⑲ Europäisches Patentamt
European Patent Office
Office européen des brevets

⑪ Publication number: **0 407 015 A1**

⑫ EUROPEAN PATENT APPLICATION

㉑ Application number: **90305186.0**

(51) Int. Cl.⁵: **C23C 22/36**, C23C 22/44

㉒ Date of filing: **15.05.90**

The title of the invention has been amended (Guidelines for Examination in the EPO, A-III, 7.3).

㉚ Priority: **15.05.89 JP 120775/89**

㊸ Date of publication of application:
09.01.91 Bulletin 91/02

(84) Designated Contracting States:
DE ES FR GB

(71) Applicant: **NIPPON PAINT CO., LTD.**
2-1-2, Oyodokita Kita-ku
Osaka-shi Osaka-fu(JP)

(72) Inventor: **Tokuyama, Akio**
9-2-208, Kourigaoka 7-chome
Hirakata-shi, Osaka 573(US)
Inventor: **Endo, Koetsu**
A28-504, I, Otokoyama Koro
Yawata-shi, Kyoto 614(JP)
Inventor: **Sobata, Tamotsu**
4-301, 2, Shirakawa 3-chome
Ibaranki-shi, Osaka 567(JP)

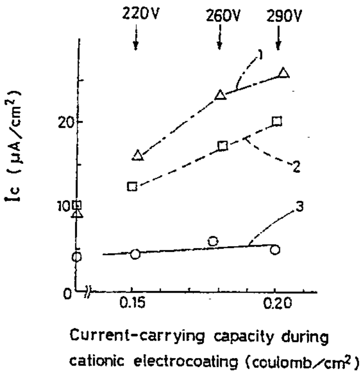
(74) Representative: **Pacitti, Pierpaolo A.M.E. et al**
Murgitroyd and Company Mitchell House 333
Bath Street
Glasgow G2 4ER Scotland(GB)

(54) Phosphate coated metal product, process for producing it, concentrate for use in the process and concentrate for replenishing the coating solution.

(57) A coating product has a zinc phosphate film for coating on a metal surface and thereon a coating film. The zinc phosphate film contains 20 ~ 42 weight % of zinc, 0.5 ~ 8 weight % of calcium, and 1.0 ~ 8 weight % of nickel.

The zinc phosphate film of this kind is obtained by treating the metal surface with dipping in an aqueous acidic phosphate-treating solution which contains at least a zinc ion, a phosphate ion, a calcium ion, a nickel ion, a fluorine compound, and an accelerator for converting into a film in specially defined concentrations and, in which the weight ratios of the calcium ion vs. the zinc ion, the nickel ion vs. the zinc ion, and the fluorine compound vs. the phosphate ion are set in specially defined ranges.

Fig. 1



EP 0 407 015 A1

COATING PRODUCT, PROCESS FOR PRODUCING, CONCENTRATED AGENT FOR TREATING WITH PHOSPHATE, AND CONCENTRATED TREATING AGENT FOR SUPPLEMENTARY USE

Background of the Invention

The present invention relates to a coating product in which, as pre-treatment (under treatment) for coating, in particular, pre-treatment for cationic electrocoating, a phosphate film is formed on a metal surface, and to a process for producing the product, a concentrated agent for treating with phosphate, and a concentrated treating agent for supplementary use.

There has been developed a method for treating with a phosphate which is suitable for treating a metal product that has a complicated uneven shape like an automobile body and also, particularly suitable for pre-treatment for the cationic electrocoating which has been widely used in recent years in the field of automotive industry (refer to Japanese Patent Gazette, showa 58-11513).

In this phosphate-treating method, is used an aqueous acidic phosphate-treating solution which, as essential components, contains a zinc ion, a phosphoric ion as well as a nitrite ion and/or a m-nitrobenzenesufonate ion in the concentrations; 0.5~ 1.5 g/l for the zinc ion, 5 ~ 30 g/l for the phosphate ion, and 0.01 ~ 0.2 g/l for the nitrite ion and/or 0.05~ 2 g/l for the m-nitrobenzenesulfonate ion. The method is carried out by first subjecting the metal surface to dipping treatment with said aqueous acidic phosphate-treating solution for 15 seconds or more at temperature of 40~ 70 °C, and followed by spraying for 2 seconds or more.

Recently in the field of automotive industry, in order to improve furthermore the corrosion-resistance in the after-coating, a steel material whose one side only is plated with zinc or a zinc alloy is beginning for use as a material for the automobile body. Like this, if a method for treating with the phosphate which is described in the forementioned Japanese Patent Gazette is applied on a metal surface where one side is an iron-based surface and the other side is a zinc-based surface, a phosphate film which has low film-quantity with uniform and dense cubic crystals as well as excellent adhesion and corrosion-resistance, which is suitable as a substratum for cationic electrocoating, can be formed on the iron-based surface, as expected. However, a film being formed on the zinc-based surface is insufficient in the resistance against brine-spraying after an application of the cationic electrocoating and, there has been found a problem that, when the process, cationic electrocoating→ intermediate coating → top coating, is completed, secondary adhesion (by dipping test of the film with cross-hatched scratches in warm water) is greatly inferior to that on the iron-based surface.

Then, as descrived above, to apply for a metal surface which has an iron-based surface and a zinc-based surface at the same time and also, to solve said problem which takes place on the zinc-based surface, there was proposed to use an aqueous acidic solution for treating with phosphate containing further a manganese ion and/or a nickel ion as a metal ion and as an essential component in a defined amount (Japanese Official Patent Provisional Publication, showa 57-152472).

Like this, for an iron-based surface or for a metal surface having both an iron-based surface and a zinc-based surface at the same time, a conversion film which is suitable for electrocoating became possible to be provided by treating with zinc phosphate by means of an immersing method and thus, the immersing method has established a firm ground for conversion treatment with zinc phosphate, of which main object is an improvement of corrosion-resistance not only for building materials and small articles, but also for wide variety of articles such as an automobile body and automobile parts which have an iron and zinc surfaces and these alloy surfaces.

However, in recent years the quality demand for corrosion-resistance in the automobile body is coming to a higher and higher degree. For example, when being repeatedly exposed to brine and subjected to atmospheric dry and wet change at a scratch in an outside plate part, it is strongly desired to prevent scab rust (scab-corrosion) occurence on an iron-based surface and to have a high degree of resistance against warm brine, but the up-to-date treating process with zinc phosphate is being unable to match the demand of a high degree like the above.

