.1 to about 1.5 g/l, of m-nitrobenzene-sulfonate ion; and

  (iii) from about 0.5 to about 5 g/l, preferably about 1 to about 4 g/l, of hydrogen peroxide (based on 100% H_2O_2).

The invention also provides an acidic aqueous composition for phosphating an iron- or zinc-based metal surface, which composition is this solution.

The invention provides also an aqueous concentrate which upon dilution with water forms a solution for use in the application of a conversion coating to iron- or zinc-based metal surfaces, which concentrate comprises:

a. at least 25 g/l of zinc ion;

b. from 2.5 to 300 parts by weight of phosphate ion;

c. from 0.1 to 30 parts by weight of manganese ion; and optionally

d. from 0.05 to 40 parts by weight of nickel ion;

the parts by weight being per 1 part by weight of zinc ion.

The invention provides also a metal substrate having an iron- or zinc-based surface, which surface is coated with a zinc phosphate conversion coating which contains from 1 to 20%, preferably 2 to 15%, especially 2 to 7%, by weight of manganese, and which coating has a non-leaf-like crystal structure on iron-based surfaces.

The metal surface can be contacted with the acidic aqueous solution by spraying the solution onto the surface of the metal, by dipping the metal surface into the solution, or by a combination of dipping and spraying steps.

In a particular, preferred, embodiment, the solution contains 0.1 to 0.4 g/l of zinc ion. In another particular, preferred, embodiment, the solution contains 1.6 to 2.0 g/l of zinc ion. In another particular, preferred, embodiment, the solution contains 0.2 to 0.5 g/l of manganese ion.

In a particularly surprising and preferred embodiment, the present process consists essentially of contacting the metal surface with the solution by spraying the metal surface with the solution by optionally after spraying dipping the metal surface in the solution. This is distinguished from a contacting which consists of dipping or dipping followed by spraying. In the present embodiment, the contacting can be by spraying more than once optionally interrupted by dipping.

Optionally, the present acidic aqueous solution may also contain one or more of the following:

(e) from about 0.1 to about 4 g/l, preferably about 0.3 to about 2 g/l, of nickel ion;

(f) from about 1 to about 10 g/l, preferably about 2 to about 8 g/l, of nitrate ion; and

(g) from about 0.05 to about 3 g/l (for example 2.1 to 3 g/l), preferably about 0.05 to about 1.9 g/l, and more preferably about 0.2 to about 1.5 g/l, of chlorate ion for both dipping and spraying use. However where a spray process is used with a zinc ion concentration of more than 1 g/l, i.e. from >1.0 g/l to about 2.0 g/l of zinc ion, then up to about 5 g/l (for example 2 to 5 g/l) of chlorate ion can be present in the solution. Use of chlorate concentrations in excess of these ranges is not advisable since at higher chlorate levels the phosphating rate becomes too rapid for satisfactory control.

The present process is carried out preferably at a temperature of from about 40° to about 70°C, especially about 45° to about 60°C, and preferably for a contact time of at least 5 seconds, more preferably at least 15 seconds, especially about 30 to about 180 seconds, and most preferably about 30 to about 120 seconds, as hereinafter discussed. The period of treatment is generally at least about 15 seconds for dipping and at least about 5 seconds for spraying. It should be noted that at temperatures below about 40°C coatings can be formed, but the coating is sparse, coating formation is relatively slow and longer times are required to form satisfactory coatings. At temperatures above 70°C, the conversion coating accelerators begin to decompose at an unacceptable rate, changing the composition of the solution and resulting in an unacceptable conversion coating; also, precipitates begin to form in the bath.

Following the present treatment, the phosphated metal surface(s) are then usually coated with a siccative coating by a known electrocoating process, preferably by the cationic electrocoating process.

The term "iron- or zinc-based metal surface" as used herein means iron-based surfaces, iron alloy-based surfaces, zinc-based surfaces, and zinc alloy-based surfaces. Zinc-based and zinc alloy-based surfaces include, for example, zinc plated steel plate formed by hot dipping, alloyed zinc plated steel plate formed by hot dipping, zinc plated steel plate formed by electroplating, and alloyed zinc plated steel plate formed by electroplating.

An important advantage of the present invention is that surfaces of metal components, such as car bodies, that contain both iron-based surfaces and zinc-based surfaces can be treated by the process of the invention with excellent results. In fact, the process of the invention produces better conversion coatings than are obtainable with conventional dip or spray treating processes, and the amount of etching of the metal surfaces during the present process is only 2/3 to 4/5 that of conventional processes, so that both the quantity of chemicals used in the process as well as sludge formation is only from 2/3 to 4/5 that of conventional processes. The present process is equally applicable to the treatment of a single metal surface of a type described above.

