



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11) **EP 1 074 640 A1**

(12) **EUROPEAN PATENT APPLICATION**  
published in accordance with Art. 158(3) EPC

(43) Date of publication:  
**07.02.2001 Bulletin 2001/06**

(51) Int. Cl.<sup>7</sup>: **C25D 11/36**

(21) Application number: **99959898.0**

(86) International application number:  
**PCT/JP99/07124**

(22) Date of filing: **17.12.1999**

(87) International publication number:  
**WO 00/36191 (22.06.2000 Gazette 2000/25)**

(84) Designated Contracting States:  
**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU  
MC NL PT SE**

• **NISHIYA, Shin**  
**Denso Corporation**  
**Kariya-shi, Aichi 448-8661 (JP)**

(30) Priority: **17.12.1998 JP 35925498**

(71) Applicant: **Denso Corporation**  
**Kariya-shi, Aichi-ken, 448-8661 (JP)**

(74) Representative:  
**Klingseisen, Franz, Dipl.-Ing. et al**  
**Patentanwälte,**  
**Dr. F. Zumstein,**  
**Dipl.-Ing. F. Klingseisen,**  
**Postfach 10 15 61**  
**80089 München (DE)**

(72) Inventors:  
• **MATSUDA, Shigeki**  
**Denso Corporation**  
**Kariya-shi, Aichi 448-8661 (JP)**

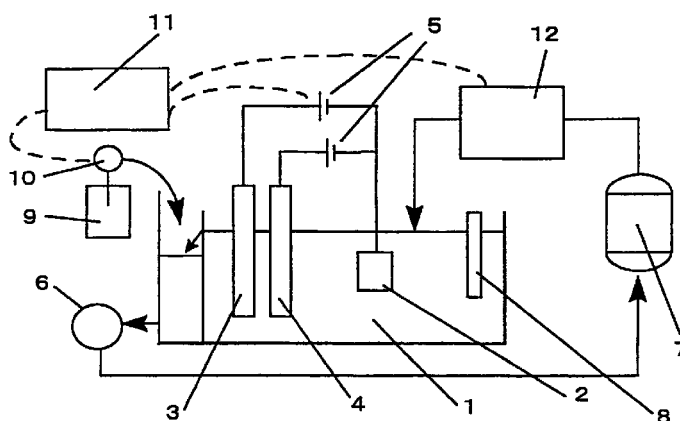
(54) **ELECTROLYTIC PHOSPHATING PROCESS AND COMPOSITE COATING FORMED ON STEEL SURFACE**

(57) The present invention provides a phosphate chemical treatment technology suitable for electrolytic treatment.

The present invention discloses a phosphate chemical treatment bath containing at least phosphate ions and phosphoric acid, nitrate ions, metal ions that form a complex with phosphate ions in the phosphate chemical treatment bath, and metal ions for which the electrical potential, at which the ions of the metal dissolved in the

phosphate chemical treatment bath are reduced and precipitate as metal, is equal to or greater than the anodic electrolytic reaction potential of water as the solvent; the concentration of metal ions other than those which are a component of the film in the treatment bath being 0-400 ppm, and the treatment bath being substantially free of solids that have an effect on the film formation reaction.

**Fig. 3**



**EP 1 074 640 A1**

**Description**

## TECHNICAL FIELD

- 5 **[0001]** The present invention relates to a method for carrying out a phosphate chemical treatment by electrolysis and a compound film formed on a steel surface.

## BACKGROUND ART

- 10 **[0002]** Japanese Unexamined Patent Publication (Saikohyo) No. 5-822481 describes an electrolytic treatment using a phosphate chemical treatment bath basically free of sludge and comprising phosphate ions, oxoacid ions containing nitrogen, and film component metal ions. This treatment bath is characterized by not allowing the formation of sludge at a pH of 2-4 and at a temperature of 40°C or less.

- 15 **[0003]** However, the phosphate chemical treatment bath of Japanese Unexamined Patent Publication (Saikohyo) No. 5-822481 uses sodium hydroxide and sodium nitrite for adjusting the pH or as accelerators that are unrelated to the film components.

**[0004]** Consequently, this method cannot be said to be an electrolytic phosphate chemical treatment method that efficiently forms a film.

- 20 **[0005]** Therefore, in consideration of the above problems, the present invention provides a phosphate chemical treatment method, that is able to efficiently form a film, and a compound film obtained by this method.

**[0006]** Prior to explaining the electrolytic phosphate chemical treatment method of the present invention, an explanation is first provided regarding the difference between "electrolytic treatment" and "non-electrolytic treatment" surface treatment technologies using aqueous solutions.

- 25 **[0007]** The difference can be clarified by discussing "plating", a wet surface treatment technology that is presently used widely.

**[0008]** Namely, there are both "electrolytic" and "non-electrolytic" methods of plating, and both methods are already used practically. However, the mechanisms of the treatment bath differ between "electrolytic" and "non-electrolytic" methods.

- 30 **[0009]** More specifically, in the case of "electroplating", the components in the solution do not react. The reaction is an electrochemical reaction that uses an external power supply for the reaction energy source. Furthermore, during "electroplating" treatment, chemicals (reducing agents) are not used for accelerating the electrolytic reaction chemically.

- 35 **[0010]** In contrast, in the case of non-electrolytic plating, the components in the solution react. In addition, instead of using an external power supply for the reaction energy source, the electrochemical reaction uses electrochemical energy (energy that forms a potential difference by a chemical reaction) formed during an oxidation reaction (anodic reaction) of a reducing agent (chemical substance having a small degree of dissociation of an aqueous solution) added to a solution and a reduction reaction (cathodic reaction) of a metal ion in solution.

**[0011]** "Plating" forms a metal film in a reduction reaction of a metal ion (cation), and phosphate chemical treatment forms a phosphate film in an oxidation reaction (dehydrogenation) of phosphate ion (anion).

40

## DISCLOSURE OF THE INVENTION

- 45 **[0012]** The inventor of the present invention considered that if electrolytic treatment and non-electrolytic treatment were possible in "plating", practical application of electrolytic treatment would be possible in addition to non-electrolytic phosphate chemical treatment of the prior art even in a phosphate chemical treatment which is the same wet surface treatment as in the plating, thereby leading to completion of the present invention.

**[0013]** The following provides an explanation of the concept of the present invention.

- 50 (1) Those items of electrolytic phosphate chemical treatment technology that were to be examined were determined by conducting a comparative study of the existing wet electrolytic surface treatment technology and the electrolytic phosphate chemical treatment technology based on an existing surface treatment technology.

(2) Preferable treatment conditions were discovered within the studied areas by studying the preferable state of the electrolytic phosphate chemical treatment reaction.

- 55 (3) The film formed by the proposed electrolytic phosphate chemical treatment method was studied.

[Existing Surface Treatment Technology]

**[0014]** Before explaining the contents of the present invention, an explanation is first provided regarding surface

treatment technology of the prior art. The technology of the electrolytic phosphate chemical treatment method of the present invention was investigated by correlating this surface treatment technology of the prior art with the electrolytic phosphate chemical treatment technology to be obtained.

**[0015]** The surface treatment technologies currently established practically, including the technology of the present invention, are classified in the manner indicated below.

**[0016]** A surface treatment technology is initially classified into a "dry surface treatment" or a "wet surface treatment". The surface treatment technology of this "wet surface treatment" is further classified into "non-electrolytic treatment" and "electrolytic treatment". Here, specific examples of surface treatment by "non-electrolytic treatment" include "non-electrolytic plating" and "non-electrolytic phosphate chemical treatment". In addition, specific examples of "electrolytic treatment" include "electroplating", "anodic oxidation" and "electrodeposition coating", and the "electrolytic phosphate chemical treatment" of the present invention belongs in the classification of "electroplating".

[Wet Surface Treatment (Discussion of Reaction Energy)]

**[0017]** As was mentioned above, wet surface treatment is classified into two types, namely "non-electrolytic treatment" and "electrolytic treatment".

**[0018]** The difference between "non-electrolytic treatment" and "electrolytic treatment" depends on the energy that promotes the reaction.

**[0019]** "Non-electrolytic treatment" is dependent on chemical energy of a chemical added to a treatment bath such as a reducing agent (plating) or an oxidizing agent (phosphate chemical treatment). In contrast, "electrolytic treatment" is dependent on electrical energy from an external power supply.

**[0020]** Consequently, in the case of "plating", the baths for "non-electrolytic plating" and "electrolytic plating" are basically different, and a "non-electrolytic plating" bath is not used for electrolytic treatment.

**[0021]** If this idea is applied to a phosphate chemical treatment method, the treatment methods during a "non-electrolytic treatment bath" and an "electrolytic treatment bath" should have contents that are basically different.

[Electrolytic Treatment in Wet Surface Treatment]

**[0022]** A schematic diagram of electrolytic treatment is shown in Fig. 1. Electrolytic treatment uses an external power supply, and is composed of three constituents broadly divided into a counter electrode, solution and article to be treated in the electrolysis tank.

**[0023]** The state in which these three constituents are involved in the electrolytic treatment reaction differs according to the type of wet electrolytic treatment. A summary of this is shown in Table 1.

Table 1

Classification of Wet Electrolytic Treatment (○: Reacts X: Does not react)					
		Counter electrode	Solution	Work piece (article to be treated)	Applied voltage level
Existing technology	Electroplating	○	X	X	10 V or more
	Anodic oxidation (aluminum materials)	X	○	○	Several tens of V or more
	Electrodeposition coating	X	○	X	100 V or more
Electrolytic phosphate chemical treatment		○	○	○	1-50 V

**[0024]** The following provides an explanation of the contents of Table 1.

**[0025]** In "electroplating", a plating film component in the form of an anode (counter electrode) (e.g., zinc electrode in the case of zinc plating) is dissolved by application of voltage or current, the dissolved plating film component passes through the solution in a complexed state, and precipitates at the cathode. For this reason, the only component that reacts is the counter electrode component that dissolves. The article to be treated is the cathode, and there is no reaction such as dissolution in the electrolysis tank.

**[0026]** In "anodic oxidation", an aluminum material in the form of an anode dissolves in the treatment bath, solvent

(water) and solute ions (anions) decompose accompanying the rise in voltage at that time, and oxygen ions ( $O^{2-}$ ) formed accompanying this decomposition and dissolved aluminum combine resulting in the formation of an aluminum oxide ( $Al_2O_3$ ) film on the surface of the aluminum material. A material that does not dissolve (react) during electrolysis is used for the counter electrode (cathode).

**[0027]** In "electrodeposition coating", voltage is applied to colloidal organic and inorganic substances dispersed in water, the colloidal substances are electrolyzed by electrophoresis or precipitation and so forth followed by precipitation on the electrode (article to be treated) surface and solidification (coated film). Namely, "electrodeposition coating" involves an electrolytic reaction of components in solution, and those which react due to application of voltage are only the water of the solvent and the colloidal contents dispersed in water. The electrodes (counter electrode and article to be treated) do not dissolve or react in any other manner.

**[0028]** In addition, it is important in "electrodeposition coating" that the solution state be maintained in a limited state (range).

**[0029]** If the solution state cannot be kept in a limited state due to changes (reactions) in solution components caused by coagulation or decomposition and so forth, it is impossible to form an effective electrodeposited coating film. Consequently, the electrodeposition coating bath is constantly maintained at a prescribed temperature and is subjected to ultrafiltration. Moreover, articles to be treated prior to electrolysis are placed in an electrolysis tank after washing with pure water to prevent entry of unnecessary ions (such as Na ions) from the previous step.

**[0030]** In contrast, the "electrolytic phosphate chemical treatment" of the present invention is completely different from the three technologies described above in that the three constituents of the "counter electrode", "solution" and "article to be treated" all dissolve and react. The reason why it was difficult to achieve practical application of this "electrolytic phosphate chemical treatment" in the prior art was because this difference was not recognized and it was therefore not possible to develop technology that accommodates this difference.

[Studied Items of Electrolytic Phosphate Chemical Treatment]

**[0031]** Table 2 identifies those items to be studied for the "electrolytic phosphate chemical treatment" in the present invention based on a study of the contents of various types of existing electrolytic treatment baths and phosphate chemical treatment baths.

