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(54) PROCEDE DE PHOSPHATATION DE SURFACES METALLIQUES UTILISANT DES SOLUTIONS SANS NICKEL

(54) PROCESS OF PHOSPHATING METAL SURFACES USING NICKEL FREE PHOSPHATING SOLUTIONS

(57) In a process of phosphating metal surfaces phosphating solutions are employed which are substantially free of nickel and contain 0.3 to 1.7 g/l Zn, 0.2 to 4.0 g/l Mn, 0.001 to 0.030, preferably 0.003 to 0.020 g/l Cu, 5 to 30 g/l phosphate (calculated as P_2O_5) in which by oxygen and/or other equivalent oxidizers the concentration of Fe(II) is kept below 0.1 g/l and which are adjusted to a pH value from 3.0 to 3.8. The weight ratio of Cu to P_2O_5 is preferably adjusted to 1 : (170 to 30,000) and Cu and P_2O_5 are preferably replenished in a weight ratio of 1 : (5 to 2000). The phosphating solutions should contain 0.3 to 1.0 g/l Zn if they are applied by spraying and should contain 0.9 to 1.7 g/l Zn if they are applied by spraying/dipping operations or by a dipping operation. The process serves particularly for the pre-treatment of metal surfaces for a succeeding painting; particularly by electro-dipcoating, and for the phosphating of steel, galvanized steel, zinc alloy-plated steel, aluminum and its alloys.

ABSTRACT

In a process of phosphating metal surfaces phosphating solutions are employed which are substantially free of nickel and contain

0.3 to 1.7 g/l Zn
0.2 to 4.0 g/l Mn
0.001 to 0.030, preferably 0.003 to o.020 g/l Cu
5 to 30 g/l phosphate (calculated as P_2O_5)

in which by oxygen and/or other equivalent oxidizers the concentration of Fe(II) is kept below 0.1 g/l and which are adjusted to a pH value from 3.0 to 3.8. The weight ratio of Cu to P_2O_5 is preferably adjusted to 1 : (170 to 30,000) and Cu and P_2O_5 are preferably replenished in a weight ratio of 1 : (5 to 2000).

The phosphating solutions should contain 0.3 to 1.0 g/l Zn if they are applied by spraying and should contain 0.9 to 1.7 g/l Zn if they are applied by spraying/dipping operations or by a dipping operation.

The process serves particularly for the pretreatment of metal surfaces for a succeeding painting, particularly by electro-dipcoating, and for the phosphating of steel, galvanized steel, zinc alloy-plated steel, aluminum and its alloys.

PROCESS OF PHOSPHATING METAL SURFACES USING NICKEL FREE PHOSPHATING SOLUTIONS

DESCRIPTION

This invention relates to a process of phosphating metal surfaces by a treatment with aqueous acid phosphating solutions which contain zinc ions, manganese ions, phosphate ions, and oxidizers, also to the use of that process for pretreating the metal surfaces for a succeeding painting, particularly by electro-dipcoating, and to the phosphating of steel, aluminum and its alloys.

Metals are phosphated to form metal phosphate layers which are firmly intergrown with the metal surface and which in themselves improve the resistance to corrosion and in combination with paints and other organic coating swill contribute to a substantial increase of the adhesion and of the resistance to subsurface corrosion. Phosphate layers serve also as an insulation against a passage of electric currents and in combination with lubricants will reduce sliding friction.

A pretreatment before a painting operation may particularly be effected by low-zinc phosphating processes, in which phosphating solutions are employed which have relatively low contents of zinc ions amounting, e.g., to 0.5 to 1.5 g/l. The phosphate layers formed on steel under such conditions will have a high content of phosphophyllite ($Zn_2Fe(PO_4)_2 \cdot 4H_2O$), which has a much higher resistance to corrosion than the hopeite ($Zn_3(PO_4)_2 \cdot 4H_2O$) deposited from relatively high-zinc phosphating solutions. If the low-zinc phosphating solutions contain also nickel ions and/or manganese ions, the protection afforded in the presence of paints will be increased further. Low-zinc processes in which, e.g., 0.5 to 1.5 g/l manganese ions and, e.g., 0.3 to 2.0 g/l nickel ione are employed are widely used as so-called three-cation processes to prepare metal surfaces for a painting operation, e.g., before a cathodic electro-dipcoating of automobile car bodies.