There have been desired to find a treating process which is a process for treating with zinc phosphate for a metal surface that has an iron-based surface or both the iron-based surface and a zinc-based surface, and with which not only a conversion film of corrosion-resistance which is suitable for coating, in particular, for electrocoating is given, but also the resistance against scab corrosion (hereinafter refered to as "scab-resistance") on the iron-based surface and the resistance against warm brine of the iron-based surface and zinc-based surface are greatly improved as well as the secondary adhesion when the intermediate and top coating on the electrocoated plate being carried out is further improved.

On the other hand, although a zinc phosphate film modified with manganese, opened in the Japanese Official Patent Provisional Publication, showa 57-152472, shows improved quality ih the cationic electrocoating film, there is limitation on the handling because the manganese compounds belong to specially defined chemical substances. Because of this, it is required to carry out the pretreatment for the electrocoating without use of the specially defined chemical substances.

Summary of the Invention

Thus, the first object of the present invention is to provide a coating product in which a conversion film having corrosion-resistance is formed in the pre-treatment suitable for the cationic electrocoating, scab-resistance of an iron-based surface as well as resistance of an iron-based surface and a zinc-based surface against warm brine are greatly improved, and also the secondary adhesion is improved when the electrocoating, intermediate coating, and top coating are carried out. The second object of the present invention is to provide a process for producing which is able to obtain a coating product such as the forementioned product by treatment at low temperature. Furthermore, the third object of the present invention is to provide concentrated agents which are used for said process.

The present inventors, as a result of extensive research to solve the forementioned subjects, found the undermentioned ① ~ ③ points with completion of this invention.

① The zinc phosphate film modified with calcium and nickel shows better coating quality than that of a film modified with manganese. That is, the zinc phosphate film modified with manganese is superior in warm brine-resistance of an iron-based surface and in water-resisting, secondary adhesion of a zinc-based surface, but does not sufficiently elevate the scab-resistance of the iron-based surface, while the zinc phosphate film modified with the specially defined calcium and nickel shows superior quality in all of the warm brine-resistance and scab-resistance of the iron-based surface as well as the water-resisting, secondary adhesion. However, if the nickel contents of the zinc phosphate film is too low, elevation of those properties, in particular, that of the water-resisting, secondary adhesion of the zinc-based surface becomes insufficient.

② Since the zinc phosphate film modified with calcium and nickel contains calcium, it is superior in alkali-resistance. Because of this, it shows particularly useful suitability for the pre-treatment in the cationic electrocoating of a thick film type, that is, in a coating method wherein an amount of heat generated during electrocoating on an interface of a product being subjected to coating is high with an increase of alkali concentration (refer to the caption for Figure 1 described later).

③ A zinc phosphate film of high quality modified with calcium and nickel can be formed by low temperature treatment with concentration management of zinc, calcium, nickel, and a fluoro compound in a specially defined range.

Accordingly, to solve the first subject, the coating product relating to the invention as claimed in the claim 1, having a zinc phosphate film for coating on a metal surface and thereon a coating film, is specialized by that the zinc phosphate film contains 20 ~ 42 weight % of zinc, 0.5 ~ 8 weight % of calcium, and 1.0 ~ 8 % weight of nickel.

In order to solve said second subject, the process for producing the coating product relating to the invention as claimed in the claim 2 is specialized by that, as a pretreatment for coating, a dipping treatment of the metal surface is carried out in an aqueous solution for treating with acidic phosphate, which contains, as essential components, at least, a zinc ion in concentration of 0.1 ~ 2 g/l, a phosphate ion in concentration of 5 ~ 40 g/l, a calcium ion in concentration of 0.5~ 4 g/l, a nickel ion in concentration of 0.5 ~ 4 g/l, a fluorine compound in concentration of 0.05 ~ 4 g/l (on a basis being converted into a fluoride ion), and an accelerator for converting into a film, in such proportion that their weight ratios are 0.5 ~ 4.0 between the calcium ion and the zinc ion (hereinafter, taking the former ion as a numerator and the latter ion as a denominator, the ratios are obtained.), 1.0 ~ 4.0 between the nickel ion and the zinc ion, and 0.05 ~ 2.0 between the fluorine compound (as being converted into the fluoride ion) and the phosphate ion, whereby a zinc phosphate film modified with calcium and nickel is formed on the metal surface.

To solve said third subject, the concentrated phosphate treating agent relating to the invention as claimed in the claim 3 is led by being diluted with water to said aqueous solution for treating with an acidic phosphate.

And to solve the third subject, the concentrated treating agent for supplementary use relating to the invention as claimed in the claim 4 is used to supplement a lacking component when the component in said aqueous solution for treating with acidic phosphate is consumed during said process.

It is preferred that said aqueous solution for treating with acidic phosphate, in case of necessity, contains a water-soluble tungsten compound in concentration of 0.005 ~ 20 g/l as the tungsten element. When being arranged like this, without deterioration in preferable quality of said zinc phosphate film modified with calcium and nickel, weight of the film can be increased, so that the effect of this invention can be displayed in a multiplication way.

Brief Description of the Drawing

Fig. 1 is a graph showing a relation between the current carrying capacity and the corrosion-causing current value Ic when cationic electrocoating of zinc phosphate film is applied.

Description of the Invention

The present invention is most effective for a case of that a metal surface having both the iron-based suface and the zinc-based surface at the same time is an object for treating, but not only this case, but also with a similar object an iron-based surface only or a zinc-based surface only as well as a zinc alloy-based surface can be treated. As said iron-based surface are cited a cold rolled steel plate, a hot rolled steel plate, and an acid-washed hot rolled steel plate. As said zinc-based and zinc alloy-based surfaces, are pratically cited, for example, a hot dipped galvanized steel plate, a hot dipped zinc alloy plated steel plate, an electro galvanized steel plate, and an electro zinc-alloyed plated steel plate. Incidentally, as far as it has said metal surface, to be wholly a metal is unnecessary.