Table 2

Comparison of Properties of Electrolytic Treatment Baths							
	Electrolytic treatment	Studied Items					
		Reaction of solution components that become film	Electrolyte tendency of bath	Bath pH control	Presence of unnecessary ions	Presence of reaction accelerator	Inorganic/organic distinction
Existing Electrolytic treatment	Electrolytic plating	No	Intermediate (complex)	No	Yes (Na <sup>+</sup> )	No	Inorganic ion reaction
	Anodic oxidation (aluminum material)	Yes (solvent)	Large (strong electrolyte bath)	Yes	No	No	Inorganic ion reaction
	Electrodeposition coating	Yes	Small (non-electrolyte bath)	Yes	No	No	Organic substance reaction

Table 2 (continued)

Comparison of Properties of Electrolytic Treatment Baths							
	Electrolytic treatment	Studied Items					
		Reaction of solution components that become film	Electrolyte tendency of bath	Bath pH control	Presence of unnecessary ions	Presence of reaction accelerator	Inorganic/organic distinction
Phosphate chemical treatment	Conventional electrolytic phosphate chemical treatment (prior art)	Yes	Small (accelerator added)	Yes	Yes (Na <sup>+</sup> )	Yes	Inorganic ion reaction
	Non-electrolytic phosphate chemical treatment (ref)	Yes	Small (weak electrolyte bath)	Yes	Yes (Na <sup>+</sup> )	Yes	Inorganic ion reaction
	Electrolytic phosphate chemical treatment (present invention)	Yes	Intermediate (complex)	Yes	No	No	Inorganic ion reaction

**[0032]** For items studied in relation to electrolytic treatment reaction control that are shared by "electrolytic plating", "anodic oxidation" and "electrodeposition coating", which are all existing forms of electrolytic treatment, the film formation reaction is carried out only on the surface of the article to be electrolyzed inside the electrolysis tank, and measures are taken to ensure that it is not carried out at other locations inside the electrolysis tank. Namely, although it is impossible to completely prevent reactions similar to the film formation reaction from occurring inside the electrolysis tank at locations other than on the surface of the article to be electrolyzed, measures are taken so that film formation on the surface of the article to be electrolyzed can be made practical.

**[0033]** From this viewpoint, the following provides an explanation of each studied item for each electrolytic treatment.

(1) Although "electroplating" involves dissolving the plated metal at an anode and then precipitating it at a cathode, the bonding of metal ions dissolved in the electrolysis tank is prevented. A complex is used as the means for preventing this bonding.

The treatment bath of "electroplating" is a complex bath of metal salts. The reason for this is to prevent bonding and precipitation of metal ions in solution (reaction of solute components in solution) while the plating metal is being dissolved from an electrode (anode) and precipitated on the cathode. A well-known example of a complex is cyano (CN) complex. The electroplating bath is normally not transparent, and although it may contain ions not involved in film formation such as Na ion, measures are taken so that the complex does not decompose in the treatment solution. As a result of these measures, only metal ions precipitate on the surface of the cathode allowing the formation of a plated film. (Since Na ions have a different precipitation potential than the plating metal ions, they do not precipitate on the cathode. This is in agreement with electrochemical principles.)

(2) "Anodic oxidation" involves electrolytic treatment using an article to be treated as the anode and an insoluble electrode as the cathode. If ions not required for the film formation reaction become involved at that time, there is an effect on both the dissolution reaction of the material (e.g., aluminum) and the oxidation (film formation) reaction. This is because dissolved aluminum ions are extremely active in the treatment bath. An anodic oxide film is formed by reacting dissolved aluminum ions with oxygen ions (O<sup>2-</sup>) formed by the decomposition of solvent in the form of

water. The contamination of the treatment solution by impurities is severely restricted to prevent the dissolved aluminum ions from reacting with other ions.

(3) "Electrodeposition coating" involves the formation of a coating film by electrolyzing a component in solution on an electrode surface. Only the solvent in the form of water and a colloidal organic substance dispersed in the water react due to application of a voltage. There is no reaction involving the dissolving of an electrode (counter electrode and article to be treated).

**[0034]** In the case of electrodeposition coating, it is important that the solution state be maintained in a prescribed state (range) that allows the formation of a satisfactory coating film. It is impossible to form an effective electrodeposited coating film if the solution state cannot be controlled due to changes (reaction) in the components in solution due to coagulation, decomposition and so forth. For this reason, the electrodeposition coating bath is maintained at a constant temperature at all times and is subjected to ultrafiltration to prevent self-coagulation of colloid components dispersed in the bath and to maintain a dispersed state.

**[0035]** In addition, the electrodeposition coating bath severely restricts contamination by inhibiting ions (e.g., Na ions), and is maintained in a state that approaches pure water. This is because the presence of inhibiting ions inhibits the precipitation reaction on the electrode surface.

**[0036]** The above technical findings obtained from the electrolytic treatment of the prior art can be summarized in the manner indicated below.

**[0037]** In the case of electrolytic treatment, it is necessary that components in solution that are involved in film formation are not allowed to react except on the electrode surface (interface), and it was found that the following measures are necessary to accomplish this.

- i: Prevention of contamination by impurities (anodic oxidation, electrodeposition coating)
- ii: Prevention of self-coagulation of components in solution by constant filtration, circulation and temperature maintenance, etc. (electrodeposition coating)
- iii: Utilization of complexes (electroplating)

**[0038]** It is believed that practical utilization of the "electrolytic phosphate chemical treatment method" in the present invention can be carried out by reflecting the above technical findings for that method. The above conclusion, "In the case of electrolytic treatment, components in solution that are involved in film formation must not be allowed to react except on the electrode surface" is a concept that is common to all forms of electrolytic surface treatment. However, the specific measures for accomplishing this vary according to each type of treatment.

**[0039]** The reason why the prior art was unable to achieve practical utilization of an efficient electrolytic phosphate chemical treatment method, which is the object of the present invention, is that specific measures could not be found to prevent components in solution, that are involved in film formation, reacting at locations other than the electrode surface.

#### [Electrolytic Phosphate Chemical Treatment Method of the Present Invention]

**[0040]** The "electrolytic phosphate chemical treatment method" of the present invention is able to embody not substantially allowing components in solution that are involved in film formation to react at locations other than the electrode surface even though electrolysis is performed.

**[0041]** In order to accomplish this, the present invention is a method of forming a film containing at least a phosphate and a metal that does not form the phosphate on the surface of an article to be treated having electrical conductivity by performing electrolytic treatment by contacting the article to be treated with a phosphate chemical treatment bath containing at least phosphate ions and phosphoric acid, nitrate ions, metal ions that form a complex with phosphate ions in the phosphate chemical treatment bath, and metal ions for which the electrical potential at which the ions dissolve in the phosphate chemical treatment bath is reduced and precipitates as metal, is equal to or greater than the anodic electrolysis reaction potential of the solvent in the form of water or equal to or greater than -0.83 V (indicated as the hydrogen standard electrode potential),

characterized by the phosphate chemical treatment bath having a concentration of metal ion other than the film component of 0-400 ppm and being substantially free of solids having an effect on the film formation reaction,

and the article to be treated being treated by electrolysis in the phosphate chemical treatment bath with a metal material that forms a complex with phosphate ions in the phosphate chemical treatment bath, and a metal material for which the electrical potential at which the ions thereof dissolved in the phosphate chemical treatment bath is reduced and precipitates as metal is equal to or greater than the anodic electrolysis reaction potential of the solvent in the form of water or equal to or greater than -0.83 V (indicated as the hydrogen standard electrode potential).

**[0042]** In particular, in the present invention, the film formation reaction can be carried out smoothly and efficiently on the surface of the article to be treated in the phosphate chemical treatment bath by minimizing reactions other than film formation in the bath as much as possible, by making the concentration of metal ions other than the film component in the phosphate chemical treatment bath 0-400 ppm, and by making the phosphate chemical treatment bath substantially free of solids having effect on the film formation reaction, and not adding an accelerator.

**[0043]** In particular, in the present invention, since the concentration of metal ions other than the film component in the phosphate chemical treatment bath is made to be 0-400 ppm and the phosphate chemical treatment bath is substantially free of solids having an effect on the film formation reaction, the film formation reaction can be carried out without being based primarily on the precipitation of phosphate from the bath, thereby being able to provide, for the first time, a film containing at least the phosphate and a metal that does not form phosphate on the surface of the article to be treated.

**[0044]** It is preferable that the phosphate chemical treatment bath contains 0-100 ppm of metal ions, other than components of the film at least containing phosphate, for film formation to be carried out efficiently.

**[0045]** A preferable example of a specific composition of the phosphate chemical treatment bath comprises a nitrate ion concentration of 6-140 g/l, a phosphate ion and phosphoric acid concentration of 0.5-60 g/l, a concentration of metal ions that form a complex with phosphate ion in the phosphate chemical treatment solution of 0.5-70 g/l, and a concentration of metal ions, in which the electrical potential resulting from ions dissolved in the phosphate chemical treatment solution being reduced and precipitating as metal is equal to or greater than the anodic electrolysis reaction potential of a solvent in the form of water or equal to or greater than -0.83 V (indicated as the hydrogen standard electrode potential), being 0-40 g/l.

**[0046]** It is preferable that the phosphate chemical treatment method does not use an acid having a degree of acid dissociation larger than the degree of acid dissociation of the phosphate ion.

**[0047]** Here, an example of an acid having a degree of acid dissociation larger than the degree of acid dissociation of phosphate ions is nitric acid.

**[0048]** If an acid having a larger degree of acid dissociation than the phosphate ions is added to the treatment bath, the film formation reaction of the phosphate on the surface of the article to be treated is inhibited in the treatment bath, thereby preventing the reaction from being carried out efficiently.

**[0049]** Metal ions that form a complex with the phosphate ions in the phosphate chemical treatment bath are preferably of at least one of metal selected from the group consisting of zinc, iron, manganese and calcium.

**[0050]** Metal ions for which the electrical potential, resulting from the ions dissolved in the phosphate chemical treatment solution being reduced and precipitating as metal, is equal to or greater than the anodic electrolysis reaction potential of the solvent in the form of water or equal to or greater than -0.83 V (indicated as the hydrogen standard electrode potential) are preferably at least metal ions selected from the group consisting of nickel ions and copper ions.

**[0051]** The present invention also provides an electrolytic phosphate chemical treatment method comprising a method of forming a film containing at least a phosphate on the surface of an electrically conductive article to be treated by contacting the article to be treated and electrolyzing it in a phosphate chemical treatment bath containing at least phosphate ions and phosphoric acid, nitrate ions and metal ions that form a complex with phosphate ions in the phosphate chemical treatment bath, wherein

the phosphate chemical treatment bath contains 0-400 ppm of metal ions, other than the component of the film, and is substantially free of solids having an effect on the film formation reaction and, the article to be treated being electrolyzed in the phosphate chemical treatment bath between metal materials that form a complex with phosphate ion in the phosphate chemical treatment bath.

**[0052]** In the case of employing this method, although the resulting film is a chemical film consisting primarily of phosphate, since 0-400 ppm of metal ions other than the components of the film are contained in the phosphate chemical treatment bath, and the phosphate chemical treatment bath is substantially free of solids having an effect on the film formation reaction, the film formation reaction in phosphate chemical treatment can be carried out efficiently.

**[0053]** It is more preferable that the concentration of metal ions other than components of the film containing at least the phosphate in the phosphate chemical treatment bath is 0-100 ppm.

**[0054]** The phosphate chemical treatment bath preferably has a nitrate ion concentration of 6-140 g/l, phosphate ion and phosphoric acid concentration of 0.5-60 g/l, and concentration of metal ion that forms a complex with phosphate ion in the phosphate chemical treatment bath of 0.5-70 g/l.

**[0055]** The phosphate chemical treatment bath preferably does not have an acid having a degree of acid dissociation larger than the degree of acid dissociation of the phosphate ions.

**[0056]** At this time, an example of an acid having a degree of acid dissociation larger than the degree of acid dissociation of the phosphate ions is nitric acid.

**[0057]** As a result of the phosphate chemical treatment bath not having an acid having a degree of acid dissociation

larger than the degree of acid dissociation of the phosphate ions, film formation can be carried out efficiently for the same reason as previously mentioned.

**[0058]** Furthermore, the metal ions that forms a complex with phosphate ions in the phosphate chemical treatment bath are preferably at least of one of metal ions selected from the group consisting of zinc ions, iron ions, manganese ions and calcium ions.