But disadvantages are due to the high content of nickel ions in the phosphating solutions used in the three-cation processes and to the high content of nickel and of nickel compounds in the resulting phosphate layers because nickel and nickel compounds are undesirable from the aspects of work place hygiene and pollution of the environment.

It is an object of the invention to provide for the phosphating of metals, particularly of steel, galvanized steel, zinc alloy-plated steel and aluminum and its alloys, a process by which phosphate layers can be formed which have approximately the same quality as the layers produced by the three-cation processes using Zn-Mn-Ni but are free of nickel and of nickel compounds.

To accomplish that object the process of the kind described first hereinbefore is carried out in accordance with the invention in such a manner that the metal surfaces are contacted with phosphating solutions which are substantially free of nickel and contain:

0.3	to	1.7	g/l	Zn
0.2	to	4.0	g/l	Mn
0.001	to	0.030	g/l	Cu
5	to	30	g/l	phosphate (calculated as P_2O_5)

with a weight ratio of copper to phosphate of 1 : (170 to 30,000) in which by oxygen and/or other equivalent oxidizers the concentration of Fe(II) is kept below 0.1 g/l and which are adjusted to a pH value from 3.0 to 3.8.

The process in accordance with the invention is particularly used to treat steel, galvanized steel, zinc alloy-plated steel, aluminum and its alloys. The term steel covers soft plain carbon steels, relatively high-strength and high-strength steels (which may be, e.g., microalloyed, or dual-phase or phosphorus-alloyed steels), and low-alloy steels. The zinc layers may be formed, e.g., by electrolysis, hot dipping and vapor deposition.

Typical qualities of zinc include pure zinc and alloys containing, e.g., Fe, Ni, Co, Al, Cr. The term aluminum and aluminum alloys covers the cast and wrought materials which are used in the metalworking industry and which may contain, e.g., Mg, Mn, Cu, Si, Zn, Fe, Cr, Ni, Ti as alloying elements.

It is a basic requirement for the process in accordance with the invention that the aqueous acid phosphating solutions must be substantially free of nickel. This means that under technical conditions the Ni concentration in the phosphating baths must be lower than 0.0002 to 0.01 g/l and is preferably below 0.0001 g/l.

Another essential feature of the invention calls for the presence of the three metal cations Zn, Mn, and Cu in the stated amounts. Particularly in the treatment of Steel, a zinc concentration below 0.3 g/l will result in the formation of a layer of much lower quality. If the zinc content exceeds 1.7 g/l, the phosphate layers formed on steel will have a much lower phosphophyllite content and the resulting phosphate layers will have a much lower quality in combination with a paint. With a content below 0.2 g/l Mn the addition of said cations will not result in detectable advantages and a further improvement of the detected quality cannot be expected with concentrations in excess of 4 g/l. The Cu concentration is between 0.001 and 0.030 g/l. Below that range the favorable effect on the formation of the layer and on the quality of the layer will be lost, and a copper content above 0.030 g/l will increasingly result in a disturbing cementation of Cu.

In the phosphating of steel, Fe will be dissolved as Fe(II) ions. The phosphating bath must contain sufficient oxygen and/or other oxidizers to prevent a steady_state Fe(II) ion concentration in excess of 0.1 g/l that is to say any Fe in excess of the above has to be transformed to Fe (III) and precipitated as iron phosphate sludge.