The metal surface to be phosphated is preferably first degreased by dipping in and/or spraying with a known alkaline degreasing agent at 50° to 60°C for a few minutes; washed with tap water; dipped in and/or sprayed with a known surface conditioner at room temperature for 10 to 30 seconds; and the thus treated metal surface then contacted with the acidic aqueous solution of the invention at about 40° to about 70°C for at least 5 seconds. Finally, the thus treated metal surface is preferably washed with tap water and then with deionized water. An acidic final chromate rinse can be employed before the rinse with deionized water.

In a preferred embodiment of the invention, use is made of a dipping procedure. In this embodiment, the acidic aqueous solution preferably contains

(a') from about 0.5 to about 1.5 g/l, more preferably about 0.7 to about 1.2 g/l, of zinc ion;

(b') from about 5 to about 30 g/l, more preferably about 10 to about 20 g/l, of phosphate ion;

(c') from about 0.6 to about 3 g/l, more preferably about 0.8 to about 2 g/l, of manganese ion; and

(d') the conversion coating accelerator, preferably that and its quantities specified above.

While these ranges are preferred, they can be adjusted within the broader limits stated above depending on the intended objects, materials and conditions used. However, certain general criteria for this dip process may be usefully stated here as follows: When the amount of zinc ion is less than about 0.5 g/l, an even phosphate film is usually not formed on an iron-based surface, and a partially blue-coloured film is often formed. When the amount of zinc ion exceeds about 1.5 g/l, then though an even phosphate film is formed, the film formed on an iron-based surface tends to be in the form of leaf-like crystals, which are unsuitable as a substrate for cationic electrocoating. When the amount of phosphate ion in the solution is less than about 5 g/l, an uneven film results. When the amount of phosphate ion exceeds about 30 g/l, no further improvement in the phosphate film is realized and hence, while not harmful, use of phosphate ion above about 30 g/l is uneconomical. When the amount of manganese ion is less than about 0.6 g/l, the manganese content in the film formed on the zinc-based surface is insufficient, resulting in inadequate adhesivity of the coating film to the phosphate substrate after cationic electrocoating. When the amount of manganese ion exceeds about 3 g/l, no further improvement in the phosphate coating is realized, and hence, it is uneconomical to use amounts in excess of about 3 g/l.

With respect to the conversion coating accelerator, when the amount of these accelerators is less than the lower amounts given above, the conversion coating on iron-based surfaces is inadequate, forming yellow rust, etc. When the amount of accelerator exceeds the higher amounts given above, a blue-coloured uneven film is formed on iron-based surfaces.

In another preferred embodiment of the invention, use is made of a spraying procedure. In this embodiment, the acidic aqueous solution desirably contains

(a") from about 0.1 to about 2.0 g/l, preferably about 0.5 to about 1.5 g/l, and more preferably about 0.7 to about 1.2 g/l, of zinc ion;

(b") from about 5 to about 30 g/l, preferably about 10 to about 20 g/l, of phosphate ion;

(c") from about 0.2 to about 3 g/l, preferably about 0.6 to about 3 g/l, of manganese ion; and

(d") the conversion coating accelerator, preferably that and its quantities specified above.

Here again, these ranges can be adjusted depending on the intended objects, materials and conditions used. However, when the amount of zinc ion is less than 0.1 g/l, an even phosphate film will seldom form on an iron-based surface, and a partially blue-coloured film is formed. On the other hand, when the amount of zinc ion is in excess of 2.0 g/l, then the film tends to be in the form of leaf-like crystals and deficient in secondary adhesion, which renders it unsuitable as a substrate for cationic electrocoating. When the amount of phosphate ion in the solution is less than about 5 g/l, an uneven film results, whereas when the amount of phosphate ion exceeds 30 g/l, no further improvement in the phosphate film is realized and hence, the use of greater quantities of phosphate is uneconomical. When the amount of manganese ion is less than about 0.2 g/l, the manganese content in the film formed on the zinc-based surface is insufficient, resulting in inadequate adhesivity of the siccative coating film to the phosphate conversion coating after cationic electrocoating. When the amount of manganese ion exceeds 3 g/l, no further improvement in the phosphate coating is realized and hence, use of a greater quantity is uneconomical. Furthermore, sport rusting of iron-based surfaces will increase. With respect to the quantities of conversion coating accelerator, very similar results to those stated above in connection with the solution for dipping use are obtained.

In addition to the dipping and spray applications described above, certain commercial conditions may warrant contacting the metal surface with the coating solution a plurality of times, such as by intermittent spraying of the metal surface, by spraying followed by dipping, or dipping followed by spraying. A combination of dipping and spraying treatments may be employed. The coating composition can be applied by these methods without a loss in coating formation. For example, the coating solution can be applied by intermittent spray, where the metal substrate is sprayed for about 5 to about 30 seconds, then allowed to stand without any coating application for about 5 to about 30 seconds, and then sprayed for at least 5 seconds, with a total spray time of at least 40 seconds. This cycle can be carried out once, twice or three times.