For the coating product relating to the present invention, as a pre-treatment for coating, in particular, for cationic electrocoating, is formed on said metal surface a phosphate film modified by that 20 % or more of zinc, 0.5 % or more of calcium, and 1.0 % or more of nickel is contained for improvement of the rust-resistance and secondary adhesion. If the calcium contents of said zinc phosphate coating film modified are less than 0.5 weight %, the warm brine-resistance on the iron-based surface does not sufficiently elevate and the water-resisting, secondary adhesion on the zinc-based and zinc alloy-based surfaces does not sufficiently elevate. Said calcium contents are preferable if those are 8 weight or less. More preferable are the 1 ~ 7 weight % for a case of the coating film being formed on the iron-based surface and the 0.5 ~ 6 weight % for a case being formed on the zinc-based and zinc alloy-based surfaces. If the calcium contents exceed 8 weight % the elevation of effects may reach the top or the warm brine-resistance on the iron-based surface may lower. Also, if said nickel contents of the zinc phosphate film modified with calcium and nickel are less than 1.0 weight %, the scab-resistance on the iron-based surface does not sufficientry elevate and the water-resisting, secondary adhesion on the zinc-based and zinc alloy-based surfaces does not sufficiently elevate. Said nickel contents are preferred if those are 8 weight % or less. More preferable are the 1.0 ~ 6 weight % for a case of the film being formed on the iron-based surface and the 1.0 ~ 6 weight % for a case being formed on the zinc-based and zinc alloy-based surfaces. If the nickel contents exceed 8 weight %, the elevation of effects may reach the top or the warm brine-resistance may lower. Also, it is preferred that the zinc contents of said zinc phosphate film modified are 20~ 42 weight %. If the zinc contents are less than 20 weight %, the warm brine-resistance on the iron-based surface may lower and, if the contents exceed 42 weight %, the scab-resistance on the iron-based surface as well as the water-resisting, secondary adhesion on the zinc-based and zinc alloy-based surfaces may lower.

The weight of said zinc phosphate film modified with calcium and nickel prefers to be 0.5 ~ 5 g/m^2 in a case of formation on the iron-based surface and more prefers to be 1.5 ~ 3 g/m^2. If the weight of the film is less than 0.5 g/m^2, the warm brine-resistance and scab-resistance on the iron-based surface may not elevate sufficiently and, if it exceeds 5 g/m^2, elevation of the effects reachs to the top and an economical disadvantage may happen. The weight of said zinc phosphate film modified with calcium and nickel, when it is formed on the zinc-based and zinc alloy-based surfaces, prefers to be 0.5 ~ 10 g/m^2 and more prefers to be 3 ~ 5 g/m^2. If the weight of the film is less than 0.5 g/m^2, the warm brine-resistance on the zinc-based and zinc alloy-based surfaces may not elevate sufficiently and, if it exceeds 10 g/m^2, the water-resisting, secondary adhesion on the zinc-based and zinc alloy-based surfaces may lower.

The process for producing a coating product relating to the present invention, for example, is carried out according to the undermentioned, but not limited within that. A metal surface is degreased by being sprayed with an alkaline degreasing agent at the temperature of 30~ 60 °C for 2 minutes and/or by being subjected to dipping treatment with the agent, rinsed with water, and then treated with spraying of a surface conditioner at room temperature for 10 ~ 30 seconds and/or with dipping. A metal surface treated with the surface conditioner is treated with dipping at the temperature of 30 ~ 70 °C for 15 seconds or more by using an aqueous solution for treating with acidic phosphate which contains a zinc ion, a phosphate ion, a calcium ion, a nickel ion, and a fluoro compound as well as an accelerator for converting into a film as the main components. Then, it is rinsed with tap water and further with deionized water, wherby a metal surface treated with coating pre-treatment is obtained. On the pre-treatment of the metal surface, for example, usual cationic electrocoating and furthermore, in case of necessity, intermediate coating and top coating are carried out to get a electrocoated product. The treating temperature for said aqueous solution for treating with acidic phosphate prefers to be 30~ 70 °C and more prefers to be 35 ~.60 °C . If temperature is lower than the range, the converting into a film is bad and the treating may require a long period and also, if it is higher than the range, decomposition of the accelerator for converting into a film and precipitation of the treating solution may take place, so that balancing of the treating solution may easily collapse and a superior film is hard to get.

The treating time for dipping prefers to be 15 seconds or more and more prefers to be 30 ~ 120 seconds. If it is less than that, a film having desired crystals may not sufficiently be formed. In a case of that an article having a complex shape such as an automobile body is treated, at first, the treating practically requires dipping for 15 seconds or more or, more preferably, for 30 ~ 90 seconds and then, spraying for 2 seconds or more or, more preferably, for 5 ~ 45 seconds. Besides, in order to rinse out the sludge adhered on the metal surface during dipping, the spray treatment is preferably carried out for as long a period as possible. Thus, the dipping treatment according to the present invention includes combination of the dipping in said aqueous solution for treating with phosphate followed by spraying.

The zinc ion which is a main component of said aqueous solution for treating with acidic phosphate prefers concentration of 0.1 ~ 2 g/l and more prefers that of 0.7 ~ 1.2 g/l. If the concentration is less than 0.1 g/l, the phosphate film is not uniformly formed on the iron-based surface and a film of blue color partly is formed. Also, if it exceeds 2 g/l, although an uniform phosphate film is formed, the phosphate film being formed on the iron-based surface easily converts into crystals of a leaf shape and also, since the calcium contents in the film become less than 0.5 weight %, the warm brine-resistance can not sufficiently be elevated and the water-resisting, secondary adhesion on the zinc-based and zinc alloy-based surfaces can not sufficiently be elevated.

In said aqueous solution for treating with acidic phosphate, the phosphate ion prefers concentration of 5 ~ 40 g/l and more prefers that of 10 ~ 20 g/l. If it is less than 5 g/l, an ununiform film is apt to be formed and also, if it exceeds 40 g/l, the elevation of effects reaches to the top resulting in waste of chemicals with an economical disadvantage.

In said aqueous solution for treating with acidic phosphate, the calcium ion prefers concentration of 0.5 ~ 4 g/l and more prefers that of 0.5 ~ 2 g/l . If it is less than 0.5 g/l, the calcium contents in a film become less than 0.5 weight %, so that the warm brine-resistance on the iron-based surface is not sufficiently elevated and the water-resisting, secondary adhesion on the zinc-based and zinc alloy-based surfaces is not sufficiently elevated. If it exceeds 4 g/l, not only the elevation of effects reachs to the top, but also the warm brine-resiastance on the iron-based surface trends to decrease with lowering of the film quantity. Besides, the weight ratio between the calcium ion and zinc ion is set in a range of 0.5~ 4. If the weight ratio is less than 0.5, calcium contents of a film become less than 0.5 weight % and, the warm brine-resistance on the iron-based surface is not sufficiently elevated and the water-resisting, secondary adhesion is not sufficiently elevated. Also, if the ratio exceeds 4, the elevation of effects reachs to the top as well as a decreasing trend in the film quantity and in the warm brine-resistance is seen.