To ensure the formation of a satisfactory phosphate layer the phosphating solution must be adjusted to a pH value between 3.0 and 3.8. The higher (lower) pH values will be employed in case of lower (higher) bath temperatures and in case of lower (higher) bath concentrations. In case of need the pH value of the bath may be adjusted by a co-use of additional cations, such as alkali ions (Na, K, NH_4, etc.), and/or alkaline earth metal ions (Mg, Ca) and/or additional anions (NO_3, Cl, SiF_6, SO_4, BF_4, etc.). The pH value of the phosphating solution may be corrected during the preparation and use of the solution by an addition of basic compounds (NaOH, Na_2CO_3, ZnO, $ZnCO_3$, $MnCO_3$ etc.) or of acids (HNO_3, H_3PO_4, H_2SiF_6, HCl, etc.) as may be required.

The quality of the phosphate layers formed by the process in accordance with the invention may be improved by an addition of up to 3 g/l Mg and/ or up to 3 g/l Ca. The concentration of each of said cations lies preferably in the range from 0.4 to 1.3 g/l. The cations may be introduced into the phosphating solution, e.g., as a phosphate or as a salt including the above-mentioned anions. The oxides, hydroxides and carbonates may also be used as a source of Mg and Ca.

If the process in accordance with the invention is carried out by a spraying operation, the Zn concentration will preferably lie between 0.3 and 1 g/l whereas for a spraying-dipping operation and for a dipping operation the bath is preferably adjusted to an Zn content between 0.9 and 1.7 g/l. The preferred Mn concentration is between 0.4 and 1.3 g/l, regardless of the mode of application.

According to a preferred feature of the invention the metal surfaces are contacted with a phosphating solution which contains 0.003 to 0.020 g/l Cu. Particularly good results will be produced if a phosphating bath is used in which the weight ratio of Cu to phosphate, calculated as P_2O_5, is 1 : (170 to 30,000), and Cu and P_2O_5 are replenished in a weight ratio of 1 : (5 to 2000).

To limit the Fe(II) concentration the phosphating solution is contacted with oxygen, such as atmospheric oxygen, and/or suitable oxidizers are added. Preferred oxidizers include nitrite, chlorate, bromate, peroxi compounds (H_2O_2, perborate, percarbonate, perphosphate, etc.), and organic nitro compounds, such as nitrobenzene sulfonates. Such oxidizers may be used alone or in combination, optionally also with weaker oxidizers such as nitrate. Suitable combinations are, e.g., nitrite-nitrate, nitrite-chlorate(-nitrate), peroxi compound-NO_3, bromate-nitrate, chlorate-nitrobenzene sulfonate(-nitrate), bromate-nitrobenzene sulfonate(-nitrate). Said oxidizers serve not only to oxidize Fe(II) ions but will also accelerate the formation of the phosphate layer. Examples of typical concentration ranges of said oxidizers in the phosphating bath will now be stated: 0.04 to 0.5 g/l nitrite; 0.5 to 5 g/l chlorate; 0.3 to 4 g/l bromate; 0.005 to 0.1 g/h peroxi compound, calculated as H_2O_2; 0.05 to 1 g/l nitrobenzene sulfonate.

In accordance with a further preferred feature of the invention the metal surfaces are contacted with phosphating solutions which additionally contain modifying compounds of the group consisting of surfactants, hydroxycarboxylic acid, tartrate, citrate, simple fluoride, borofluoride, silico-fluoride. An addition of a surfactant (e.g., 0.05 to 0.5 g/l) will improve the phosphating of slightly greased metal surfaces. Hydroxycarboxylic acids, such as tartaric acid, citric acid and/or their salts, in concentrations in the range from, e.g., 0.03 to 0.3 g/l, will distinctly decrease the weight of the phosphate layer. A simple fluoride will promote the phosphating of metals which can be attacked only with difficulty and will reduce the minimum phosphating time and increase the surface area covered by the phosphate layer. This may be accomplished, e.g., by F contents of 0.1 to 1 g/l. Besides, the controlled addition of simple fluoride will permit a formation of crystalline phosphate layers on aluminum and its alloys. BF_4 and SiF_6 will also increase the aggressiveness of the phosphating baths and this will become distinctly apparent in the treatment of hot-galvanized surfaces. Such additions are made, e.g., in amounts of 0.4 to 3 g/l.

The phosphating process in accordance with the invention can be carried out by spraying, spraying-dipping and dipping operations. The bath temperatures lie usually between 40 and 60 °C.