Furthermore, in treating metal components having complicated surface profiles, such as car bodies, the components can be subjected first to dipping treatments for about 15 seconds or more, preferably about 30 to about 90 seconds, and then to spray treatment with the solution for about 2 seconds or more, preferably for about 5 to about 45 seconds. In order to wash out the sludge which adheres during dipping, the spray treatment is preferably carried out for as long a period within the above range as the speed of the production line will permit. Dipping treatment is preferred to spray treatment, but dipping followed by spraying is more preferred. Alternatively however the coating can be applied by first spraying the metal surface for from about 2 to about 15 seconds, and then dipping the metal surface into the coating solution for at least about 15 seconds, preferably from about 90 to about 120 seconds. This method of applying the coating composition helps to eliminate "hash" marks on the metal surface as the metal surface enters the dip coating solution. The "hash" marks result when the conveyor system fails to move the substrate at a constant velocity, or when the substrate "sways" in a direction perpendicular to the direction of conveyor movement.

Of course, the above-mentioned treating times and treating sequences can be changed according to the composition of the metal substrate to be treated and the treating solution and conditions to be used.

For spray applications, the coating solution is conveniently applied at a spraying pressure of from about 0.5 to about 2 Kg/cm^2.

Irrespective of the application means and the contacting solution used, the resulting phosphate film present on the zinc-based surface should preferably contain from about 1.0 to about 20% by weight, more preferably from about 2 to about 18% by weight, and most preferably from about 5 to about about 18% by weight of manganese ion, which is very important for the subsequent cationic electrocoating. The zinc ion is usually present in from about 28 to about 45% by weight, preferably about 28 to about 40% by weight. When nickel ion is used in the solution, then from about 0.3 to about 4% by weight, preferably about 0.5 to about 4% by weight of nickel is usually present in the coating. The remainder of the coating is usually phosphate and water, except for quantities of other ions such as sodium, calcium and magnesium, which usually total less than 1% by weight. It has also been found that as the content of manganese in the bath increases, increased manganese coating results. However, increasing the manganese level of the coating above the ranges given above does not improve coating quality.

As examples of sources of zinc ions for use in the invention, one or more of the following can be employed: zinc oxide, zinc carbonate, and zinc nitrate. As examples of sources of phosphate ions, one or more of the following can be used: sodium phosphate, zinc phosphate, and manganese phosphate. As examples of sources of manganese ions, one or more of the following can be employed: manganese carbonate, manganese nitrate, manganese chloride, and manganese phosphate. As examples of sources of conversion coating accelerators, sodium nitrite, ammonium nitrite, sodium m-nitrobenzene-sulfonate, and hydrogen peroxide can be employed. With respect to the optional ingredients that can be present in the acidic aqueous solution, the addition of nickel ion to the manganese-containing composition results in further improvement in the performance of the phosphate conversion coating, so that the adhesion and the corrosion-resistance of the film produced by cationic electrocoating are also further improved.

As sources of the optional ingredients, nickel carbonate, nickel nitrate, nickel chloride, nickel phosphate, etc. can be used for nickel ions; sodium nitrate, ammonium nitrate, zinc nitrate, manganese nitrate, nickel nitrate, etc. for nitrate ions; and chloric acid, sodium chlorate, ammonium chlorate, etc. for chlorate ions.

The acidic aqueous treating solutions are conveniently prepared by diluting an aqueous concentrate which contains a number of the solution ingredients in proper weight ratios, and then adding other ingredients as needed to prepare the treating solutions. The concentrates are advantageously formulated to contain zinc ion, phosphate ion and manganese ion, and optionally nickel ion, in a weight proportion of

0.1 to 2 : 5 to 30 : 0.2 to 3 : 0.1 to 4 .

The concentrates are preferably formulated to contain at least about 25 g/l , and more preferably from about 50 g/l to 130 g/l, of zinc ion.

The phosphated metal surface is preferably rinsed and electrocoated.

The invention is illustrated by the following Examples.

EXAMPLES I - XIV

Examples I to IX are Examples of the process and compositions of the invention. Examples X to XIV are Examples using known compositions, given for comparison purposes. The treating process used, which is common to all of Examples I - XIV, is given below, with the aqueous coating compositions of each Example being set forth in Table 1, while the metal treated and the test results obtained following the phosphate treatment are given in Table 2.

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

(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 5N5", 0.1% by weight) at room temperature for 15 seconds;

(d) the metal surfaces were then dipped into the acidic aqueous solution specified in Table 1 at 52°C for 120 seconds;

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

(f) the metal surfaces were then dipped into deionized water at room temperature for 15 seconds;

(g) the surfaces were then dried in hot air at 100°C for 10 minutes. At this stage, the appearance and film weight of the treated metal surfaces was determined, with the results set forth in

Table 2; and

(h) 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 180 V., 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.