In said aqueous solution for treating with acidic phosphate, the nickel ion prefers concentration of 0.5 ~ 4 g/l and more prefers that of 0.5 ~ 2 g/l. If the concentration is less than 0.5 g/l, the nickel contents in a film become less than 1 weight %, so that the scab-resistance on the iron-based surface is not sufficiently elevated and the water-resisting, secondary adhesion on the zinc-based and zinc alloy-based surfaces is not sufficiently elevated. If the concentration exceeds 4 g/l, not only the elevation of effects reachs to the top, but also there is seen a decreasing trend of the warm brine-resistance on the iron-based surface with decresing quantity of the film. Besides, the weight ratio between the nickel ion and the zinc ion is set in a range of 1.0 ~ 4.0. If the weight ratio is less than 1.0, the nickel contents in the film become less than 1.0 weight % and, the scab-resistance on the iron-based surface and the water-resisting, secondary adhesion on the zinc-based surface are not elevated and also, if the weight ratio exceeds 4.0, the elevation of effects reachs to the top as well as a decreasing trend of the film quantity and of the warm brine-resistance on the iron-based surface is seen.

In the aqueous solution for treating with acidic phosphate, the fluorine compound prefers, on a basis being converted into a fluoride ion, concentration of 0.05 ~ 4 g/l and more prefers that of 0.1 ~ 2 g/l . If the concentration is less than 0.05 g/l, the phosphate-treating at low temperature is not attained, so that the calcium contents in the film become less than 0.5 weight % and then, the warm brine-resistance on the iron-based surface is not sufficiently elevated and the water-resisting, secondary adhesion on the zinc-based and zinc alloy-based surfaces is not sufficiently elevated. If the concentration exceeds 4 g/l, not only the elevation of effects reachs to the top resulting in an economical disadvantage, but also there is seen a decreasing trend of the warm brine-resistance on the iron-based surface with decresing quantity of the film. Besides, in said aqueous solution for treating with acidic phosphate, the weight ratio between the fluorine compound and the phosphate ion is set in a range of 0.05 ~ 2 which is calculated on a basis being converted into the orthophosphate ion (PO_4). If the weight ratio is less than 0.05, the calcium contents in the film become less than 0.5 weight % and thus, the warm brine-resistance on the iron-based surface is not sufficiently elevated as well as the water-resisting, secondary adhesion on the zinc-based and zinc alloy-based surfaces is not elevated. Also, if the weight ratio exceeds 2, the elevation of effects reachs to the top resulting in an economical disadvantage.

Said aqueous solution for treating with acidic phosphate prefers to contain, in case of necessity, a water-soluble tungsten compound in concentration of 0.005~ 20.0 g/l calculated on a basis being converted into the tungsten element and more prefers to contain the compound in concentration of 0.05 ~ 10 g/l. If the amount of the water-soluble tungsten compound is less than the above range, the effect on increase of the film weight quantity without deterioration of the film quality can not be obtained and, if the amount exceeds the above range, an sufficiently good effects are not obtained and instead, the amount of chemicals for use increases resulting in an economical disadvantage.

In said aqueous solution for treating with acidic zinc phosphate, as an accelerator for converting into a film, for example, at least one kind of agent selected from a nitrite ion, m-nitrobenzenesulfonate ion, and hydrogen peroxide is used. The nitrite ion prefers concentration of 0.01 ~ 0.2 g/l and more prefers that of 0.04 ~ 0.15 g/l. The m-nitrobenzenesulfonate ion prefers concentration of 0.05 ~ 2 g/l and more prefers that of 0.1 ~ 1.5 g/l. The hydrogen peroxide prefers concentration of 0.5 ~ 5 g/l, calculated on a basis being converted into 100 % H_2O_2, and more prefers that of 1 ~ 4 g/l. If these accelerators for converting into a film does not reach to the above concentration range, sufficient conversion into a film on the iron-based surface is not attained and instead, conversion into a yellow rust occurs and, if the agent exceeds the above concentration range, an ununiform film of blue color is apt to be formed on the iron-based surface.

As resources for said zinc ion, for example, zinc oxide, zinc carbonate, and zinc nitrate etc. are used. The phosphate ion is supplied from, for example, phosphoric acid, zinc phosphate, and calcium phosphate etc. The calcium ion is supplied from, for example, calcium carbonate, calcium nitrate, calcium chloride, and calcium phosphate etc. The nickel ion is supplied from, for example, nickel carbonate, nickel nitrate, nickel chloride, and nickel phosphate etc. The fluoro compound is supplied from, for example, hydrogen fluoride (hydrofluoric acid), fluoboric acid, fluosilic acid, and these metal salts (for example, a zinc salt and a nickel salt, but a sodium salt is excluded because an expected effect is not attained) and so on. The water-soluble tungsten compounds of suitable use are, for example, a tungstate such as sodium tungstate and ammonium tungstate, borotungstic acid, phosphotungstic acid, phosphotungstate, and in addition, particularly silicotungstic acid and silicotungstate.

Besides, said aqueous solution for treating with acidic phosphate may contain only the forementioned essential components, or besides the essential components, may contain, for example, a nitrate ion and a chlorate ion etc., respectively by alone or in combination of the two or more kinds. The nitrate ion prefers concentration of 1~ 10 g/l and more prefers that of 2 ~ 8 g/l. The chlorate ion prefers concentration of 0.05 ~ 2 g/l and more prefers that of 0.2 ~ 1.5 g/l. As resources for these components, for example, for the nitrate ion are used sodium nitrate, ammonium nitrate, zinc nitrate, and nickel nitrate etc., and for the chlorate ion are used sodium chlorate and ammonium chlorate etc.

The aqueous solution for treating with acidic phosphate of said composition is obtained by diluting with water the concenrated phosphate-treating agent relating to the present invention. The aqueous solution for treating with acidic phosphate used in the pre-treatment for electrocoating etc. is not generally marketed in a concentration adjusted for acutual use and, instead, has been arranged as a concentrated solution for preparing in use. The concentrated phosphate-treating solution should contain, for getting the treating solution of said composition by diluting 1 ~ 4 g of the concentrated phosphate-treating solution with 100 ml of water (1 ~ 4 w/v %), sufficient amounts of the zinc ion resources, phosphate ion resource, calcium ion resource, nickel ion resource, and fluorine compound resource and, in case of necessity, the water-soluble tungsten compound resource, but should not contain a sodium derivative and a manganese derivative. If the fluoride ion and sodium ion coexists, a problem of precipitate formation may take place when said treating solution is prepared. Also, no use of a manganese derivative is an important point. Besides, use of a sodium derivative is not completely prohibited, but in a case of that a sodium derivative (for example, sodium nitrite, sodium nitrate, sodium chlorate, and sodium tungstate etc.) is used, it is necessary to add it into the treating bath in form of a separated solution .