**[0059]** Electrolysis using the article to be treated as the anode may be performed in the phosphate chemical treatment method.

**[0060]** Electrolysis using the article to be treated as the cathode may also be performed in the phosphate chemical treatment method.

**[0061]** Electrolysis using the article to be treated as the anode followed by electrolysis using the article to be treated as the cathode may also preferably be performed in the phosphate chemical treatment method.

**[0062]** As a result of performing this electrolysis, a film formation reaction can be carried out on the surface of the article to be treated after exposing a fresh surface by etching the surface of the article to be treated. Consequently, a film can be obtained having improved adhesion with the surface of the article to be treated.

**[0063]** Cathodic electrolytic treatment, in which electrolytic treatment is performed using the article to be treated of the phosphate chemical treatment method as the cathode, is preferably an electrolytic phosphate chemical treatment method composed of at least one of either an electrolytic treatment in which a metal material identical to the metal for which ions dissolved in the phosphate chemical treatment bath is reduced and precipitated, and/or an electrically conductive material that is insoluble in the phosphate chemical treatment bath, is used for the anode, or an electrolytic treatment in which the metal material that forms a complex in the phosphate chemical treatment bath is used for the anode.

**[0064]** As a result of using this treatment method, the component ratio of phosphate that forms the film and the metal that does not form the phosphate can be suitably adjusted, thereby making it possible to form a film having the desired properties on the surface of the article to be treated.

**[0065]** Cathodic electrolytic treatment, in which electrolytic treatment is performed using the article to be treated of the phosphate chemical treatment method as the cathode, is preferably an electrolytic phosphate chemical treatment method composed of one cycle of treatment consisting of performing electrolytic treatment in which a metal material identical to the metal to which ions dissolved in the phosphate chemical treatment bath are reduced and precipitated, and/or an electrically conductive material, that is insoluble in the phosphate chemical treatment bath, is used for the anode, followed by performing electrolysis in which the metal material that forms a complex in the phosphate chemical treatment bath is used for the anode, and performing this cycle at least once.

**[0066]** As a result of using this treatment method, a thick film can be formed having the desired properties as previously described.

**[0067]** Cathodic electrolytic treatment, in which electrolytic treatment is performed using the article to be treated of the phosphate chemical treatment method as the cathode, is preferably an electrolytic phosphate chemical treatment method comprising performing electrolytic treatment by separating an electrolysis tank in which electrolytic treatment is performed, in which a metal material identical to the metal for which ion dissolved in the phosphate chemical treatment bath is reduced and precipitated, and/or an electrically conductive material that is insoluble in the phosphate chemical treatment bath, is used for the anode, and an electrolysis tank in which electrolytic treatment is performed, in which the metal material that forms a complex in the phosphate chemical treatment bath is used for the anode.

**[0068]** As a result of using this treatment method, providing separate electrolysis tanks makes it possible to independently control the respective component precipitation reactions, thereby making it even easier to form a film having the desired properties.

**[0069]** Furthermore, the metal material identical to the metal for which metal dissolved in the phosphate chemical treatment bath is reduced and precipitated is preferably at least one of metal selected from the group consisting of nickel and copper.

**[0070]** The metal material that forms a complex in the phosphate chemical treatment bath is preferably at least one of metal selected from the group consisting of zinc, iron, manganese and calcium.

**[0071]** If the article to be treated is not contacted with the phosphate chemical treatment bath, it is preferable that the metal material used as the anode, during electrolytic treatment in which the article to be treated is used for the cathode, is used as the cathode, a material insoluble in the phosphate chemical treatment bath is used as the anode, and a voltage of 5 V or less is applied between the anode and cathode.

**[0072]** If the article to be treated is not contacted with the phosphate chemical treatment bath, it is preferable that the metal material used as the anode, during electrolytic treatment in which the article to be treated is used for the cathode, is used as the cathode, a material insoluble in the phosphate chemical treatment bath is used as the anode, and a voltage, at which the cathode substantially does not dissolve, is applied between the anode and cathode.

**[0073]** In this manner, by implementing measures when the article to be treated is not contacted with the phosphate chemical treatment bath, dissolution of the metal material can be inhibited when not treating the article to be treated.



**[0074]** It is preferable to remove a portion of the phosphate chemical treatment bath from a bath tank having the phosphate chemical treatment bath, to thermodynamically stabilize the energy state of the portion as a liquid, of the phosphate chemical treatment bath, and to later return it to the bath tank.

**[0075]** It is preferable to remove a portion of the phosphate chemical treatment bath from a bath tank having the phosphate chemical treatment bath, and remove the solids that precipitated during phosphate chemical treatment during the course of the film formation reaction, followed by returning it to the bath tank.

**[0076]** As a result of using this method, for example, unavoidably formed reaction products (sludge) and nitrides (such as  $\text{NO}_2$ ) formed by reduction of nitrate ion other than on the surface of the article to be treated by the electrolysis reaction can be removed from the treatment bath. Consequently, superfluous reactions other than the reaction for film formation can be inhibited in the treatment bath.

**[0077]** When replenishing components of the phosphate chemical treatment bath, it is preferable to remove a portion of the phosphate chemical treatment bath, and add replenishing liquid containing treatment bath components at a concentration higher than the concentration of at least one component among the components that compose the phosphate chemical treatment bath with respect to the bath that has been removed.

**[0078]** Replenishment of the treatment bath can be performed easily according to this method.

**[0079]** The present invention provides an electrolytic phosphate chemical treatment method for electrolytic treatment using an article to be treated as the cathode comprising a reaction in which a metal, for which the electrical potential at which ions dissolved in a phosphate chemical treatment bath are reduced and precipitate as the metal, is equal to or greater than the anodic electrolysis reaction potential of a solvent in the form of water or equal to or greater than  $-0.83\text{ V}$  (indicated as the hydrogen standard electrode potential), is dissolved in the phosphate chemical treatment bath, is reduced by electrolytic treatment from a cationic state and precipitates on the surface of the article to be treated, and a reaction in which a metal ion that complexes with phosphate ions in the phosphate chemical treatment bath precipitates as phosphate crystal corresponding to dehydrogenation of the phosphate ions.

**[0080]** According to this treatment method, since two different reactions can be carried out simultaneously in the treatment bath, a desired compound film can be formed on the surface of the article to be treated.

**[0081]** Furthermore, metal ions that complex with phosphate ions are preferably at least of one metal selected from the group consisting of Fe, Zn, Mn, Ca and Mg.

**[0082]** The metal for which the electrical potential at which ions dissolved in the phosphate chemical treatment bath is reduced and precipitates as metal is equal to or greater than the anodic electrolysis reaction potential of the solvent in the form of water or greater than or equal to  $-0.83\text{ V}$  (indicated as the hydrogen standard electrode potential), is preferably at least of one metal selected from the group consisting of Ni, Cu, Fe and Zn.

**[0083]** It is preferable that the composition of the treatment bath, when performing electrolytic treatment, be such that the ratio of the concentration of metal ions that complex with phosphate ions (g/l) to the concentration of phosphate ions and phosphoric acid (g/l) be 0.1 or more.

**[0084]** By making the ratio of the concentration of metal ions that complex with phosphate ions (g/l) to the concentration of phosphate ions and phosphoric acid (g/l) 0.1 or more, and more preferably 0.25 or more, phosphoric acid ( $\text{H}_3\text{PO}_4$ ) is able to exist in the form of phosphate ions ( $\text{H}_2\text{PO}_4^-$ ) in the treatment bath, thereby making it possible to inhibit the oxidation reaction of phosphate ions on the cathode surface. In addition, this also controls the phosphoric acid present in the treatment bath.

**[0085]** During the electrolytic phosphate chemical treatment in which electrolytic treatment is performed using the article to be treated as the cathode, when starting the electrolytic treatment, it is preferable to vary the voltage applied between the metal materials that form the anode and cathode.

**[0086]** Moreover, it is preferable that the variation in the applied voltage during the start of electrolytic treatment be in the form of pulses. As a result of using this method, even if a film starts to be formed at only a specific location on the article to be treated during the initial stage of film formation on the surface of the article to be treated, the location where the film is formed can be forcibly changed each time the electrolytic treatment voltage changes. Consequently, a film can be formed uniformly on the surface of the article to be treated.

**[0087]** The present invention provides a compound film composed of a metal that does not form a phosphate and a phosphate compound on a steel surface, wherein the metal and phosphate compound that compose the film are dispersed throughout the film.

**[0088]** The present invention provides a compound film composed of a metal that does not form a phosphate and a phosphate compound on a steel surface, wherein at least the metal that does not form a phosphate is present on the uppermost surface of the film.

**[0089]** The present invention provides a compound film composed of a metal that does not form a phosphate and a phosphate compound on a steel surface, wherein the film does not exhibit peaks other than the inevitable peak of phosphate in X-ray diffraction analysis.

**[0090]** The present invention provides a compound film composed of a metal that does not form a phosphate and a phosphate compound on a steel surface, wherein the number of atoms of the metal that does not form a phosphate

is at least 0.25 the number of phosphorus atoms that compose the phosphate crystal.

**[0091]** The metal that does not form a phosphate is preferably at least one of metal selected from the group consisting of Ni, Cu, Fe and Zn.

**[0092]** In addition, the metal that forms a phosphate compound is preferably at least one of metal selected from the group consisting of Fe, Zn, Mn, Ca and Mg.

**[0093]** The steel preferably contains at least 95 wt% iron (Fe) when the whole steel is taken to be 100 wt%.

**[0094]** The X-ray diffraction analysis is preferably performed by ESCA or EDX analysis.

#### BRIEF DESCRIPTION OF THE DRAWINGS

**[0095]**

Fig. 1 is a schematic drawing showing an overview of electrolytic treatment.

Fig. 2 is an outline drawing of an electrolytic reaction system.

Fig. 3 is a block diagram showing the composition of an electrolytic phosphate chemical treatment apparatus.

Fig. 4 is a perspective view of an article to be treated of Example 1 and Comparative Example 1.

Fig. 5 is an EDX analysis chart of the flat portion of the article to be treated in Example 1.

Fig. 6 is an EDX analysis chart of the outer peripheral portion of the article to be treated in Example 1.

Fig. 7 is an EDX analysis chart of the flat portion of the article to be treated in Comparative Example 1.

Fig. 8 is an EDX analysis chart of the outer peripheral portion of the article to be treated in Comparative Example 1.

Fig. 9 is a GDS analysis chart of the flat portion of the article to be treated in Example 1.

Fig. 10 is a GDS analysis chart of the outer peripheral portion of the article to be treated in Example 1.

Fig. 11 is a GDS analysis chart of the flat portion of the article to be treated in Comparative Example 1.

Fig. 12 is a GDS analysis chart of the outer peripheral portion of the article to be treated in Comparative Example 1.

Fig. 13 is a perspective view of the article to be treated of Example 2 and Comparative Example 2.

Fig. 14 is an EDX analysis chart of the flat portion of the article to be treated in Example 2.

Fig. 15 is an EDX analysis chart of the flat portion of the article to be treated in Comparative Example 2.

Fig. 16 is an EDX analysis chart of the flat portion of the article to be treated in Example 3.

Fig. 17 is an EDX analysis chart of the outer peripheral portion of the article to be treated in Example 3.

Fig. 18 is an EDX analysis chart of the flat portion of the article to be treated in Comparative Example 1.

Fig. 19 is an EDX analysis chart of the outer peripheral portion of the article to be treated in Comparative Example 1.

Fig. 20 is an SEM micrograph of the flat portion of the article to be treated in Example 3.

Fig. 21 is an analytical photograph of phosphorus of the flat portion of the article to be treated in Example 3.

Fig. 22 is an analytical photograph of zinc of the flat portion of the article to be treated in Example 3.

Fig. 23 is an analytical photograph of nickel of the flat portion of the article to be treated in Example 3.

Fig. 24 is an analytical photograph of iron of the flat portion of the article to be treated in Example 3.

Fig. 25 is an SEM micrograph of the outer peripheral portion of the article to be treated in Example 3.

Fig. 26 is an analytical photograph of phosphorus of the outer peripheral portion of the article to be treated in Example 3.

Fig. 27 is an analytical photograph of zinc of the outer peripheral portion of the article to be treated in Example 3.