For a treatment of steel and aluminum, contacting times of, e.g., 1 to 5 minutes will be sufficient for a deposition of uniformly covering phosphate layers. On the other hand, contacting times shorter than

10 seconds are often sufficient in the treatment of galvanized steel so that the process can also be carried out in coil coating plants.

Before being contacted with the phosphating solution, the surfaces are usually cleaned and rinsed and are often treated with activators based on titanium phosphate.

The phosphate layers formed by the phosphating process in accordance with the invention are finely crystalline and effect a uniform coverage. The weight per unit of area is usually between 1.5 and 4.5 g/m^2 in the treatment of steel, galvanized steel and zinc alloy-plated steel and between 0.5 and 2.5 g/m^2 in the treatment of aluminum and its alloys.

During the phosphating treatment, components of the phosphating solution are consumed, e.g., by incorporation in the phosphate layer, sludge formation, mechanical losses of bath solution remaining on the treated metal surfaces or in the sludge to be carried off, or by oxidation-reduction reactions and also decomposition. For that reason the analysis of the phosphating solution must be monitored and the deficient components must be replenished.

The phosphate layers may be used to advantage, inter alia, for protection against corrosion, to facilitate cold working and for electrical insulation. They are preferably used to prepare metal surfaces for a painting operation, particularly by elextro-dipcoating, and particularly good results will be produced in a combination with a cathodic electro-dipcoating. Before the painting operation the phosphate layers are preferably treated with passivating postrinsing agents based, e.g., on Cr(VI), Cr(VI)-Cr(III), Cr(III), Cr(III)-fluozirconate, Al(III), AI(III)-fluozirconate, because this will further improve the adhesion of the paint and its resistance to migration under the paint.

The invention will be explained more in detail with reference to the following examples:

Examples

Sheets of steel, galvanized steel, and aluminum were degreased with an alkaline cleaning agent and rinsed with water and after an optional activating pretreatment with a solution which contained titanium phosphate were phosphated by a treatment with phosphating solutions 1 to 12 at 50°C. In all cases, uniformly covering phosphate layers were formed, which in combination with a paint applied by cathodic electro-dipcoating and further painting (automobile-type treatment) provided a high resistance to corrosion and migration under the paint.

	1	2	3	4	5	6
Zn (g/l)	0.7	0.7	0.9	0.8	0.8	0.7
Mn (g/l)	1	0.8	1	1	1	1
Mg (g/l)	-	0.8	-	1	-	-
Cu mg/l	5	3	5	3	5	4
Na (g/l)	3.47	2.13	4.68	2.86	3.67	5.82
Ca (g/l)	-	1.3	-	-	-	-
P_2O_5 (g/l)	12	12	14	14	13	13
NO_2 (g/l)	0.07	0.07	0.09	0.09	-	0.17
ClO_3 (g/l)	-	-	-	-	-	-
NBS (g/l)	-	-	-	-	-	-
H_2O_2 (g/l)	-	-	-	-	0.03	-
NO_3 (g/l)	3	3	4	4	3	7
Cl (g/l)	-	-	-	=	-	-
F (g/l)	-	-	0.3	0.3	-	0.1
SIF_6 (g/l)	-	-	-	-	-	1.2
pH	3.4	3.4	3.4	3.4	3.4	3.4
TA	20.1	20.3	23.4	23.7	21.8	25.0
Application	S	S	S	S	S	S
LW (g/m^2) on steel	2.7	2.3	2.5	2.3	1.8	2.5
LW (g/m^2) on galvanized steel	2.8	2.5	2.3	2.4	1.9	2.8
LW (g/m^2) on aluminum	-	-	2.2	2.0	-	0.8