The concentrated treating agent for supplementary use relating to the present invention is used to supplement a lacking component when the component in the aqueous solution for treating with acidic phosphate is consumed during the pre-treatment for coating such as cationic electrocoating. That is, when said aqueous solution for treating with acidic phosphate is used on the pre-treatment for cationic electrocoating, all the components are not consumed in the same proportion, but a component is consumed in an one-sided manner. Because of this, a suplementation of the consumed component is carried out by adding the concentrated treating agent for suplementary use into said aqueous solution for treating with acidic phosphate. The concentrated treating agent for suplementary use is excemplified as the undermentioned A, A′, and B.

Method for preparing the concentrated treating agent for suplementary use A

To 28 weight parts (hereinafter simply referred to as 「 part 」) of water were added 45 parts of 75 % phosphoric acid, and 5 parts of 70 % nitric acid, and then 10 parts of zinc white (zinc oxide) were added and dissolved. Furthermore, 5 parts of calcium carbonate and 5 parts of nickel carbonate were added and dissolved, and after cooling, 2 parts of 40 % fluosilicic acid were added with good mixing, whereby 100 parts in total of the concentrated treating agent were obtained.

Method for preparing the concentrated treating agent for supplementary use A′

The method for preparing the concentrated treating agent for supplementary use A was repeated except that 27.9 parts of water and 0.1 part of silicotungstic acid were dissolved, whereby 100 parts in total of the concentrated treating agent A′ were obtained.

Method for preparing the concentrated treating agent for supplementary use B

To 60 parts of water were dissloved 35 parts of sodium nitrite and 5 parts of sodium chlorate to get 100 parts in total of the concentrated treating agent for supplementary use.

But the compositon of this concentrated treating agent for supplementary use and the method for preparing it are not limited within the forementioned examples.

Besides, the forementioned explanation is mainly given in accordance with the case of electrocoating, but the present invention is not limited to the electrocoating and can be used in the other kinds of coating.

By that calcium and nickel are contained in 0.5 ~ 8 weight % and 1.0 ~ 8 weight %, respectively, in the zinc phosphate film, the warm brine-resistance and scab-resistance on the iron-based surface are enhanced without use of manganese and also, the water-resisting, secondary adhesion on the zinc-based and zinc alloy-based surfaces are enhanced. In addition, the scab-resistance is elevated more than the case of manganese modification.

A zinc phosphate film modified with calcium and nickel is formed on a metal surface by that, as pre-treatment, dipping treatment of the metal surface is carried out in an aqueous solution for treating with acidic phosphate, which contains, as essential components, at least a zinc ion, a phosphate ion, a calcium ion, a nickel ion, and a fluorine compound as well as an accelerator for converting into a film and also, contains a zinc ion in concentration of 0.1~ 2 g/l, a phosphate ion in concentration of 5 ~ 40 g/l, a calcium ion in concentration of 0.5~ 4 g/l, a nickel ion in concentration of 0.5 ~ 4 g/l , and a fluorine compound in concentration of 0.05 ~ 4 g/l (on a basis being converted into a fluoride ion) in such proportion that their weight ratios are 0.5 ~ 4.0 between the calcium ion and the zinc ion, 1.0 ~ 4.0 between the nickel ion and the zinc ion, and 0.05 ~ 2.0 between the fluorine compound (as being converted into the fluoride ion) and the phosphate ion, and a coating film thus-formed by the low temperature treatment shows, as pre-treatment especially as pre-treatment in electrocoating, sufficient effects on the adhesion as well as the corrosion-resistance for a metal surface having both the iron-based and zinc-based surfaces at the same time. Besides, the use of manganese is unnecessary.

When the aqueous solution for treating with acidic phosphate further contains a water-soluble tungsten compound in concentration of 0.005 ~ 20.0 g/l (calculated on a basis being converted into the tungsten element), the film thickness can be increased without deterioration in quality of the zinc phosphate film and with enhancing properties of the film.

Hereinafter, concrete examples and examples for comparison in the present invention are shown, but the invention is not limited within the undermentioned examples.

Examples 1 ~ 9 anf examples for comparison 1 ~ 8

As metals for treatment, a hot dipped zinc alloy plated steel plate and a cold rolled steel plate were used.

Seventeen kinds of aqueous solutions for treating with acidic zinc phosphate having the composition shown in Table 1 were prepared.

Surfaces of said two kinds of metals for treating were treated at the same time according to the undermentioned processes.

(a) Degreasing → (b) water rinsing → (c) surface conditioning → (d) conversion (dipping treatment) → (e) water rinsing → (f) deionized-water rinsing → (g) drying → (h) electrocoating

(a) Degreasing :

Using an alkaline degreasing agent (Surf Cleaner SD 250, made by Nippon Paint Co., Ltd., 2 weight % humidity dipping treatment was carried out at 40 °C for 2 minutes.

(b) Water rinsing :

Using tap water, rinsing was carried out at room temperature for 15 seconds.

(c) Surface conditioning :

Using a surface-conditioning agent (Surf Fine 5N-5, made by Nippoon Paint Co., Ltd., 0.1 weight % concentration), dipping treatment was carried out at room temperature for 15 seconds.

(d) Conversion :

Using said aqueous solution for treating with acidic zinc phosphate, dipping treatment was carried out for 120 seconds at the temperature shown in Table 1.

(e) Water rinsing :

Using tap water, rinsing was carried out at room temperature for 15 seconds.

(f) Deionized-water rinsing :

Using deionized-water, rinsing was carried out at room temperature for 15 seconds.

(g) Drying :

Drying was carried out with hot air at 100 °C for 10 minutes.

Besides, for a converted plate thus-obtained, the film was dissolved by using a chromic acid solution, the weight of the dissolved film determined, and the amounts of zinc, calcium, nickel, and manganese in the film-dissolved solution were determined with an atomic absorption analysis method, and thus the contents of each metal in the film (weight %) were determined.

(h) Electrocoating :

A cationic electrocoating composition (Power Top U-1000 Grey, made by Nippon Paint Co., Ltd.) was coated so as to make a dry film of thickness 35 µm after baking (voltage 240 V, current-carrying capacity 0.16 coulombs/cm^2, electricity-applying time 3 minutes), and the surface was baked at 170 °C for 20 minutes.

A part of the electrocoated plates thus-obtained were used for the hot brine dipping test. The other remaining electrocoated plates were coated with an intermediate coating compositon (Orga TO 4811 Grey, made by Nippon Paint Co., Ltd., melamine-alkyd resin base) by spraying so as to make a dry film of thickness 30µm after baking, and the surfaces were baked at 140 °C for 20 minutes. Then, they were coated with a top coating composition (Orga TO 630 Dover White, made by Nippon Paint Co., Ltd., melamine-alkyd resin base) by spraying so as to make a dry film of thickness 30 µm after baking, and the surfaces were baked at 140 °C for 20 minutes, to obtain coated plates having in total the 3-coatings and 3-bakings, which were then subjected to the adhesion test and scab-corrosion test.