A second sample of each electrocoated plate so obtained was coated with an intermediate coating material (Nippon Paint Co., "ORGA TO778 Gray") to 30 µ thickness, followed by baking at 140°C for 20 minutes, and a top coating material (Nippon Paint Co., "ORGA TO626 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. The coated plates were subjected to the adhesion test, and with the cold rolled steel plate, 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 1mm 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 was 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). Test results are shown in Table 2.

Table 1

Composition of Acidic Aqueous solution, g/l	Ex.I	Ex.II	EX.III	Ex.IV	EX.V	EX.VI	EX.VII	EX.VIII	EX.IX	EX.X	EX.XI	EX.XII	EX.XIII	EX.XIV
Zn	1.0	1.0	1.0	1.0	1.0	1.0	1.0	0.7	1.2	0.69	0.8	1.0	1.0	3.0
PO_4	14.0	14.0	14.0	14.0	14.0	14.0	14.0	10.0	20.0	11.40	14.0	14.0	14.0	20.0
Mn	0.8	2.0	2.0	0.8	0.8	2.0	0.8	0.8	0.8	—	—	0.5	0.3	0.8
Ni	—	—	2.0	0.3	2.0	0.3	0.3	0.3	0.3	0.38	0.5	—	0.3	0.3
NO_2	0.06	0.06	0.06	0.06	0.06	0.06	—	0.06	0.06	0.07	0.08	0.06	0.06	0.06
H_2O_2	—	—	—	—	—	—	1.0	—	—	—	—	—	—	—
NO_3	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	1.6	3.0	4.0	4.0	4.0
ClO_3	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	1.49	0.5	0.7	0.7	0.7
BF_4	—	—	—	—	—	—	—	—	—	0.8	—	—	—	—
Fe(III)	—	—	—	—	—	—	—	—	—	0.018	—	—	—	—
Total Acidity (point)	17.5	19	19	18	20	19.5	18	18	24	14.5	17	17	17	26
Acidity of Free Acid (point)	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.7	1.0	0.8	0.9	0.9	0.9	1

Table 2

Metal	Test item	EX.I	EX.II	EX.III	EX.IV	EX.V	EX.VI	EX.VII
Hot dipped zinc alloy plated on steel plate	Film appearance	good evenness & density	good evenness & density	good evenness & density	good evenness & density	good evenness & density	good evenness & density	good evenness & density
	Film weight (g/m^2)	3.2	2.8	2.6	3.0	3.1	2.7	3.2
	Brine spray (ave. in mm)	2.5	2.0	1.5	1.5	1.5	1.5	1.5
	Adhesivity							
	2 mm cuts	100/100	100/100	100/100	100/100	100/100	100/100	100/100
	1 mm cuts	100/100	100/100	100/100	100/100	100/100	100/100	100/100
Electro-plated zinc on steel plate	Film appearance	good evenness & density	good evenness & density	good evenness & density	good evenness & density	good evenness & density	good evenness & density	good evenness & density
	Film weight (g/m^2)	2.5	2.0	2.4	2.2	2.4	2.4	2.1
	Brine spray (ave. in mm)	3.5	3.0	2.0	2.5	2.0	2.0	3.0
	Adhesivity							
	2 mm cuts	100/100	100/100	100/100	100/100	100/100	100/100	100/100
	1 mm cuts	80/100	90/100	100/100	95/100	100/100	100/100	100/100
Electro-plated zinc alloy on steel plate	Film appearance	good evenness & density	good evenness & density	good evenness & density	good evenness & density	good evenness & density	good evenness & density	good evenness & density
	Film weight (g/m^2)	3.2	2.9	2.6	3.1	3.2	2.8	3.0
	Brine spray (ave. in mm)	2.0	2.0	1.5	2.0	1.5	1.5	2.0
	Adhesivity							
	2 mm cuts	100/100	100/100	100/100	100/100	100/100	100/100	100/100
	1 mm cuts	100/100	100/100	100/100	100/100	100/100	100/100	100/100
cold rolled steel plate	Film appearance	good evenness & density	good evenness & density	good evenness & density	good evenness & density	good evenness & density	good evenness & density	good evenness & density
	Film weight (g/m^2)	2.5	2.2	2.2	2.3	2.2	2.0	2.2
	Brine spray (ave. in mm)	1.5	1	>1	1	$1 \geq$	1	1
	Adhesivity							
	2 mm cuts	100/100	100/100	100/100	100/100	100/100	100/100	100/100
	1 mm cuts	100/100	100/100	100/100	100/100	100/100	100/100	100/100
	Spot rusting (ave. in mm)	0.96	1.00	0.88	0.98	0.91	0.96	0.97

Table 2 (continued)