	7	8	9	10	11	12
Zn (g/l)	0.7	1.3	1.5	1.3	1.3	1.4
Mn (g/l)	1	1.5	0.7	1	1	1.2
Mg (g/l)	-	-	1.2	-	-	0.8
Cu mg/l	4	5	4	3	4	5
Na (g/l)	3.69	3.92	1.80	4.39	4.78	5.4
Ca (g/l)	-	-	-	-	-	-
P_2O_5 (g/l)	6	10	10	11	16	18
NO_2 (g/l)	0.17	0.17	0.15	0.11	-	-
ClO_3 (g/l)	-	-	-	-	2	3
NBS (g/l)	-	-	-	-	0.6	0.5
H_2O_2 (g/l)	-	-	-	-	-	-
NO_3 (g/l)	7	8	7	6	3	-
Cl (g/l)	-	-	-	-	-	4
F (g/l)	0.1	-	-	0.1	-	-
SIF_6 (g/l)	1.2	-	-	1.2	-	-
pH	3.6	3.3	3.3	3.3	3.3	3.3
TA	14.6	18.6	18.3	22.8	26.9	30.6
Application	S	D	D	D	D	D
LW (g/m^2) on steel	2.3	3.2	3.0	3.3	2.1	2.0
LW (g/m^2) on galvanized steel	2.7	3.4	3.2	3.5	2.0	2.0
LW (g/m^2) on aluminum	0.7	-	-	0.6	-	-

Explanations

NBS = nitrobenzene sulfonate sodium salt

TA = total acid = consumption of 0.1 N NaOH in ml for 10 ml bath sample against phenolphtalein

LW = weight of layer

S = spraying

D = dipping

The Fe(II) concentration is less than 0.1 g/l in all baths.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A process of phosphating metal surfaces by a treatment with aqueous acid phosphating solutions which contain zinc ions, manganese ions, phosphate ions, and oxidizers, characterized in that the metal surfaces are contacted with phosphating solutions which contain:

less than		0,01	g/l	Ni
0.3	to	1.7	g/l	Zn
0.2	to	4.0	g/l	Mn
0.001	to	0.030	g/l	Cu
5	to	30	g/l	phosphate (calculated as P_2O_5)

with a weight ratio of copper to phosphate of 1 : (170 to 30,000); in which by at least one of said oxidizers the concentration of Fe(II) is kept below 0.1 g/l and which are adjusted to a pH value from 3.0 to 3.8.

2. A process according to claim 1, characterized in that the metal surfaces are contacted with phosphating solutions which additionally contain Mg and/or Ca in amounts from greater than 0 to 3.0 g/l each.

3. A process according to claim 1 or 2, characterized in that the metal surfaces are contacted by spray application with phosphating solutions which contain 0.3 to 1.0 g/l Zn.

4. A process according to claim 1 or 2, characterized in that the metal surfaces are contacted by

spray/dip application or by dip application with phosphating solutions which contain 0.9 to 1.7 g/l Zn.

5. A process according to any one of claims 1 to 4, characterized in that the metal surfaces are contacted with phosphating solutions which contain 0.4 to 1.3 g/l Mn.

6. A process according to any one of claims 1 or 5, characterized in that the metal surfaces are contacted with phosphating solutions which contain 0.003 to 0.020 g/l Cu.

7. A process according to any one of claims 1 or 6, characterized in that Cu and P_2O_5 are replenished in a weight ratio of 1 : (5 to 2000).

8. A process according to any one of claims 1 to 7, characterized in that the metal surfaces are contacted with phosphating solutions which contain nitrite, chlorate, bromate, peroxi compounds or organic nitro compounds, as oxidizers.

9. A process according to any one of claims 1 to 8, characterized in that the metal surfaces are contacted with phosphating solutions which additionally contain modifying compounds selected from the group consisting of surfactants, hydroxycarboxylic acids, tartrate, citrate, simple fluoride, borofluoride and silicofluoride.

10. The use of the process according to any one of claims 1 to 9, for pretreating metal surfaces for a succeeding painting by electro-dipcoating.

11. The use of the process according to any one of claims 1 to 9, for phosphating steel, galvanized steel, zinc alloy-plated steel, aluminum and its alloys.

12. A process according to claim 8, wherein the metal surfaces are contacted with phosphating solutions which contain nitrobenzene sulfonate.