Fig. 28 is an analytical photograph of nickel of the outer peripheral portion of the article to be treated in Example 3.

Fig. 29 is an analytical photograph of iron of the outer peripheral portion of the article to be treated in Example 3.

**[0096]** Next, a more detailed explanation is provided of the action and effect described above while making a comparative study of the prior art.

**[0097]** To begin with, according to Japanese Unexamined Patent Publication (Saikohyo) No. 5-822481, which describes an electrolytic phosphate chemical treatment method of the prior art, components of a phosphate chemical treatment bath having the same composition as non-electrolytic phosphate chemical treatment were used.

**[0098]** Namely, in non-electrolytic phosphate chemical treatment of the prior art, the treatment bath is extremely active and the bath composition is easily decomposed in order to form a film by reacting the components in the treatment bath. This is because the reaction in the bath solution cannot occur unless the treatment bath is active. In order to activate the treatment bath, namely, in order to chemically decompose (oxidize: dehydrogenate) the phosphoric acid, measures were taken in which sodium hydroxide and so forth are added to the non-electrolytic phosphate chemical treatment bath of the prior art to adjust the pH (hydrogen ion concentration) to within the prescribed range, or nitrite ions were added as an oxidation accelerator to accelerate the reaction. As a result of adding these chemicals, phosphate chemical treatment contains a large amount of Na ions, and as a result, the non-electrolytic phosphate chemical treatment bath contains large amounts of impurities (unnecessary substances) that do not form a phosphate film.

**[0099]** The electrolytic phosphate chemical treatment method of the prior art used such a phosphate chemical treatment bath that contains components other than film components.

**[0100]** Consequently, these components other than film components inhibit the formation of the phosphate chemical treatment film to be formed on the surface of the article to be treated, thereby preventing the formation of an efficient film on the surface of the treated portion.

**[0101]** In contrast, the phosphate chemical treatment bath of the present invention is composed so that the concentration of ions, such as Na ions, not involved in the film formation reaction, which are metal ions other than the film components, in the phosphate chemical treatment bath, is 400 ppm or less, and preferably 100 ppm or less. As a result, the stability of the treatment bath as a solution is improved considerably resulting in a composition that does not form a sludge. Moreover, a composition can be employed in which only the components in solution are allowed to react on the electrode surface as a result of electrolytic treatment, while the treatment bath only reacts on the electrode surface during electrolytic treatment, and reactions are substantially prevented from taking place at other times and other locations.

**[0102]** Moreover, it is preferable to employ the following means as a means for ensuring that the reaction only takes place on the electrode surface during electrolytic treatment in the treatment bath, while reactions substantially do not take place at other times and at other locations.

**[0103]** Namely, as an example of such a means, it is preferable to remove a portion of the phosphate chemical treatment bath from a bath tank having the phosphate chemical treatment bath to thermodynamically stabilize the energy state of the portion of the phosphate chemical treatment bath as a liquid and then return it to the bath tank, and remove a portion of the phosphate chemical treatment bath from a bath tank having the phosphate chemical treatment bath, pass it through a filter for removing solids precipitated during phosphate chemical treatment in film formation reaction process, and return it to the bath tank.

**[0104]** In addition, in the case the article to be treated is not in contact with the phosphate chemical treatment bath, it is preferable to apply a voltage of 5 V or less between the anode and cathode while using for the cathode the metal material used as an anode during electrolytic treatment in which the article to be treated was used for the cathode, and using for the anode a material that is insoluble in the phosphate chemical treatment bath, and if the article to be treated is not in contact with the phosphate chemical treatment bath, it is preferable to apply a voltage between the anode and cathode so that the cathode does not substantially dissolve, using for the cathode the metal material used as anode during electrolytic treatment using the article to be treated for the cathode, and using for the anode a material that is insoluble in the phosphate chemical treatment bath.

**[0105]** Moreover, when replenishing components of the phosphate chemical treatment bath, it is preferable to remove a portion of the phosphate chemical treatment bath and add replenishing liquid containing treatment bath components at concentrations at least one of which is higher than the concentration of the component of the components that compose the phosphate chemical treatment bath relative to the removed bath liquid to the portion removed from the electrolysis tank.

**[0106]** In addition, it is preferable that the composition of the treatment bath when performing electrolytic treatment is such that the ratio of the concentration of metal ions that complex with phosphate ions (g/l) to the concentration of phosphate ions and phosphoric acid (g/l) is 0.1 or more.

**[0107]** As a result of performing the above measures, the phosphate chemical treatment bath is substantially free of solids that have an effect on the film formation reaction, and the reaction only takes place on the electrode surface during electrolytic treatment, while reactions substantially do not take place at other times and at other locations.

**[0108]** Furthermore, similar to the "electrolytic phosphate chemical treatment method" of the present invention, although "electrodeposition coating", in which a film is formed by reacting components in a solution, requires the utmost care to prevent coagulation and decomposition of the components in solution, since the solution is organic, this can be accommodated by preventing contamination by impurities, constantly filtering and maintaining the treatment bath at a prescribed temperature.

**[0109]** Since the "electrolytic phosphate chemical treatment method" of the present invention involves electrolysis in an inorganic acid solution, it is preferable to make the accommodations described above in addition to the measures of electrodeposition coating.

**[0110]** Moreover, since the present invention is substantially free of metal ions other than metal ions that compose a component of film formation such as Na as in the prior art, metal ions that form a complex with phosphate ions in the phosphate chemical treatment bath are able to exist in the phosphate chemical treatment bath as a complex. Consequently, even though metal ions are dissolved in solution, they exist in a stable form in the treatment bath, making it possible to inhibit phenomena such as the formation of sludge in the treatment bath and to induce the film precipitation reaction only on the surface of the article to be treated.

**[0111]** This is equivalent to the cyano complex frequently being used in electroplating of the prior art, in that this cyano complex does not decompose in the solution, but rather only decomposes on the surface of the cathode where the charge is concentrated and precipitates in the form of a metal film.

**[0112]** In addition, complexes have been used in the past even in non-electrolytic phosphate chemical treatment

baths of the prior art. Namely, metal ions (such as  $\text{Fe}^{3+}$ ,  $\text{Zn}^{2+}$  or  $\text{Mn}^{2+}$ ) that precipitate as a phosphate compound on a metal surface are dissolved in solution by forming a complex with phosphate ions. However, since the phosphate ion complex used in non-electrolytic phosphate chemical treatment baths of the prior art contained ions such as Na ions resulting in an active (unstable) state, the stability of the complex is low in comparison with a cyano complex and so forth used in electrolytic plating. Thus, even in the case of non-electrolytic treatment, the complex is easily dissolved and forms a film and sludge, and the treatment does not use the present invention in any way.

**[0113]** Furthermore, with respect to complex stability, a cyano complex is stable and, in the case of non-electrolytic treatment (non-electrolytic plating), the complex is not dissociated (decomposed). For this reason, a cyano complex is only used in electrolytic plating.

**[0114]** If the stability of a phosphate ion complex could be increased, that complex would not decompose easily. The reason why the stability of phosphate ion complex used in non-electrolytic phosphate chemical treatment baths of the prior art is low is because the pH of the bath is adjusted (and Na ions and so forth are added for that purpose) resulting in phosphate ions being dissociated (decomposed by oxidation) easily. In electrolytic phosphate chemical treatment baths, pH adjustment of the bath is not performed by addition of  $\text{Na}^+$ . For this reason, the stability of the phosphate ion complex can be increased. In the case of a treatment bath in which the stability of the phosphate ion complex is large, there is no decomposition and a film is not formed in the absence of electrolysis. In addition, during electrolysis, since there is no decomposition of the phosphate ion complex in solution as in electroplating and a film is formed as a result of the phosphate ion complex decomposing only on the cathode surface where the charge is concentrated, there is basically no formation of sludge, and the treatment bath is maintained in a transparent state.

**[0115]** If the phosphate ion complex is excessively stable, it is unsuitable for film formation by cathodic electrolysis. For this reason, it is necessary to maintain the stability of the phosphate ion complex within a suitable range.

**[0116]** In order to achieve this in the present invention, it is preferable that the treatment bath composition when electrolytic treatment is performed be such that the ratio of the concentration of metal ions that complex with phosphate ions (g/l) to the ratio of the concentration of phosphate ions and phosphoric acid (g/l) is 0.1 or more. As a result, the stability of the complex can be secured.

#### [Study of Characteristics of Electrolytic Phosphate Chemical Treatment]

**[0117]** In addition to purification methods such as prevention of contamination by impurities and bath filtration as well as the measures taken regarding the complex, it is also necessary to employ measures for accommodating the unique characteristics of an electrolytic phosphate chemical treatment in order to use this electrolytic phosphate chemical treatment practically.

**[0118]** The following provides an explanation of these unique characteristics.

**[0119]** In the electrolytic phosphate chemical treatment of the present invention, it is preferable that the above phosphate chemical treatment method comprises performing electrolytic treatment using the above article to be treated for the anode followed by electrolytic treatment using the article to be treated for the cathode.

**[0120]** In this case, it is preferable that a film forming metal (such as Fe, Ni or Zn) be used for the anode, and the article to be treated be used for the cathode.

**[0121]** Furthermore, there are the two cases indicated below in which a metal material is installed in the electrolysis tank as an anode.

(1) A metal for which the electrode material dissolves to become a film forming component

(2) An insoluble material for which the electrode material does not dissolve or only slightly dissolves

**[0122]** The cathodic electrolytic treatment uses both the above electrode materials or only uses one of the electrode materials. A summary of their classification is shown in Table 3.

Table 3

Classification of Cathodic Electrolytic Treatment			
Type of anode material	Cathodic electrolysis voltage	Description	
(1) Metal materials that dissolve and precipitate easily and become a film component	Small	Metals that form phosphate compounds	Fe, Zn
		Metals for which metal ions dissolved in solution are reduced and precipitate as metal elements that dissolve easily and can be precipitated	Cu
(2) Materials that are only slightly soluble or insoluble	Large	Materials having a high dissolution voltage that do not form phosphates.	Ni and other insoluble materials

**[0123]** In the case of (1) in which a metal that dissolves and becomes a film component is used for the anode, the anode material dissolves electrochemically by the action of an external power supply and after being present in an ionic state dissolved in solution, precipitates (solidifies) on the cathode to form a film.

**[0124]** In the case of (2) in which an insoluble material that does not dissolve or only slightly dissolves is used for the anode, cations dissolved in solution are acted on by an external power supply and precipitate on the cathode. These cases are used according to the properties of the phosphate chemical film to be formed.

**[0125]** As described in Table 3, "metals that form phosphate compounds (such as Fe and Zn)" dissolve and precipitate relatively easily (at low voltages) even under conditions of phosphate chemical treatment baths of the prior art as has been demonstrated in the non-electrolytic treatment. However, metals that become "solids for which metal ions dissolved in a phosphate chemical treatment bath are reduced and precipitate as metal elements" include metals that easily dissolve and precipitate under conditions of non-electrolytic phosphate chemical treatment baths of the prior art (for example, Cu), as well as metals that require a large voltage and current to dissolve and precipitate (for example, Ni).

**[0126]** If a metal requiring a large voltage and current to dissolve and precipitate (for example, Ni) is precipitated by supplying it to a treatment bath only by dissolving it from an electrode serving as the anode, a large voltage and current is required. This electrolytic treatment results in a relatively large voltage and current being applied to the entire treatment bath. However, this type of electrolytic treatment (requiring a large voltage and current) cannot be said to be suitable for electrolysis of metals (Fe and Zn) that can be electrolyzed by applying a low voltage and form phosphate compounds.

**[0127]** The inventor of the present invention recognized that there is basically two systems for "cathodic electrolytic treatment" as characteristics of electrolytic phosphate chemical treatment. The inventor of the present invention also thought that these two cathodic electrolytic treatment systems should be used appropriately by recognizing the differences between these two systems according to the required properties of the film. Namely, the composition of the treatment bath and the metal material used for the anode are determined according to the required film, and electrolytic treatment (voltage and current) is used appropriately corresponding to that treatment bath and electrode material.

**[0128]** Recognition of the fact that cathodic electrolytic treatment can be basically divided into two systems suggests that it is necessary to accommodate two different systems for practical application of electrolytic phosphate chemical treatment. Namely, different accommodations are required in the case of using "a metal material that dissolves and precipitates easily and becomes a film component" and "a material that is only slightly soluble or insoluble".