Metal	Test item	EX.VIII	EX.IX	EX.X	EX.XI	EX.XII	EX.XIII	EX.
Hot dipped zinc alloy plated on steel plate	Film appearance	good evenness & density	good evenness & density	good evenness & density	good evenness	good evenness	good evenness	good evenness
	Film weight(g/m^2)	2.9	2.7	4.5	4.5	4.0	4.2	4.6
	Brine spray (ave.in mm)	1.5	1.5	5.5	3.5	4.0	3.5	4.0
	Adhesivity							
	2 mm cuts	100/100	100/100	35/100	58/100	68/100	52/100	0/100
	1 mm cuts	100/100	100/100	0/100	0/100	0/100	0/100	0/100
Electro-plated zinc on steel plate	Film appearance	good evenness & density	good evenness & density	good evenness & density	good evenness	good evenness	good evenness	good evenness
	Film weight(g/m^2)	2.3	2.3	3.7	3.5	3.3	3.5	3.8
	Brine spray (ave.in mm)	2.5	2.5	10.5	6.5	6.0	7.0	8.0
	Adhesivity							
	2 mm cuts	100/100	100/100	0/100	24/100	33/100	25/100	0/100
	1 mm cuts	100/100	95/100	0/100	0/100	0/100	0/100	0/100
Electro-plated zinc alloy on steel plate	Film appearance	good evenness & density	good evenness & density	good evenness & density	good evenness	good evenness	good evenness	good evenness
	Film weight(g/m^2)	3.0	2.9	4.3	4.0	3.6	3.8	4.5
	Brine spray (ave.in mm)	2.0	2.0	5.0	3.0	3.0	3.5	3.0
	Adhesivity							
	2 mm cuts	100/100	100/100	20/100	64/100	52/100	48/100	0/100
	1 mm cuts	100/100	100/100	0/100	3/100	12/100	6/100	0/100
cold rolled steel plate	Film appearance	good evenness & density	good evenness & density	blue colored uneven	good evenness & density	good evenness & density	good evenness & density	good evenness
	Film weight(g/m^2)	2.2	2.0	0.8	3.1	2.9	3.0	3.4
	Brine spray (ave.in mm)	1	1	4	1.5	1.5	1.5	3.0
	Adhesivity							
	2 mm cuts	100/100	100/100	100/100	100/100	100/100	100/100	0/100
	1 mm cuts	100/100	100/100	80/100	100/100	100/100	100/100	0/100
	Spot rusting (ave.in mm)	0.96	0.98	3.10	1.10	1.30	1.30	2.52

In Table 2 above, the brine spray and spot rusting results each indicate average values (mm) of the largest diameter of blisters and rust spots, respectively.

EXAMPLES XV - XXXI

Examples XV to XXV are Examples of the process and compositions of the invention. Examples XXVI to XXXI are Examples using known compositions, given for comparison purposes.

The treating process used, which is common to all of Examples XV - XXXI, is given below, with the aqueous coating composition of each Example being set forth in Table 3, while the metal treated and the test results obtained following the phosphate treatment are given in Table 4.

Samples of all four metal surfaces specified in Table 4 were treated simultaneously according to the following procedure:

(a) degreasing, using an alkaline degreasing agent (Nippon Paint Co., "RIDOLINE S102", 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 sprayed with the acidic aqueous solution specified in Table 3 at 52°C for 120 seconds, (in Ex. XXVI, first sprayed for 15 seconds, spraying discontinued for 15 seconds, and again sprayed for 105 seconds) spraying pressure -0.8 Kg/cm^2 (gauge pressure);

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

(e) the metal surfaces were then dipped into deionized water at room temperature for 15 seconds;

(f) the surfaces were then dried in hot air at 100°C for 10 minutes. At this stage, the appearance and film weight of the treated metal surfaces were determined, with the results set forth in Table 4; and

(g) 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 180 V., 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.

A second sample of each electrocoated plate so obtained was coated with an intermediate coating material (Nippon Paint Co., "ORGA TO778 Gray") to 30 μ thickness, followed by baking at 140°C for 20 minutes, and a top coating material (Nippon Paint Co., "ORGA TO626 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. The coated plates were subjected to the adhesion test, and with the cold rolled steel plate, 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 was 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 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 4.

(D) Determination of Mn in coating:

A phosphated plate was dipped in a 5% aqueous chromic acid solution (75°C) for 5 minutes, and the weight of the conversion coating was calculated from the weight difference of the plate before and after this treatment. Next, the amount of manganese dissolved out and contained in the aqueous chromic acid was determined by the atomic-absorption method, and manganese in the conversion coating was calculated therefrom.

Mn(%) in the conversion coating = $W_M/Wc \times 100$ (%)

$$Wc = W_1 - W_2/S$$

$$W_M = A.M/S$$

wherein

W_1 stands for weight (g) of plate before chromic acid treatment;

W_2 stands for weight (g) of plate after chromic acid treatment;

S is surface area (m^2) of plate;

Wc is the coating weight per square metre (g/m^2);

A stands for volume (l) of chromic acid solution used;

M stands for amount of Mn determined by atomic-absorption method (g/l); and

W_M stands for amount of Mn in unit area (m^2) of coating.