For the hot brine dipping test, cross cuts were made on the electrocoated plate, which was then dipped in a 5 % brine solution (55 °C) for 480 hours. An adhesive tape was applied on the cut portion and then peeled off. The maximum width of the coating film peeled was determined as a result from the dipping test.

For the adhesion test, the coated plate was dipped in deionized water at 40 °C for 20 days and provided with grids (100 squares each) which were made at 1 mm intervals and 2 mm intervals using a sharp cutter. To each surface of the plate thus-treated, an adhesive tape was applied, after which it was peeled off and the number of remaining coated squares on the coated plate was counted as the adhesive test result.

For the scab-corrosion test, cross cuts were made on the coated plate using a sharp cutter, which was then subjected to a 10 cycles' anti-corrosion test, each cycle consisting of a 5 % brine spraying test (JIS-Z-2371, 24 hours) → a humidity test (temperature 40 °C, relative humidity 85 %, 120 hours) → followed by standing in a room (24 hours). After the test, the maximum width of corroded portions such as a thread rust and a scab on the coated surface was determined as the scab-corrosion test result.

The results obtained are shown in Table 2.

Table 1 (Part 1/2)

		example 1	example for comparison 1	example for comparison 2	example for comparison 3	example for comparison 4	example 2	example 3	example 4
composition of aqueous solution for treating with acidic phosphate (g/l)	Zn	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.5
	Ca	1.0	1.0	1.0	0	0	2.0	1.0	2.0
	Ni	1.5	1.5	0	3.0	0	1.0	1.5	2.0
	Mn	0	0	0	0	1.5	0	0	0
	PO_4	14.0	14.0	14.0	14.0	14.0	14.0	14.0	20.0
	fluorine compound (converted into fluorine)	1.0 ※1	0	1.0 ※1	1.0 ※1	1.0 ※1	1.0 ※2	1.0 ※1	1.0 ※1
	NO_2	0.06	0.06	0.06	0.06	0.06	0.06	0	0.06
	H_2O_2	0	0	0	0	0	0	1.0	0
	NO_3	6.0	6.0	6.0	9.0	6.0	8.0	8.0	8.0
	ClO_3	0.7	0.7	0.7	0.7	0.7	0	0.7	0.7
	Cl	0	0	0	0	0	0	0	0
	tungsten compound (converted into tungsten)	0	0	0	0	0	0	0	0
	total acidity (point)	20.5	19.0	19.8	21.0	20.2	20.5	19.8	25.4
	free acidity (point)	0.9	0.8	0.9	1.0	0.9	0.9	0.9	1.0
	Ca/Zn (weight ratio)	1.0	1.0	1.0	0	0	2.0	1.0	1.3
	Ni/Zn (weight ratio)	1.5	1.5	0	3.0	0	1.0	1.5	1.3
	F/PO_4 (weight ratio)	0.07	0	0.07	0.07	0.07	0.07	0.07	0.05
temperature (℃)		40	40	40	40	40	40	40	40

(Note) ※1…SiF_4 ※2…BF_4 ※3… sodium tungstate ※4… silicotungstic acid
The F/PO_4 is a weight ratio between a fluorine compound calculated with converting into fluorine and a phosphate compound calculated with converting into orthophosphoric acid.

Table 1 (Part 2/2)

		example for comparison 5	example for comparison 6	example for comparison 7	example 5	example 6	example 7	example 8	example 9	example for comparison 8
composition of aqueous solution for treating with acidic phosphate (g/l)	Zn	0.92	2.0	1.0	1.0	1.0	1.0	1.0	1.0	0.7
	Ca	0.50	1.0	3.0	3.0	1.0	1.0	3.0	1.0	0.6
	Ni	1.33	1.5	1.5	1.5	3.0	1.5	1.5	3.0	0.3
	Mn	0	0	0	0	0	0	0	0	0
	PO_4	13.8	14.0	14.0	14.0	14.0	14.0	14.0	14.0	22.6
	fluorine compound (converted into fluorine)	0	1.0 ※1	0.5 ※1	1.0 ※1	1.0 ※1	1.0 ※1	1.0 ※1	1.0 ※1	0.5 ※1
	NO_2	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.1
	H_2O_2	0	0	0	0	0	0	0	0	0
	NO_3	7.9	8.0	8.0	8.0	8.0	6.0	8.0	8.0	2.7
	$C\ell O_3$	3.9	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0
	$C\ell$	1.8	0	0	0	0	0	0	0	0
	tungsten compound (converted into tungsten)	0	0	0	0	0	1.0 ※3	0.2 ※4	0.2 ※4	0
	total acidity (point)	15.0	21.0	21.5	21.5	21.0	20.6	21.5	21.1	31.2
	free acidity (point)	0.7	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.8
	Ca/Zn (weight ratio)	0.54	0.5	3.0	3.0	1.0	1.0	3.0	1.0	0.86
	Ni/Zn (weight ratio)	2.7	0.75	1.5	1.5	3.0	1.5	1.5	3.0	0.43
	F/PO_4 (weight ratio)	0	0.07	0.036	0.07	0.07	0.07	0.07	0.07	0.02
temperature (℃)		50	40	40	40	40	40	40	40	40

(Note) ※1…SiF_6 ※2…BF_4 ※3… sodium tungstate ※4… silicotungstic acid

The F/PO_4 is a weight ratio between a fluorine compound calculated with converting into fluorine and a phosphate compound calculated with converting into orthophosphoric acid.

Table 2 (Part 1/2)

material	item evaluated		example 1	example for comparison 1	example for comparison 2	example for comparison 3	example for comparison 4	example 2	example 3	example 4
hot dipped zinc alloy plated steel plate	weight of film (g/m²)		4.2	3.0	4.3	3.8	3.5	4.1	4.0	4.1
	zinc contents (weight %)		38.3	39.8	39.5	38.0	36.0	38.3	38.2	37.8
	calcium contents (weight %)		0.9	0.1	1.0	0	0	1.2	0.8	1.0
	nickel contents (weight %)		1.3	0.6	0	2.6	0	1.0	1.4	1.7
	manganese contents(weight %)		0	0	0	0	5.1	0	0	0
	water-resisting secondary adhesion	grids of 2 mm interval	100/100	30/100	45/100	100/100	100/100	100/100	100/100	100/100
		grids of 1 mm interval	100/100	0/100	8/100	80/100	100/100	100/100	100/100	100/100
cold rolled steel plate	weight of film (g/m²)		2.0	1.0	2.1	1.8	2.0	2.0	2.1	2.1
	zinc contents (weight %)		26.0	30.7	27.4	28.3	26.5	24.5	26.1	24.9
	calcium contents (weight %)		4.0	0.1	4.1	0	0	6.0	3.8	4.5
	nickel contents (weight %)		1.5	0.7	0	3.2	0	1.0	1.6	2.1
	manganese contents(weight %)		0	0	0	0	5.0	0	0	0
	warm brine-resistance (coming off) (mm)		1.0	13.0	1.5	10.5	3.5	1.0	1.0	1.0
	scab-resistance (rust · scab width) (mm)		3.0	15.0	6.5	2.9	10.5	3.3	2.9	2.9