**[0129]** In the case of using "metal materials that dissolve and precipitate easily and become film components (such as Fe, Zn or Cu)" of Table 3 for the anode, those metals dissolve easily in the phosphate chemical treatment bath even if voltage is not applied (even in the absence of electrolysis). If this phenomenon (action) is left undisturbed, these metal ions dissolve in the treatment bath even when treatment is not performed. As a result, the state of the treatment bath ends up changing to a state that does not allow treatment to be performed. Consequently, there is a need to provide a means for inhibiting that dissolution. This is the first accommodation to be made.

**[0130]** It is preferable to take the following measures as specific examples of measures to be taken as means for inhibiting dissolution:

(1) controlling the surface area of the metal electrode (anode) during electrolytic treatment,  
 (2) controlling the electrolysis current of the metal electrode (anode) during electrolytic treatment, and  
 (3) performing weak electrolysis (dormant electrolysis) to a degree that the metal used for the cathode does not dissolve (to a degree that the solution components do not decompose) while using an insoluble electrode for the anode and a metal electrode that dissolves easily (Fe, Zn, Cu) for the cathode, when electrolysis is dormant, with this electrolysis to be referred to as "dormant electrolysis".

**[0131]** The second accommodation is made with respect to the case of using "a material that is only slightly soluble or insoluble".

**[0132]** For example, although required as a film component, in the case of a metal (such as Ni) for which sufficient dissolution cannot be obtained even if electrolyzed using a metal for the anode, it is impossible to obtain all of the metal ions required for the film components by dissolving from the electrode. In this case, the supply of metal ions to the treatment bath is preferably performed by adding dissolved metal ions to the treatment bath. Cathodic electrolytic treatment is targeted only at the electrolytic reaction (reduction and precipitation) at the cathode. If this is done, the electrolysis voltage for incorporating, for example, Ni into the film components can be reduced in comparison with the case of assuming film formation by dissolving Ni from the anode. This type of contrivance is preferable for practical application of electrolytic phosphate chemical treatment.

[Reactions Composing Electrolytic Phosphate Chemical Treatment]

**[0133]** The present invention forms a novel electrochemical phosphate chemical treatment reaction as a result of providing an environment for carrying out electrolytic phosphate chemical treatment reactions. The following provides an explanation of a summary of this.

[General Perception of Electrochemical Reactions]

**[0134]** The electrolytic phosphate chemical treatment reaction of the present is basically free of sludge.

**[0135]** Electrochemical reaction systems are composed of an anodic reaction and cathodic reaction. The anodic reaction is an oxidation reaction that takes place at the anode. In addition, the cathodic reaction is a reduction reaction that takes place at the cathode. In an electrochemical reaction system, the electrode potential is defined so that the potential of the cathodic reaction is higher than that of the anodic reaction.

**[0136]** In addition, if the anode undergoes an anodic reaction, then the corresponding solvent and anion are believed to undergo a cathodic reaction. If a cation undergoes a cathodic reaction, then the corresponding solvent and anion are believed to undergo an anodic reaction.

**[0137]** A summary of the electrochemical reaction system formed in electrolytic treatment is shown in Fig. 2.

**[0138]** As shown in Fig. 2, the electrochemical reaction system is divided into (1) "reaction system between electrodes separated in a solution" and (2) "reaction system on the surfaces of identical electrodes not separated in a solution".

**[0139]** The "reaction system between electrodes separated in a solution" of (1) forms an anode-cathode reaction system between the separated electrodes. A breakdown of this reaction system is given below.

(1)-1 Electrochemical reaction system involving cations between electrodes (anodic reaction at the anode and cathodic reaction at the cathode)

(1)-2 Electrochemical reaction system involving anion and solvent between electrodes (cathodic reaction at the anode and anodic reaction at the cathode)

**[0140]** The "reaction system on the surface of identical electrodes not separated in a solution" of (2) forms an anode-cathode reaction system among cations, and anions and solvent on the surfaces of identical electrodes. A breakdown of this reaction system is indicated below.

(2)-1 Anodic reaction of cations, and cathodic reaction of anions and solvent, on the anode surface

(2)-2 Cathodic reaction of cations, and anodic reaction of anions and solvent, on the cathode surface

**[0141]** Electrochemical reaction systems composed of a cathodic reaction and anodic reaction are formed in cases in which an electrochemical reaction system is formed regardless of "non-electrolytic treatment" or "electrolytic treatment". However, electrochemical reaction systems of "non-electrolytic treatment" are composed only of cathodic and anodic reactions on the same surface. In Fig. 2, these are the reactions of (2)-1 and (2)-2, and are composed between a metal (solid) and solution (liquid).

[0142] There are cases in which electrochemical reaction systems are composed only of one pair of cathodic and anodic reactions, and cases in which electrochemical reaction systems are composed multiple pairs of cathodic and anodic reactions. As shown in Fig. 2, the electrochemical reaction system of phosphate chemical treatment is a complex system composed of multiple pairs of cathodic and anodic reactions. This complexity makes it difficult to control the reaction system.

[Composition of the Electrochemical Reaction System in Electrolytic Phosphate Chemical Treatment]

[0143] In the case of the "cathodic electrolytic treatment" of electrolytic phosphate chemical treatment, when Fe, Zn, Ni or Cu is used for the film-forming metal electrode (anode), the reactions are organized as shown in Table 4. Furthermore, in the following example, iron (steel material) is treated with a phosphate chemical treatment bath containing zinc ion, nickel ion, phosphate ion and nitrate ion (phosphate chemical treatment bath).

Table 4 Classification of Electrolytic Phosphate Chemical Treatment Reactions (Cathodic Treatment)

	Anodic Reactions	Cathodic Reactions
Anode Surface	1. Dissolution (oxidation) reaction of metal electrode (Fe, Zn, Ni, Cu, etc.) $\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e} \text{ (-0.44 V) (1)}$ $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e} \text{ (-0.23 V) (2)}$ $\text{Ni} \rightarrow \text{Ni}^{2+} + 2\text{e} \text{ (-0.23 V) (3)}$ $\text{Cu} \rightarrow \text{Cu}^+ + \text{e} \text{ (0.52 V) (4)}$ $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{e} \text{ (0.77 V) (5)}$	1. Reduction reaction of nitrate ion system $(\text{NO}_3^- \rightarrow \text{NO}_2^- \rightarrow \text{NO})$ $\text{NO}_3^- + 3\text{H}^+ + 2\text{e} \rightarrow \text{HNO}_2 + \text{H}_2\text{O} \text{ (0.94 V) (6)}$ $\text{NO}_3^- + 4\text{H}^+ + 3\text{e} \rightarrow \text{NO} + 2\text{H}_2\text{O} \text{ (0.96 V) (7)}$ $\text{NO}_3^- + 2\text{H}^+ + 2\text{e} \rightarrow \text{NO}_2^- + \text{H}_2\text{O} \text{ (0.84 V) (8)}$ 2. Reduction reaction of water (solvent) $\text{O}_2 + 4\text{H}^+ + 4\text{e} \rightarrow 2\text{H}_2\text{O} \text{ (1.23 V) (18)}$
Cathode Surface (Surface of Article to be Treated)	1. Oxidation reaction of phosphate ion system $(\text{H}_3\text{PO}_4 \rightarrow \text{H}_2\text{PO}_4^- \rightarrow \text{PO}_4^{3-})$ $\text{H}_3\text{PO}_4 \rightarrow \text{H}^+ + \text{H}_2\text{PO}_4^- \text{ (9)}$ $\text{H}_2\text{PO}_4^- \rightarrow 2\text{H}^+ + \text{PO}_4^{3-} \text{ (10)}$ 2. Crystallization reaction in which the charge of phosphorylation when metal ions bond with phosphate ions does not change (Zn, Fe, Mn, Ca ion, etc.) $2\text{PO}_4^{3-} + 2\text{Zn}^{2+} + \text{Fe}^{2+} \rightarrow \underline{\text{Zn}_2\text{Fe}(\text{PO}_4)_2} \text{ (11)}$ $\text{M}^{x+} \text{ (metal ions) } + n(\text{PO}_4^{3-}) \rightarrow \underline{\text{M}(\text{PO}_4)_n} \text{ (12)}$ 3. Oxidation reaction of water (solvent) $\text{H}_2 + 2\text{OH}^- \rightarrow 2\text{H}_2\text{O} + 2\text{e} \text{ (-0.83 V) (19)}$	1. Reduction reaction of metal ions accompanying change in charge (reduction of Ni, Cu, (Fe, Zn) etc. ions) $\text{Ni}^{2+} + 2\text{e} \rightarrow \underline{\text{Ni}} \text{ (-0.23 V) (13)}$ $\text{Cu}^+ + \text{e} \rightarrow \underline{\text{Cu}} \text{ (0.52 V) (14)}$ $\text{Fe}^{2+} + 2\text{e} \rightarrow \underline{\text{Fe}} \text{ (-0.44 V) (15)}$ $\text{Zn}^{2+} + 2\text{e} \rightarrow \underline{\text{Zn}} \text{ (-0.77 V) (16)}$ $\text{Fe}^{3+} + \text{e} \rightarrow \text{Fe}^{2+} \text{ (0.77 V) (17)}$ Note: Underlined portions indicated film components.

[0144] As was previously mentioned, the electrochemical interelectrode reaction mediated by an external power supply basically consists of two systems. The first is the reaction system between the electrodes consisting of a dissolution reaction of the film forming metal (electrode) at the anode (cathodic reaction), and a precipitation reaction of dis-

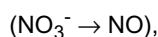
solved metal ion on the surface of the cathode (article to be treated) (cathodic reaction). The other reaction system is an electrochemical reaction system on the surface of the same electrodes. This consists of a dissolution (oxidation) reaction of metal at the anode and a reduction reaction of the solution components (nitrate ion and water), and an oxidation reaction of solution components (phosphate ions and water) and a reduction reaction of metal ions at the cathode. Furthermore, metal (such as Zn, Fe or Mn) ions that forms a phosphate complex accompanying oxidation (dehydrogenation) of phosphate ions on the surface of the cathode precipitates on the surface of the cathode as a phosphate.

[Electrochemical Reactions of the Phosphate Chemical Treatment Reaction - 1 (Non-Electrolytic Treatment Reaction)]

**[0145]** Non-electrolytic phosphate chemical treatment reactions are carried out such that the anodic and cathodic reactions in the above table are carried out on the same surface without polarization into an anode and a cathode.

**[0146]** The reason why non-electrolytic phosphate chemical treatment is primarily targeted only at steel materials is because an environment is created so that the electrochemical reaction system is spontaneously formed even in the absence of electrolysis between the phosphate chemical treatment bath and treatment bath.

**[0147]** Furthermore, chlorine ions ( $\text{Cl}^-$ ) are added when the article to be treated is copper (Cu). In addition, fluorine ions ( $\text{F}^-$ ) are added in the case the article to be treated is aluminum (Al). When fluorine ions ( $\text{F}^-$ ) are added, it becomes easy to dissolve (oxidize) the Al and, inside the treatment bath (even in the absence of electrolysis), an electrochemical reaction system is formed relating to phosphate chemical treatment. Consequently, a phosphate chemical film is formed in the same manner as steel. However, fluorine ions ( $\text{F}^-$ ) are not incorporated into the film nor are they reduced in the manner of nitrate ions



vaporized (gassified) or removed from the solution. Thus, it is necessary to prepare a fresh treatment bath when fluorine ions have exceeded the prescribed concentration.

**[0148]** Since an electrochemical reaction system is formed on the same surface in the case of a non-electrolytic phosphate chemical treatment reaction, dissolution of material (article to be treated) is limited by film formation. For this reason, the thickness of the film cannot be increased without destroying the film. In order to obtain a thick film, since excessive continuation of the reaction causes the reaction to be accompanied by dissolution of the material (article to be treated), a rough film results. This is the reason why thick films formed by a non-electrolytic treatment (heated bath), and used for cold forging press working lubrication substrate treatment, are rough.