Table 3

Composition of Acidic Aqueous solution, g/l	Ex.XV	Ex.XVI	Ex.XVII	EX.XVIII	EX.XIX	EX.XX	EX.XXI	EX.XXII
Zn	1.0	1.0	1.0	1.0	1.0	1.0	0.7	1.2
PO_4	14.0	14.0	14.0	14.0	14.0	14.0	10.0	20.0
Mn	0.8	2.0	0.8	0.8	2.0	0.8	0.8	0.8
Ni	—	—	0.3	2.0	0.3	0.3	0.3	0.3
NO_2	0.06	0.06	0.06	0.06	0.06	—	0.06	0.06
H_2O_2	—	—	—	—	—	1.0	—	—
NO_3	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
ClO_3	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
BF_4	—	—	—	—	—	—	—	—
Fe(III)	—	—	—	—	—	—	—	—
Total Acidity (point)	17.5	19	18	20	19.5	18	18	24
Acidity of Free Acid (point)	0.7	0.7	0.7	0.7	0.7	0.7	0.6	0.7
Spraying pressure (Kg/cm^2)	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8

Table 3 (continued)

Composition of Acidic Aqueous solution, g/l	Ex.XXIII	Ex.XXIV	Ex.XXVI	EX.XXVII	EX.XXVIII	EX.XXIX	EX.XXX	EX.XXXI
Zn	1.0	1.2	0.69	0.8	1.0	1.0	3.0	0.1
PO_4	14.0	20.0	11.4	14.0	14.0	14.0	20.0	5.0
Mn	0.8	0.8	—	—	0.5	0.3	0.8	0.8
Ni	0.3	0.3	0.38	0.5	—	0.3	0.3	0.3
NO_2	0.08	0.06	0.07	0.08	0.06	0.06	0.06	0.06
H_2O_2	—	—	—	—	—	—	—	—
NO_3	4.0	4.0	1.6	3.0	4.0	4.0	4.0	4.0
ClO_3	—	2.5	1.49	0.5	1.5	1.5	1.5	0.3
BF_4	—	—	0.8	—	—	—	—	—
Fe(III)	—	—	0.018	—	—	—	—	—
Total Acidity (point)	18	24	14.5	17	17	17	26	8
Acidity of Free Acid (point)	0.7	0.7	0.6	0.7	0.7	0.7	0.7	0.2
Spray. pressure (Kg/cm^2)	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8

In Example XXV, the same composition as specified in Example XV was used, but intermittent spraying, i.e., spraying (15 sec) — standing (15 sec.) — spraying (105 sec.) was used.

Table 4

Metal	Test item	EX.XV	EX.XVI	EX.XVII	EX.XVIII	EX.XIX	EX.XX	EX.XXI
Hot dipped zinc alloy plated on steel plate	Film appearance	good evenness & density	good evenness & density	good evenness & density	good evenness & density	good evenness & density	good evenness & density	good evenness & density
	Film weight (g/m^2)	2.6	2.2	2.4	2.5	2.2	2.6	2.3
	Brine spray (ave. in mm)	2.5	2.0	1.5	1.5	1.5	1.5	1.5
	Adhesivity 2 mm cuts	100/100	100/100	100/100	100/100	100/100	100/100	100/100
	1 mm cuts	100/100	100/100	100/100	100/100	100/100	100/100	100/100
Electro-plated zinc on steel plate	Film appearance	good evenness & density	good evenness & density	good evenness & density	good evenness & density	good evenness & density	good evenness & density	good evenness & density
	Film weight (g/m^2)	2.0	1.6	1.8	1.9	1.9	1.7	1.8
	Brine spray (ave. in mm)	3.5	3.0	2.5	2.0	2.0	3.0	2.5
	Adhesivity 2 mm cuts	100/100	100/100	100/100	100/100	100/100	100/100	100/100
	1 mm cuts	80/100	90/100	95/100	100/100	100/100	100/100	100/100
Electro-plated zinc alloy on steel plate	Film appearance	good evenness & density	good evenness & density	good evenness & density	good evenness & density	good evenness & density	good evenness & density	good evenness & density
	Film weight (g/m^2)	2.6	2.3	2.5	2.6	2.2	2.4	2.4
	Brine spray (ave. in mm)	2.0	2.0	2.0	1.5	1.5	2.0	2.0
	Adhesivity 2 mm cuts	100/100	100/100	100/100	100/100	100/100	100/100	100/100
	1 mm cuts	100/100	100/100	100/100	100/100	100/100	100/100	100/100
cold rolled steel plate	Film appearance	good evenness & density	good evenness & density	good evenness & density	good evenness & density	good evenness & density	good evenness & density	good evenness & density
	Film weight (g/m^2)	1.8	1.5	1.8	1.8	1.6	1.8	1.8
	Brine spray (ave. in mm)	2.0	1.5	1.5	1.0	1.5	1.5	1.5
	Adhesivity 2 mm cuts	100/100	100/100	100/100	100/100	100/100	100/100	100/100
	1 mm cuts	100/100	100/100	100/100	100/100	100/100	100/100	100/100
	Spot rusting (ave. in mm)	0.96	1.00	0.98	0.91	0.96	0.97	0.96