Table 2 (Part 2/2)

material	item evaluated		example for comparison 5	example for comparison 6	example for comparison 7	example 5	example 6	example 7	example 8	example 9	example for comparison 8
hot dipped zinc alloy plated steel plate	weight of film (g/m²)		4.0	6.0	2.5	2.5	3.0	4.4	2.7	3.3	4.3
	zinc contents (weight %)		39.4	39.4	36.5	36.5	37.2	38.2	36.4	37.1	40.3
	calcium contents (weight %)		0.1	0.3	3.0	3.0	0.8	0.8	3.0	0.8	0.1
	nickel contents (weight %)		1.0	0.8	0.8	1.0	2.5	1.3	1.1	2.6	0.2
	manganese contents (weight %)		0	0	0	0	0	0	0	0	0
	water-resisting secondary adhesion	grids of 2 mm interval	45/100	100/100	100/100	100/100	100/100	100/100	100/100	100/100	10/100
		grids of 1 mm interval	8/100	80/100	80/100	100/100	100/100	100/100	100/100	100/100	0/100
cold rolled steel plate	weight of film (g/m²)		1.9	3.5	1.0	1.0	1.5	2.4	1.6	2.0	2.5
	zinc contents (weight %)		30.4	29.9	23.5	23.5	25.5	26.2	24.5	25.6	30.4
	calcium contents (weight %)		0.1	0.8	7.0	7.0	3.0	3.8	6.5	2.8	0.5
	nickel contents (weight %)		1.0	0.8	0.8	1.0	3.0	1.6	1.0	3.0	0.3
	manganese contents (weight %)		0	0	0	0	0	0	0	0	0
	warm brine-resistance (coming off) (mm)		9.0	4.0	5.0	5.0	4.5	1.0	3.0	1.0	9.0
	scab-resistance (rust · scab width) (mm)		5.5	6.0	6.0	5.0	3.0	2.9	3.3	2.9	12.0

As seen in Table 1 and Table 2, all the coating products in the examples 1 ~ 9, when compared with those in the examples for comparison 1 ~ 8, showed better quality in the water-resisting secondary adhesion on the zinc-based surface as well as in the warm brine-resistance and the scab-resistance on the iron-based surface. Especially, in the examples 7 ~ 9, since the weight of film on the cold rolled steel plate increased without deteriolation in quality of film and the warm brine-resistance was elevated, an effect of water-soluble tungsten compound is clear. Since those in the examples for comparison 1 and 5 do not contain a fluoro compound in the aqueous solution for treating with acidic zinc phosphate, the calcium contents in the film are considered to be low. Since the example for comparison 2 does not contain nickel, the water-resisting secondary adhesion and scab-resistance are especially inferior and, since the example for comparison 3 does not contain calcium, the warm brine-resistance is especially inferior. Since the example for comparison 4 does not use calcium and nickel, but manganese, the scab-resistance is inferior.

Since the example for comparison 6 shows in the treating solution a weight ratio between the nickel ion and zinc ion as lower than 1.0, the nickel contents in the film is less than 1.0 weight %, and, as a result, the water- resisting secondary adhesion on the zinc-based surface and the scab-resistance on the cold rolled steel plate are both bad. Since in the treating solution the example for comparison 8 shows a weight ratio between the nickel ion and zinc ion as lower than 1.0 and a weight ratio between the fluorine compound converted in to the fluorine element and the phosphate ion converted into the orthophosphoric acid as lower than 0.05, the nickel contents in the film is less than 1 weight %, and, as a result, the scab-resistance on the cold rolled steel plate is bad.

The alkali-resisting solubilities of zinc phosphate films on the conversion-treated plates in said example 1, and examples for comparison 3 and 4 are shown in Fig. 1. The curve 1 is for the example for comparison 3, the curve 2 for the example for comparison 4, and the curve 3 for the example 1. The conversion-treated plates were subjected to cationic electrocoating under a condition of three kinds of electric currents (boosted from 0 volt to a set voltage during 30 seconds and treated with currents of a set voltage of 220 V and a constant voltage of 260 and 290 V for 2.5 minutes) and the alkali-resisting solubilities were determined with variation of a corroding current value (Ic) for a conversion-treated plates in which a wet coating film that is before putting together by baking and hardening was dissolved in tetrahydrofuran. As the Ic value is smaller and smaller, the corroding is harder. The corroding current value (Ic) was determined under a condition of that an area in contact with the solution was 1 cm^2 and the electrolyte was a 3 weight % solution of sodium chloride of 20 °C. The cross axis indicates current-carrying capacity during cationic electrocoating. As seen in Fig. 1, the product from the example 1 hardly suffers coating film damage.

The coating product relating to the invention as claimed in claim 1 has a zinc phosphate film being formed as pre-treatment for coating which contains zinc in an amount of 20 ~ 42 weight %, calcium in an amount of 0.5 ~ 8 weight %, and nickel in an amount of 1.0 ~ 8 weight % and, thus, the scab-resistance on the iron-based surface and the warm brine-resistance on the iron-based and zinc-based surfaces are greatly improved, and further improvement of the secondary adhesion is shown when the electrocoating, intermediate coating, and top coating are performed on said film.

In the process for producing a coating product relating to the invention as claimed in claim 2, since the pre-treatment for coating is carried out by using an aqeous solution for treating with acidic phosphate of the above composition, the scab-resistance on the iron-based surface and the warm brine-resistance on the iron-based and zinc- based surfaces are greatly improved, and a zinc phosphate film, in which further improvement of the secondary adhesion is shown when the electrocoating, intermediate coating, and top coating are performed, can be formed by treatment at low temperature.

The concentrated phosphate treating agent relating to the invention as claimed in claim 3 is used, with proper dilution by water, for preparing the aqueous solution for treating with acidic phosphate, which is used for forming a zinc phosphate film modified with calcium and nickel with low temperature treatment.