**[0149]** In addition, since non-electrolytic phosphate chemical treatment reactions are electrochemical reaction systems on the same surface that do not use an external power supply, reduction and precipitation reactions of metal ions accompanying a change in charge are severely limited. Consequently, even in a treatment bath containing Ni ions, reduction and precipitation of Ni is only extremely slight. (Precipitation of Ni is only possible in the initial stage of film formation when Fe dissolves.) Therefore, the film that is formed is composed mainly of phosphate. This is the basis for referring to conventional non-electrolytic treatment as phosphate chemical treatment.

[Electrochemical Reactions of the Phosphate Chemical Treatment Reaction - 2 (Anodic Electrolytic Treatment)]

**[0150]** If a film is formed only in anodic electrolytic treatment in electrolytic phosphate chemical treatment, the reaction system is basically the same as non-electrolytic treatment. The function of anodic treatment is to promote the "dissolution (oxidation) reaction of the metal electrode" of Table 4. The "dissolution (oxidation) reaction of the metal electrode" is the first reaction that initiates the phosphate chemical treatment (film formation) reaction system. That reaction (dissolution of the article to be treated) is carried out easily and reliably by anodic electrolytic treatment. As a result, the phosphate film that is formed has excellent adhesion with the article to be treated (material). However, it is not possible to increase the thickness of the film.

**[0151]** In the case of forming a film by performing cathodic electrolytic treatment subsequent to anodic electrolytic treatment, the role of the anode is limited to the dissolution (oxidation) reaction of the metal electrode and the reduction reaction of water. In anodic electrolytic treatment, dissolution of the article to be treated is carried out reliably, and the film is formed in the following cathodic electrolytic treatment.

**[0152]** For this reason, in the case of forming a film by anodic electrolytic treatment only, the composition of the treatment bath differs from the case of forming a film by a combination of anodic electrolytic treatment and cathodic electrolytic treatment.

**[0153]** Furthermore, in the case of performing anodic electrolytic treatment only, a material is selected for the cathode serving as the opposing electrode that does not dissolve in the phosphate chemical treatment bath. For this reason, a material such as titanium that does not dissolve in the chemical treatment bath is used for the cathode.



## [Electrochemical Reactions of the Phosphate Chemical Treatment Reaction - 3 (Cathodic Treatment)]

**[0154]** A method combining anodic treatment and cathodic treatment is employed for electrolytic phosphate chemical treatment. In this case, the function of anodic treatment is to dissolve the surface of the article to be treated and ensure adhesion of the film. The cathodic treatment performs formation of the film.

**[0155]** Furthermore, anodic treatment can be omitted depending on the particular case. It can be omitted when, in the case of not requiring a tight adhesion of the film, and in the case the material tends to dissolve even in the absence of electrolysis because the pH of the electrolytic phosphate chemical treatment bath is lower than a conventional non-electrolytic treatment bath, the dissolution reaction of the material is carried out even in the absence of electrolysis.

**[0156]** In conventional non-electrolytic phosphate chemical treatment, the "dissolution reaction of the article to be treated" and the "reaction relating to film formation" take place on the same surface. However, in the cathodic electrolytic treatment of the present invention, the "dissolution reaction of the article to be treated" does not take place on the surface of the article to be treated serving as the cathode as shown in Table 3. Only the "reaction relating to film formation" takes place on the surface of the article to be treated (cathode).

**[0157]** There are three reaction systems for the electrochemical reaction system involved in cathodic electrolytic treatment according to the classification described in Fig. 2. These are as follows:

i. Oxidation-reduction (dissolution-precipitation) reaction system of metal ions between the electrodes (anode and cathode) ((1)-1 in Fig. 2)

ii. Oxidation-reduction reaction system of anions and solvent (water) between the electrodes (anode and cathode) ((2)-2 in Fig. 2)

iii. Anodic reaction of anions and solvent (water) and cathodic reaction of metal ion on the surface of the cathode ((2)-2 and (1)-3 in Fig. 2)

**[0158]** The following provides explanations of each of these reaction systems.

i. Oxidation-reduction (dissolution-precipitation) reaction system of metal ions between the electrodes (anode and cathode) ((1)-1 in Fig. 2) This interelectrode reaction is formed from a cathodic reaction on the surface of the cathode (reduction and precipitation of metal ion) and an anodic reaction on the surface of the anode (dissolution of metal). This reaction is an electrolytic reaction that uses an external power supply. Since the surface of the cathode is subjected to large electrochemical energy in terms of the cathodic reaction, a precipitation reaction can be carried out accompanying a change in charge (reduction). The cathodic precipitation reaction is a precipitation reaction accompanied by a change in charge (reduction) of a metal ion such as nickel, copper, iron or zinc, and causes the metal ion to bond to the substrate metal using an action similar to electroplating. Furthermore, although metals for which phosphates of iron or zinc and so forth form the film precipitate preferentially as phosphate unaccompanied by a change in charge, the dissolution and precipitation potential accompanying a change in charge is greater than or equal to the anodic reaction potential of water (-0.83 V), and allows precipitation as metal by changing the charge.

ii. Oxidation-reduction reaction system of anions and solvent (water) between the electrodes (anode and cathode) ((1)-2 and (2)-3 in Fig. 2)

This interelectrode reaction is formed from an anodic reaction on the surface of the cathode (dissociation and oxidation of phosphate ion, and formation of phosphate and oxidation of solvent (water)), and a cathodic reaction on the surface of the anode (reduction of nitrate ion and reduction of solvent (water)). As a result of the formation of this electrochemical reaction system, the resulting phosphate crystals are securely bound electrochemically to the surface of the cathode.

iii. Anodic reaction of anions and solvent (water) and cathodic reaction of metal ion on the surface of the cathode ((2)-2 in Fig. 2)

**[0159]** This reaction system is formed between an oxidation reaction of water (anodic reaction of formula (19)), and a cathodic precipitation reaction (formulas (13), (14), (15) and (16)) accompanied by a change in charge (reduction) on the surface of the cathode. As a result of the formation of this reaction system, it is possible to directly precipitate a metal for which the electrical potential, at which ions dissolved in the phosphate chemical treatment bath are reduced and precipitate as metal (dissolution-precipitation equilibrium potential), is roughly equal to or greater than -0.83 V, the anodic reaction potential of water (hydrogen standard electrode potential). As was previously stated, in electrochemical reaction systems, the electrical potential of the cathodic reaction is defined as being higher than that of the anodic reaction. Thus, as a result of forming this reaction system, it is guaranteed that it is possible to precipitate metal ions having a dissolution-precipitation equilibrium potential greater to or equal to that of zinc (dissolution-precipitation equilibrium potential (hydrogen standard electrode potential) = -0.77 V). Namely, metals that can be precipitated in are determined.

**[0160]** Metals having a low dissolution-precipitation equilibrium potential such as sodium (dissolution-precipitation equilibrium potential (hydrogen standard electrode potential) = -2.7 V) and potassium (dissolution-precipitation equilibrium potential (hydrogen standard electrode potential) = -2.9 V) cannot be precipitated by electrolysis and do not form a film. For this reason, these metal ions hinder electrolytic treatment film formation.

5 **[0161]** Furthermore, Zn, Fe and so forth can theoretically be precipitated by changing their charge as metals. However, Zn, Fe and so forth typically exist in the treatment bath by forming a complex with phosphate ions. Precipitation as a phosphate is also more favorable in terms of energy. For this reason, Zn, Fe and so forth preferentially exist as phosphates in the film.

10 **[0162]** In the cathodic electrolytic treatment of the present invention, together with making the metal ions other than components of the above film about 0-400 ppm, and preferably 0-100 ppm or less, since this treatment is substantially free of solids having an effect on the film formation reaction, metals that do not form phosphates can be incorporated in the compound film, making it possible for the compound film itself to approach the properties of conventional "plating". Consequently, the phosphate chemical film that is formed receives a high level of electrochemical energy, enabling it to be securely adhered and fixed on the cathode (article to be treated).

15 **[0163]** In the present invention, the oxidation-reduction (dissolution-precipitation) reaction system of metal ions between the electrodes (anode-cathode) is formed continuously by connecting an external power supply. For this reason, Ni and other metals can be reduced and precipitated and then distributed during the entire film formation process. In addition, it is also possible to contain only a specific metal or not contain certain metals. Namely, the cathode treatment film formation reaction can be controlled.

20

#### [Characteristics of Electrolytic Phosphate Chemical Treatment Films]

**[0164]** It is particularly noteworthy in the present invention that precipitation of metal accompanying a change in charge is possible throughout the entire duration of film formation. This is the same phenomenon as "electroplating".

25 **[0165]** Namely, the electrolytic phosphate film can be said to be a "phosphate-containing compound electroplated film". In other words, a film can be formed on the uppermost surface of the phosphate chemical film in which the ratio of the atomic number density is such that metal that does not form a phosphate (e.g., Ni) is contained in a greater amount than 1/4 the phosphorus (P) that serves as the element that forms the phosphate. (Refer to the results of EDX film analysis of Table 10 and Example 1, and the results of EDX film analysis of Table 16, Example 4 and Example 5.)  
30 This film is a film that cannot be realized with conventional non-electrolytic treatment in which a film is formed by utilizing the crystallization action of phosphate.

**[0166]** (The ratio of atomic number density Ni/P = 1/4 corresponds to the fact that  $\text{Ni/Zn}_3(\text{PO}_4)_2$  is present in a ratio of 1/2.)

35 **[0167]** Furthermore, as a result of not performing cathodic electrolytic treatment of the metal accompanying a change in charge, precipitation of metal accompanying a change in charge can be completely eliminated in the same manner as non-electrolytic treatment. (Refer to the results of EDX film analysis of Table 12 and Example 2.)

**[0168]** Moreover, another characteristic of the electrolytic phosphate chemical treatment film of the present invention is that, when the film is analyzed with X-rays, a film is found to be formed that does not have a peak corresponding to phosphate crystals. (Refer to Example 3 in Table 16, Fig. 16 and Fig. 17.) This is also possible because precipitation of metal (e.g., Ni) accompanying a change in charge is able to occur throughout the entire duration of film formation. Namely, this is thought to be the result of precipitation of phosphate crystals being subordinate to precipitation of metal (e.g., Ni) accompanying a change in charge, and the phosphate crystals being finely dispersed in the metal component. Although the film of Example 3 contains phosphorus (P) and Zn and is a film that contains phosphate, phosphate crystals are dispersed with Ni metal. This is shown in the EPMA elementary analysis photographs (Table 17, Figs. 20-29) taken in the cross-sectional direction of the film. This film can be referred to as a "phosphate-containing compound electroplated film".

45 **[0169]** As has been described above, in the present invention, an electrolytic phosphate chemical treatment was developed that is suitable for the general principle of electrochemical reactions.

**[0170]** Namely, the present invention is able to provide a phosphate chemical treatment method for forming a phosphate chemical film that is able to form a film composed of phosphate and metal from a film consisting primarily of phosphate crystals of the prior art.

**[0171]** Moreover, a compound film obtained with the present invention is able to contain a metal material that is not a phosphate.

55 **[0172]** Thus, this novel phosphate chemical treatment allows the obtaining of compound films that can be adapted to numerous metal materials in the same manner by which electroplating is adapted regardless of the type of metal.

## BEST MODE FOR CARRYING OUT THE INVENTION

## [Configuration of Electrolytic Phosphate Chemical Treatment]

5 **[0173]** Electrolytic phosphate chemical treatment is composed of (1) an apparatus, (2) treatment bath composition, (3) treatment bath electrochemical conditions, and (4) an electrolysis method.

**[0174]** To begin with, an explanation is provided of the apparatus used for the present electrolytic phosphate chemical treatment method using Fig. 3.

**[0175]** Fig. 3 shows the composition during cathodic electrolytic treatment.

10 **[0176]** Here, 1 is the phosphate chemical treatment bath of the present invention, 2 is the article to be treated, 3 and 4 are working electrodes, with 3 being a working electrode comprised of a metal material that forms a complex with phosphate in the phosphate chemical treatment bath with the phosphate chemical treatment bath, and 4 being a working electrode comprised of a metal material for which the electrical potential at which ions dissolved in the phosphate chemical treatment bath are reduced and precipitate as metal is equal to or greater than the anodic electrolytic reaction potential of water as the solvent or greater than or equal to -0.83 V (indicated as the hydrogen standard electrode potential).