Table 4 (continued)

Metal	Test item	EX.XXII	EX.XXIV	EX.XXV	EX.XXVI	EX.XXVII	EX.XXVIII	EX.XXI
Hot	Film appearance	good evenness	good evenness	good evenness	good evenness	good evenness	good evenness	good evenness
dipped		& density	& density	& density	& density			
zinc	Film weight(g/m²)	2.2	2.0	2.2	3.5	3.6	3.2	3.4
alloy	Brine spray							
plated	(ave.in mm)	1.5	3.0	1.5	5.5	3.5	4.0	3.5
on	Adhesivity							
steel	2 mm cuts	100/100	100/100	100/100	35/100	58/100	68/100	52/100
plate	1 mm cuts	100/100	100/100	100/100	0/100	0/100	0/100	0/100
Electro–	Film appearance	good evenness	good evenness	good evenness	good evenness	good evenness	good evenness	good evenness
plated		& density	& density	& density	& density			
zinc on	Film weight(g/m²)	1.8	1.7	1.8	3.0	2.8	3.0	2.8
steel	Brine spray							
plate	(ave.in mm)	2.5	4.0	2.0	10.5	6.5	6.0	7.0
	Adhesivity							
	2 mm cuts	100/100	90/100	100/100	0/100	24/100	33/100	25/100
	1 mm cuts	95/100	80/100	100/100	0/100	0/100	0/100	0/100
Electro–	Film appearance	good evenness	good evenness	good evenness	good evenness	good evenness	good evenness	good evenness
plated		& density	& density	& density	& density			
zinc	Film weight(g/m²)	2.3	2.2	2.0	3.4	3.2	2.9	3.0
alloy	Brine spray							
on	(ave.in mm)	2.0	2.5	1.5	5.0	3.0	3.0	3.5
steel	Adhesivity							
plate	2 mm cuts	100/100	100/100	100/100	20/100	64/100	52/100	48/100
	1 mm cuts	100/100	95/100	100/100	0/100	8/100	12/100	6/100
cold	Film appearance	good evenness	good evenness	good evenness	blue color	good evenness	good evenness	good evenness
rolled		& density	& density	& density	uneven	& density	& density	& density
steel	Film weight(g/m²)	1.6	1.5	1.6	0.7	2.5	2.3	2.4
plate	Brine spray							
	(ave.in mm)	1.5	2.0	1.02	4.5	2.0	2.0	2.0
	Adhesivity							
	2 mm cuts	100/100	100/100	100/100	100/100	100/100	100/100	100/100
	1 mm cuts	100/100	100/100	100/100	80/100	100/100	100/100	100/100
	Spot rusting							
	(ave.in mm)	0.98	0.98	0.87	3.10	1.10	1.30	1.30

Table 4 (continued)

Metal	Test item	EX.XXIII	EX.XXX	EX.XXXI
Hot dipped zinc alloy plated on steel plate	Film appearance	good evenness & density	good evenness	good evenness
	Film weight(g/m^2)	2.4	3.7	2.0
	Brine spray (ave.in mm)	2.5	4.0	4.5
	Adhesivity			
	2 mm cuts	100/100	0/100	60/100
	1 mm cuts	100/100	0/100	0/100
Electro-plated zinc on steel plate	Film appearance	good evenness & density	good evenness	good evenness
	Film weight(g/m^2)	1.9	3.0	1.8
	Brine spray (ave.in mm)	3.5	8.6	7.5
	Adhesivity			
	2 mm cuts	100/100	0/100	34/100
	1 mm cuts	95/100	0/100	0/100
Electro-plated zinc alloy on steel plate	Film appearance	good evenness & density	good evenness	good evenness
	Film weight(g/m^2)	2.2	3.6	2.2
	Brine spray (ave.in mm)	2.5	3.0	4.0
	Adhesivity			
	2 mm cuts	100/100	0/100	68/100
	1 mm cuts	100/100	0/100	12/100
cold rolled steel plate	Film appearance	good evenness & density	good evenness	yellow rust uneven
	Film weight(g/m^2)	1.2	2.2	1.1
	Brine spray (ave.in mm)	2.0	3.5	4.5
	Adhesivity			
	2 mm cuts	100/100	0/100	80/100
	1 mm cuts	100/100	0/100	30/100
	Spot rusting (ave.in mm)	1.00	4.52	5.02