The concentrated treating agent for supplementary use relating to the invention as claimed in claim 4 is used for adjusting the component in the aqueous solution for treating with acidic phosphate, which is used to form a zinc phosphate film modified with calcium and nickel.

When the aqueous solution for treating with acidic phosphate contains a water-soluble tungsten compound in concentration of 0.005 ~ 20 g/l which is calculated on a basis being converted into the tungsten element, the zinc phosphate film modified with calcium and nickel is able to increases the film weight without deterioration in quality of the film.

Claims

1. A coating product having a zinc phosphate film for coating on a metal surface and thereon a coating film, which said zinc phosphate film contains 20 ~ 42 weight % of zinc, 0.5 ~ 8 weight % of calcium, and 1.0 ~ 8 weight % of nickel.

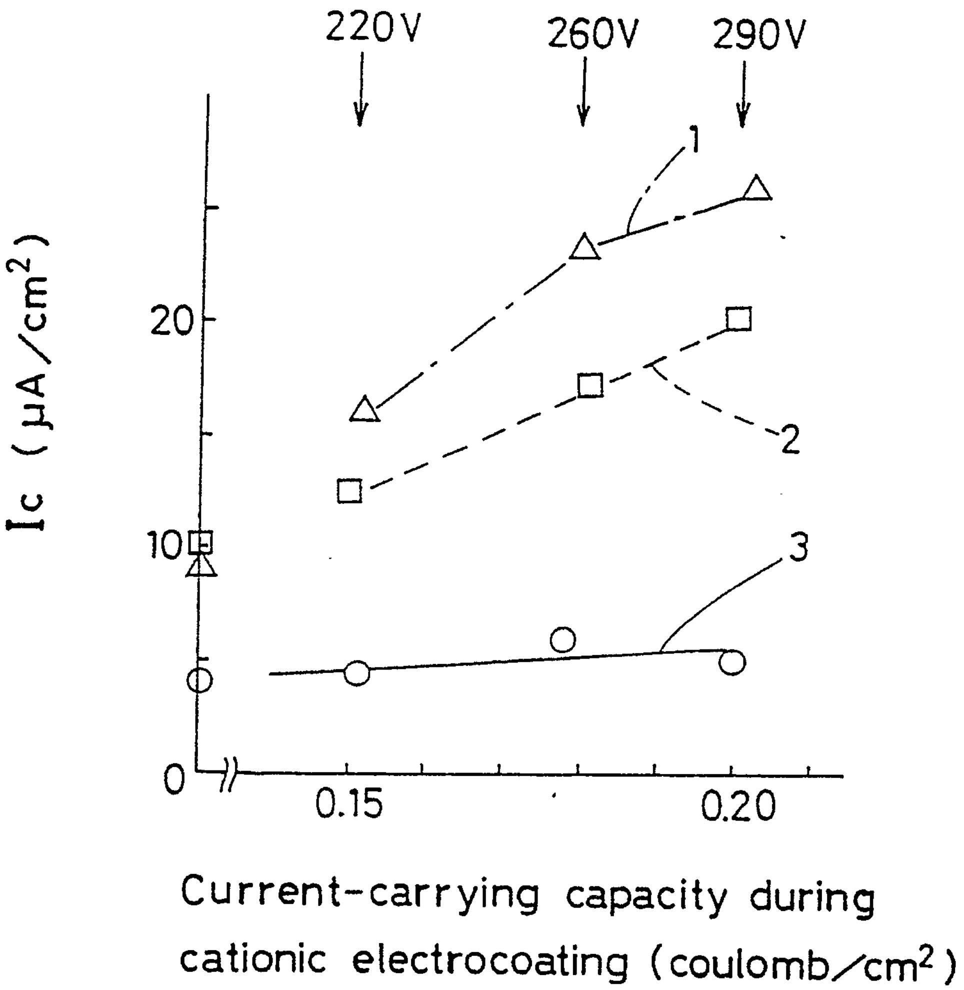
2. A process for producing a coating product which forms on a metal surface a zinc phosphate film modified with calcium and nickel, wherein formation of the film is carried out with, as pre-treatment for coating, dipping treatment of the metal surface in an aqueous solution for treating with acidic phosphate which contains at least a zinc ion in concentration of 0.1 ~ 2 g/l , a phosphate ion in concentration of 5 ~ 40 g/l, a calcium ion in concentration of 0.5 ~ 4 g/l, a nickel ion in concentration of 0.5 ~ 4 g/l, a fluorine compound in concentration of 0.05 ~ 4 g/l, which is calculated on a basis being converted into the fluoride ion, and an accelerator for converting into a film as the essential components, in such proportion of that the weight ratio between the calcium ion and zinc ion is 0.5~ 4.0, that between the nickel ion and zinc ion is 1.0 ~ 4.0, that between the fluorine compound (calculated on a basis being converted into the fluoride ion) and the phosphate ion is 0.05~ 2.0.

3. A concentrated phosphate-treating agent for leading, by diluting with water, to said aqueous solution for treating with acidic phosphate used for said process as claimed in claim 2.

4. A concentrated treating agent for supplementary use used to supplement a lacking component when the component in said aqueous solution for treating with acidic phosphate is consumed during said process as claimed in claim 2.

5. The process for producing a coating product as claimed in claim 2, the concentrated phosphate-treating agent as claimed in claim 3, or the concentrated treating agent for supplementary use wherein the aqueous acidic phosphate-treating solution contains a water-soluble tungsten compound in concentration of 0.005~ 20 g/l which is calculated on a basis being converted into the tungsten element.

Fig. 1


220V
260V
290V
1
2
3
Ic (μA/cm²)
20
10
0
0.15
0.20
Current-carrying capacity during cationic electrocoating (coulomb/cm²)

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 90 30 5186

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.5)
X	EP-A-0 018 841 (NIPPON PAINT CO.) * Claims 1,8,9,14,17,18; page 12, example 3 *	1,2	C 23 C 22/36 C 23 C 22/44
Y	* Page 12, example 3 *	3,5	
Y	EP-A-0 155 547 (GERHARD COLLARDIN GmbH) * Claims 1-4; page 8, line 33 - page 9, line 4 *	3	
Y	EP-A-0 015 020 (METALLGESELLSCHAFT AG) * Claims 1-3 *	5	
A	FR-A-1 391 804 (THE LUBRIZOL CORP.)		
A	EP-A-0 045 110 (METALLGESELLSCHAFT AG)		
A	FR-A-2 111 665 (THE LUBRIZOL CORP.)		

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

C 23 C 22/00

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	14-08-1990	TORFS F.M.G.

CATEGORY OF CITED DOCUMENTS

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

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

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P0401)