**[0177]** In addition, 5 is a power supply that applies a voltage between the article to be treated 2 and working electrodes 3 and 4, 6 is a filtration/circulation pump for removing a portion of phosphate chemical treatment bath 1 from inside the bath tank containing phosphate chemical treatment bath 1 and thermodynamically stabilizing the energy state as liquid of phosphate chemical treatment bath 1, and 7 is a filter that removes solids that have precipitated in phosphate chemical treatment bath 1 during the course of the film formation reaction.

**[0178]** 8 is a dormant electrolytic anode comprised of an inert material with respect to the phosphate chemical treatment bath used when the article to be treated does not make contact with the phosphate chemical treatment bath, 9 is a replenishing chemical having a higher concentration than the concentration of components of phosphate chemical treatment bath 1, and 10 is a chemical replenishment pump for adding replenishing chemical to the treatment bath.

25 **[0179]** 11 is a control computer for controlling the amount of replenishing chemical added, the applied voltage and so forth based on information from sensor 12 that measures the pH, the ORP and other parameters of the treatment bath.

**[0180]** The following provides an explanation of the present invention based on Fig. 3.

30 **[0181]** In the present invention, the article to be treated (article to be treated) is connected to the cathode by means of a direct current power supply, and the electrode composed of metal that forms a phosphate film or a conducting material that is insoluble in the bath (to be referred to as a working electrode) is connected to the anode. Furthermore, during anodic electrolytic treatment, the article to be treated is connected to the anode and the conducting material insoluble in the bath is connected to the cathode.

35 **[0182]** There is only one of working electrode (counter electrode) in the case of anodic electrolytic treatment.

**[0183]** Although there are cases in which there is only one of working electrode in the case of cathodic electrolytic treatment, multiple types (materials) may also be used as electrodes. In addition, it is preferable to install a direct current power supply used for electrolysis for each working electrode. This is to prevent occurrence of the phenomenon in which a large amount of current flows to the electrode arranged in a location where current flows easily while current does not flow to the electrode arranged in a location where current does not easily in the case of connecting a plurality of the same type of electrodes to a single direct current power supply.

40 **[0184]** The dormant electrolytic electrode is installed in the electrolysis tank. The dormant electrolysis electrode (anode) uses a conducting material that is insoluble in the bath. The role of this electrode is to prevent dissolution of the working electrodes when an article to be treated (article to be treated) is not being treated (when electrolysis is dormant). When electrolysis is dormant, this insoluble conducting material is used as the anode, and the working electrodes are used as cathodes, and they are connected to a direct current power supply. When this is done, only extremely slight electrolysis takes place to an extent that does not cause the working electrodes to dissolve. This electrolysis is referred to as dormant electrolysis. As a result of this dormant electrolysis, decomposition of the treatment bath is prevented by preventing the working electrodes from dissolving in the bath when electrolysis is dormant.

50 **[0185]** The circulation pump is used for filtering and circulating the treatment bath. In addition, a filter is used to remove any sludge that is formed. When electrolytic treatment is completed and current to the article to be treated is stopped, a phenomenon occurs in which charge that has accumulated on the article to be treated is released into the treatment bath. At this time, a portion of the film is released into the bath. Sludge forms when this accumulates. If these phenomena are allowed to continue, sludge is formed continuously. Filtration and circulation of the treatment bath inhibits these phenomena.

55 **[0186]** A pH electrode, ORP electrode, EC (electrical conductivity) electrode, thermometer electrode and so forth are installed in the sensor electrode tank. These electrodes cannot be installed in the treatment tank since electrolysis current flows in this tank. They must therefore be installed separately.

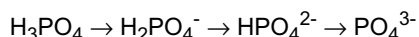
**[0187]** The replenishing chemical tank and chemical replenishment pump are installed for adding chemicals. It is preferable that chemicals be added to the portion (of the tank) following separation from the electrolysis tank in the filtration and circulation path of the treatment bath. This is because, since slight hydrolysis is taking place in the electrolysis tank at all times, even when dormant, making the electrolysis tank extremely electrochemically active, if active chemical is added to that active tank at a concentration greater than the treatment bath, the chemical component ions react before dissolving in the bath resulting in greater susceptibility to the formation of sludge.

**[0188]** The control computer is installed for suitably performing electrolytic treatment (reaction).

**[0189]** The following provides a description of the degree of dissociation of phosphoric acid. The electrolytic phosphate chemical treatment bath of the present invention has a pH of 0.5-5.0. The main factor that causes a change in the phosphate chemical treatment bath is dissociation of phosphoric acid ( $\text{H}_3\text{PO}_4$ ), one of the components of the treatment bath (phosphate chemical treatment bath). Namely, phosphoric acid ( $\text{H}_3\text{PO}_4$ ) dissolves and the acid dissociation coefficient (pKa) of phosphoric acid becomes larger. The acid dissociation coefficient (pKa) is the logarithmic value of the inverse of the dissociation constant, and the larger that value, the lower the degree of dissociation of the acid. Namely, it indicates that the strength of the acid is low.

**[0190]** Although the degree of dissociation of pure phosphoric acid ( $\text{H}_3\text{PO}_4$ ) is such that  $\text{pKa} = 2.15$ , the degree of dissociation of  $\text{H}_2\text{PO}_4^-$ , in which  $\text{H}^+$  has dissociated from  $\text{H}_3\text{PO}_4$ , is such that  $\text{pKa} = 7.2$ . This indicates that  $\text{H}_2\text{PO}_4^-$  is a weaker acid than  $\text{H}_3\text{PO}_4$ .

**[0191]** Although the treatment bath contains phosphate ions, the state of the ions changes (becomes reduced), as indicated below, due to electrolysis:



and finally, becomes phosphate (e.g.,  $\text{Zn}_2\text{Fe}(\text{PO}_4)_3$ ), which in turn becomes the film.

**[0192]** For this reason,  $\text{H}_3\text{PO}_4$  in the treatment bath constantly dissociate to  $\text{H}_2\text{PO}_4^-$ . This indicates that, whether the state of phosphoric acid in the treatment bath is primarily in the form of  $\text{H}_3\text{PO}_4$  or primarily in the form of  $\text{H}_2\text{PO}_4^-$ , this results in a considerable difference in the degree of acid activity of the treatment bath.

**[0193]** In the case phosphoric acid is primarily in the state of  $\text{H}_3\text{PO}_4$ , the degree of acid activity of the treatment bath is relatively large, and stabilizes in the direction of consuming acid ( $\text{H}^+$ ) in the treatment bath (direction in which phosphoric acid dissociates). Namely, although a solution primarily containing  $\text{H}_3\text{PO}_4$  consumes acid ( $\text{H}^+$ ), the target of that consumption is the consumption of acid ( $\text{H}^+$ ) by dissolving Fe electrode immersed in the treatment bath. This action results in the decomposition of the treatment bath and the formation of sludge.

**[0194]** This being the case, a treatment bath consisting primarily of  $\text{H}_3\text{PO}_4$  contains a large amount of acid ( $\text{H}^+$ ), and, due to the large ratio at which acid ( $\text{H}^+$ ) is contained, the ratio of metal ion that dissolves in the treatment bath becomes correspondingly small. As a result, the ratio of "metal (Zn, Fe, Mn, etc.) component ion that becomes phosphate and enters the film/(phosphate ion and phosphoric acid)" becomes relatively small.

**[0195]** On the other hand, if the treatment bath is composed primarily of  $\text{H}_2\text{PO}_4^-$ , it contains a large amount of metal ions instead of acid ( $\text{H}^+$ ), and the ratio of metal ion that dissolves in the treatment bath becomes larger. As a result, the ratio of "metal (Zn, Fe, Mn, etc.) component ion that becomes phosphate and enters the film/(phosphate ion and phosphoric acid)" becomes relatively large.

**[0196]** This indicates that the degree of dissociation of phosphoric acid in the treatment bath can control the ratio of "metal (Zn, Fe, Mn, etc.) component ion that becomes phosphate and enters the film/(phosphate ion and phosphoric acid)". Namely, the treatment bath can be stabilized during electrolysis by controlling the "metal (Zn, Fe, Mn, etc.) component ion that becomes phosphate and enters the film/(phosphate ion and phosphoric acid)". The reason for focusing on the metal (Zn, Fe, Mn, etc.) component ions that become phosphate and enter the film is because those metal ions form a complex with phosphate ion ( $\text{H}_2\text{PO}_4^-$ ) in solution that results in stabilization of phosphate ion ( $\text{H}_2\text{PO}_4^-$ ). For this reason, even if metal (Ni, Cu, etc.) ions that do become a phosphate are dissolved, since they do not become a complex of phosphate ions ( $\text{H}_2\text{PO}_4^-$ ), they do not contribute to stabilization of the treatment bath.

**[0197]** Furthermore, the ratio of "metal (Zn, Fe, Mn, etc.) component ions that becomes phosphate and enter the film/(phosphate ion and phosphoric acid)" can be indicated as the ion concentration (g/l) ratio.

**[0198]** In consideration of practical application, stabilization of the treatment bath is extremely important when considering its flow during volume production.

**[0199]** In the case of an electrolytic phosphate chemical treatment bath containing phosphate ions, nitrate ions, metal (Zn, Fe, Mn, etc.) component ions that become a phosphate and enter the film, and metal (Ni, Cu, etc.) ions that do not become a phosphate, the ratio of the "concentration of metal (Zn, Fe, Mn, etc.) component ions that becomes phosphate and enters the film (g/l)/(concentration of phosphate ions and phosphoric acid (g/l))" is suitably within the range of 1/10 (= 0.1) or more, and preferably within the range of 1/4 (= 0.25) to 3.

**[0200]** If the above ratio is 0.1 or less, the ratio of pure phosphoric acid ( $\text{H}_3\text{PO}_4$ ) of the treatment bath increases resulting reduced stability of the treatment bath. (Although the concentration of Zn ions is 0.4 g/l and that of phosphate

ions is 7.6 g/l in Example 1, since the surface area of the Fe electrode is 380 cm<sup>2</sup>/electrode and the amount of electrolysis is 51 A/8 electrodes, the amount of electrolysis of Fe is large in comparison with the other examples. For this reason, the ratio of the "concentration of metal (Zn, Fe, Mn, etc.) component ions that becomes phosphate and enters the film (g/l)/(concentration of phosphate ions and phosphoric acid (g/l))" is assumed to be 0.1 or more.)

**[0201]** In addition, the upper limit of the above ratio is determined by the "solubility in the treatment bath of metal (Zn, Fe, Mn, etc.) component ions that become phosphate and enters the film" and from a practical viewpoint.

**[0202]** In the present invention, the above metal ions that become a phosphate and enter the film dissolve nitrate and form a solution (treatment bath). Zinc nitrate and manganese nitrate are compounds that have a large solubility. Electrolysis can be performed by adding phosphate at about 1-10 g/l to zinc nitrate solution or zinc nitrate + nickel nitrate solution. In this case, the main factor that causes clouding of the treatment bath and inhibits film formation is the solubility of the solution. In the case of electrolytic phosphate chemical treatment, although treatment is premised on Zn, Ni and so forth dissolving, in the case of dissolving as zinc nitrate, it is possible to dissolve 100 g/l of zinc. Thus, if limited by solubility, the upper limit of the "concentration of metal (Zn, Fe, Mn, etc.) component ions that become phosphate and enters the film (g/l)/(concentration of phosphate ions and phosphoric acid (g/l))" is about 10-100.

**[0203]** Another factor that determines the upper limit is the "practical viewpoint". This is based on the fact that chemical concentrations are typically required to be low. Judging from this viewpoint, an upper limit of the "concentration of metal (Zn, Fe, Mn, etc.) component ions that become phosphate and enter the film (g/l)/(concentration of phosphate ions and phosphoric acid (g/l))" of about 4 is considered to be reasonable. (However, since Fe ions cannot exist in solution as ferrous ion (Fe<sup>2+</sup>) but only as ferric ion (Fe<sup>3+</sup>), and ferric ions have strong coagulating properties that result in the formation of sludge when added to the treatment bath, they cannot be used in the replenishing liquid.)

#### [Treatment Bath Composition]

**[0204]** The electrolytic phosphate chemical treatment bath is basically classified into the components indicated below.