CLAIMS

1. A process for phosphating an iron- or zinc-based metal surface comprising contacting the metal surface with an acidic aqueous solution characterised in that the solution contains:
   (a) from 0.1 to 2.0 g/l of zinc ion;
   (b) from 5 to 30 g/l of phosphate ion;
   (c) from 0.2 to 3 g/l of manganese ion; and
   (d) a conversion coating accelerator.
2. A process according to claim 1 characterised in that the solution contains 0.1 to 0.4 g/l of zinc ion.
3. A process according to claim 1 characterised in that the solution contains 1.6 to 2.0 g/l of zinc ion.
4. A process according to any one of claims 1-3 characterised in that the solution contains 0.2 to 0.5 g/l of manganese ion.
5. A process according to any one of the preceding claims consisting essentially of contacting the metal surface with the solution by spraying the metal surface with the solution and optionally after spraying dipping the metal surface in the solution.
6. A process according to claim 5 characterised in that the contact is by spraying the metal surface with the solution for about 2 - 15 seconds, followed by dipping the metal surface in the solution for at least 15 seconds.
7. A process according to claim 5 characterised in that the contact is by spraying the metal surface with the solution for at least 5 seconds.
8. A process according to claim 7 characterised in that the treatment is carried out by one to three intermittent spray cycles, each cycle consisting of first spraying for 5 to 30 seconds, then discontinuing spraying for 5 to 30 seconds, and then finally spraying again for at least 5 seconds, the total spray treatment time for each cycle being at least 40 seconds.

9. A process according to any one of claims 5, 7 and 8 characterised in that the contact is by spraying the metal surface with a solution containing:

(a) from 0.5 - 2, preferably 0.5 - 1.5 g/l of zinc ion;
(b) from 10 to 20 g/l of phosphate ion;
(c) from 0.6 to 3 g/l of manganese ion; and
(d) a conversion coating accelerator.

10. A process according to any one of the preceding claims characterised in that the solution also contains 0.05 - 3 g/l, preferably 0.05 - 1.9 g/l, of chlorate ion.

11. A process according to any one of claims 5 and 7-9 characterised in that the contact is by spraying the metal surface with the solution and the solution contains from 2 to 5 g/l of chlorate ion and from >1 to 2 g/l of zinc ion.

12. A process according to any one of the preceding claims characterised in that the metal treated includes both an iron-based surface and a zinc-based surface.

13. A process according to any one of the preceding claims characterised in that the phosphated metal surface is rinsed and electrocoated.

14. An acidic aqueous composition for phosphating an iron- or zinc-based metal surface characterised in that the composition is a solution defined in any one of claims 1-4 and 9-11.

15. An aqueous concentrate which upon dilution with water forms a solution for use in the application of a conversion coating to iron- or zinc-based metal surfaces, characterised in that the concentrate contains zinc ion, phosphate ion and manganese ion (as well as optionally nickel ion) in weight ratios of

0.1 - 2 : 5 - 30 : 0.2 - 3 (: 0.1 - 4).

16. A concentrate according to claim 15, which contains

at least 25 g/l, and preferably from 50 to 130 g/l, of zinc ion.

17. A metal substrate having an iron- or zinc-based surface characterised in that the surface is coated with a zinc phosphate conversion coating which contains from 1 to 20% of manganese, and which coating has a non-leaf-like crystal structure on iron-based surfaces.

European Patent Office

EUROPEAN SEARCH REPORT

Application number

EP 83 30 4846

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. ³)
X	EP-A-0 018 841 (NIPPON PAINT) * Claims 1-3,8,9,17 *	1-4,9 10	C 23 F 7/08
X	* Claims 18-29; page 9, lines 22-26 *	5,7,8	
X	* Page 2, lines 28-34; examples 4-6; page 17; claims 30-32 * ---	12-14 17	
X	EP-A-0 060 716 (NIPPON PAINT) * Claims 1,2,6,8,9-11; example page 14 * ---	1-4,12 -14	TECHNICAL FIELDS SEARCHED (Int. Cl. ³)
X	EP-A-0 056 881 (METALLGESELLSCHAFT) * Claims 1,3,4,5,9; examples 2,6, page 7; page 6, lines 7-20; page 2, line 34 - page 3, line 8 *	1-7,9 10,12- 14,17	C 23 F 7/08 C 23 F 7/10 C 23 F 7/12
Y	* Examples 2,6, page 7; claims * --- -/-	9-17	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	18-04-1984	TORFS F.M.G.

CATEGORY OF CITED DOCUMENTS

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Application number

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Page 2

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. ³)
Y	EP-A-0 036 689 (METALLGESELLSCHAFT AG) * Claims 1-4; page 4, lines 19-30 * -----	9-17	
			TECHNICAL FIELDS SEARCHED (Int. Cl. ³)

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D : document cited in the application
L : document cited for other reasons
& : member of the same patent family, corresponding document