**[0205]** Namely, the treatment bath has anions in the form of (1) nitrate ion (oxoacid (oxyacid) ion containing nitrogen, provided that the nitrate ion is not obtained by dissolving nickel nitrate or zinc nitrate, and is not supplied from nitric acid (HNO<sub>3</sub>)) and (2) phosphate ions. In addition, the treatment bath has cations in the form of (1) metal ions such as zinc, manganese, calcium and iron that crystallizes as phosphate in the film and which forms a complex with phosphate ions in the phosphate chemical treatment bath, and (2) metal ions such as nickel and copper that precipitate (form a film) due to a change in charge (reduction) of the metal ions, and for which the precipitation equilibrium potential as dissolved metal is greater than or equal to -0.83 V (hydrogen standard electrode potential), which is the anodic electrolysis potential of water.

**[0206]** This classification of the treatment bath composition is characterized by being classified into four components corresponding the role of the treatment bath components in the film formation reaction. This type of viewpoint (recognition) is not found in conventional phosphate chemical treatment.

**[0207]** Furthermore, components other than those indicated above can also be added as necessary. Examples of such components include fluorine ions in the case of targeting aluminum materials, and chlorine ions in the case of targeting copper materials.

**[0208]** In the case of non-electrolytic treatment, the only metal ions that are precipitated (formed a film) due to a change in charge (reduction) of the metal ions were nickel ions in the case of treating steel. Moreover, since nickel precipitates only at the iron interface, it cannot be present on the uppermost surface of the film. This indicates that precipitation accompanying a change in the charge of nickel takes place only corresponding to dissolution of iron. Since there is no dissolution of iron at locations other than the steel interface, nickel does not precipitate at those locations. This indicates the characteristic of non-electrolytic treatment films of the prior art. Namely, films obtained by non-electrolytic treatment are films that consist primarily of phosphate.

**[0209]** However, in the present embodiment, the range of metal ions such as nickel that precipitate (form a film) due to a change in charge (reduction) of the metal ions can be expanded in an environment in which they can be reduced using an external power supply in an electrolyte solution. In principle, metal ions having a dissolution-precipitation equilibrium potential (cathodic precipitation reaction potential) that is equal to or greater than the anodic electrolysis reaction potential of water on the surface of the cathode (-0.83 V) in electrolytic treatment are able to precipitate. Examples of such metals include copper, nickel, iron, zinc, tin, lead and chromium.

**[0210]** In addition, there are also cases in which it is desirable that the treatment bath only contains a trace amount (0.1 g/l or less) or is completely free of metal ions that precipitate (form a film) due to a change in charge (reduction) of the metal ion. This is true in cases in which the metal ion decreases the adhesion of the film to the material. It is desirable that films used in cold forging working lubrication treatment of steel be formed from uniform zinc phosphate crystals for which adhesion with the material is decreased. This is because a high degree of adhesion leads to poor lubricating properties. In order to form this type of film, it is necessary that the bath be free of metal ions such as nickel

that precipitates due to change in charge (reduction).

**[0211]** Furthermore, the composition of the treatment bath should be made to contain as few substances not involved in film formation as possible. For this reason, with respect to cations (metal ions), contamination by sodium ions that are used in degreasers should be restricted. Sodium ions, potassium ions, chlorine ions and sulfate ions ( $\text{SO}_4^{2-}$ ) should also not be contained in any chemical that is added to phosphate chemical treatment.

**[0212]** It is desirable that the amount of sodium ions and other unnecessary ions be as low as possible. As an actual means for accommodating this, the use of softened water should be avoided in preliminary washing. It is thought to be desirable to make the concentration of sodium ion and other unnecessary ions in the treatment bath 400 ppm or less, and preferably 100 ppm or less, as a general rule.

**[0213]** Next, the following defines the preferable composition for each item.

**[0214]** The concentration of nitride ions is preferably 6-140 g/l, the concentration of phosphate ions and phosphoric acid is preferably 0.5-60 g/l, the concentration of at least one of metal ion such as zinc, manganese, iron or calcium that forms a complex with phosphate ions in the phosphate chemical treatment bath is preferably 1-70 g/l, and the concentration of at least one of metal ion such as nickel, copper, iron, zinc or chromium that is dissolved and reduced in the phosphate chemical treatment bath and for which the potential of precipitation as metal is greater than or equal to the anodic electrolysis reaction potential of the solvent in the form of water or greater than or equal to -0.83 V (indicated as the hydrogen standard electrode potential) is preferably 0-40 g/l.

[Treatment Bath Electrochemical Conditions]

**[0215]** Those parameters that define the electrochemical conditions of the treatment bath consist of pH, ORP (oxidation-reduction potential), EC (electrical conductivity) and temperature. In the case of non-electrolytic treatment, the energy that promotes the electrical chemical reaction was dependent on the chemical energy possessed by the chemical treatment bath. For this reason, it is necessary to precisely define the electrochemical reaction conditions that define the status of the electrochemical reaction. In the case of electrolytic treatment, however, the energy that promotes the electrochemical reaction is dependent on an external power supply. Namely, the degree to which electrochemical conditions promote the reaction is small in comparison with non-electrolytic treatment. For this reason, it is not necessary to precisely define the electrochemical conditions of the treatment bath.

**[0216]** This corresponds to aggressive management of electrochemical conditions not being performed in practical electrolytic treatment such as "electroplating".

**[0217]** The following indicates the preferable ranges of each parameter.

**[0218]** To begin with, the preferable pH range is 0.5-5. The reason for the wide range for pH is to accommodate the composition of the treatment bath. As a general rule, the treatment bath of the present embodiment is an electrolyte treatment bath that does not contain substances that are not involved in film formation. For this reason, at a pH of 4 and above, the treatment bath is able to exist without formation of sludge.

**[0219]** The ORP (oxidation-reduction potential) of the treatment bath reflects the composition of the treatment bath. Table 3 shows the reaction formulas of reactions that are involved in electrolytic phosphate chemical treatment. The reaction that has the highest reaction potential is the cathodic decomposition reaction of water (1.23 V). In addition, the reaction that exhibits the lowest reaction potential is similarly the anodic electrolysis reaction of water (-0.83 V). For this reason, the ORP of the treatment bath of the present invention is preferably between -0.83 V and 1.23 V in principle.

**[0220]** Moreover, it is preferably within the range of 0-1 V (hydrogen standard electrode potential).

**[0221]** EC (electrical conductivity) also reflects the composition of the treatment bath. In addition, the method for measuring conductivity is not strictly standardized. EC is preferably within the range of 4-60 mS as determined by typical measurement methods.

**[0222]** A treatment bath temperature within the range of 10-90°C is preferable when considering film formation only. This is because the treatment bath is stable with respect to heat since it does not contain ions not involved in film formation, and the use of an external power supply for promoting the reaction enables energy to be supplied even at low temperatures.

**[0223]** The practical temperature differs according to the composition of the treatment bath.

[Electrolysis System (Control of the Cathodic Electrolytic Phosphate Chemical Treatment Reaction)]

**[0224]** Actual control of the cathodic electrolytic treatment reaction is performed by combining the three constituent features of the working electrode (anode) material, treatment bath composition, electrolysis method and conditions according to the properties of the film formed.

**[0225]** The following provides an explanation of each constituent feature.

**[0226]** A metal material that forms a film is selected for the working electrode (anode) material. Typical examples of such metals include iron, zinc, nickel and copper. In addition to these metals, manganese-containing alloys, calcium-

containing alloys and magnesium alloys, which form phosphate compounds, can also be used. In addition, metal materials, such as tin and lead, that have a standard electrode potential greater than or equal to - 0.83 V may also be used. These metals can be used as the anode either alone or as a combination of a plurality of materials.

**[0227]** The composition of the treatment bath (anions and cations) has been previously described. In the present embodiment, however, although the treatment bath does not contain anions other than nitrate ions and phosphate ions as a general rule, depending on the type of treated material, there are cases in which other ions can be contained. For example, in the case of forming a phosphate chemical treatment film on copper, the addition of chlorine ions can also be considered. Although active during anodic treatment, chlorine ions undergo the following anodic reaction relative to copper.



**[0228]** Since CuCl is incorporated in the film, chlorine ions do not remain in the treatment bath and increase, if suitably added.

**[0229]** In addition, in the case of performing film treatment on an aluminum material, a small amount of fluorine ions can be added for the purpose of promoting the dissolution reaction of aluminum. In this case, although the fluorine ions do not become a film component, they are effective for promoting the dissolution reaction of the aluminum material. For this reason, addition of a small amount of fluorine ions is allowed to the extent of supplying the portion taken out from the treatment bath.

**[0230]** The electrolysis method and conditions refers to what voltage and current is applied between the selected working electrode (anode) and article to be treated (cathode). The electrolysis method and conditions vary according to the type of working electrode selected and the type of film formed. There are generally two types of working electrodes used, namely "a metal (zinc, iron, etc.) that crystallizes as phosphate" and "a metal (nickel, copper, etc.) that precipitates following reduction of metal ions".

**[0231]** In order to ensure adhesion with the metal, it is preferable to first perform electrolysis using "a metal (nickel, copper, etc.) that precipitates following reduction of metal ions" for the working electrode, and then perform electrolysis using "a metal (zinc, iron, etc.) that crystallizes as phosphate" for the working electrode alone or use a combination of two types of electrolyses.

**[0232]** In order not to ensure adhesion of a film with the metal, it is preferable to only perform electrolysis using "a metal (zinc, iron, etc.) that crystallizes as phosphate" for the working electrode.

**[0233]** The normal range of the electrolysis voltage is 1-50 V, and that of the electrolysis current is 0.01-10 A/dm<sup>2</sup>. In addition, there are no particular provisions for electrolysis time.

**[0234]** Various types of films can be formed by making adjustments in the cathodic electrolytic treatment. For example, it is possible to form a film containing a large amount of zinc by using a bath containing a large amount of zinc and using a zinc electrode. Such films are applied for cold forging working substrates.

**[0235]** In addition, a film can be formed containing a large amount of nickel on the surface of a steel material by performing electrolysis using a bath containing a large amount of nickel ions and using first a nickel electrode and then performing electrolysis using a nickel electrode and an iron electrode, respectively. Films containing large amounts of nickel have excellent adhesion with iron base materials (substrates) and are therefore suited for coating substrates.

[Differences regarding Electrolytic Treatment of the Prior Art]

**[0236]** Differences regarding the electrolytic phosphate chemical treatment method of the prior art are shown in Table 5 to further clarify the characteristics of the present embodiment.

**[0237]** The basic difference is the composition of the treatment bath. In contrast to the treatment bath of the present embodiment being "a bath that is free of impurities and suitable for reacting components in solution in an electrolytic reaction", the electrolytic treatment bath of the prior art is "a bath containing impurities that inherits the contents of non-electrolytic treatment baths", thereby making them considerably different with respect to this point.

Table 5

Differences in Electrolytic Treatment Reactions (Between the Prior Art and the Present Invention)		
	Prior Art	Present Example
Treatment Bath Composition	(1) Phosphate ions, nitrate ions (2) Film forming metal ions (3) Cation not involved in film formation (Na <sup>+</sup> , etc.) (4) Promoter (nitrite ions, ions having a low degree of dissociation)	(1) Phosphate ions, nitrate ions (2) Film forming metal ions
Electrochemical conditions of treatment bath	pH = 2-4 ORP = 460-860 mV Temperature = 20-40°C	pH = 0.5-5 ORP = 200-1000 mV Temperature = 10-90°C
Electrolysis conditions	Voltage = 0-10 V Current = 0.01-4 A/dm <sup>2</sup>	Voltage = 0-50 V Current = 0.01-10 A/dm <sup>2</sup>

## [Discussion of Electrolytic Phosphate Chemical Films]

**[0238]** Next, an explanation is provided of films that can be obtained in the present embodiment.

**[0239]** As was previously described, the contents of the electrochemical reaction of the film formation reaction of the present embodiment differ from those of the method of prior art. As shown in the classification of cathodic electrolytic treatment reactions (Table 4), the contents of the electrochemical reaction of the present embodiment consist primarily of an "interelectrode electrolytic reaction".

**[0240]** However, prior arts, including Japanese Unexamined Patent Publication No. 5-822481, do not assume this type of "interelectrode electrolytic reaction". The intent of Japanese Unexamined Patent Publication No. 5-822481 is to provide an electrolytic reaction for reinforcing the electrochemical reaction in non-electrolytic phosphate chemical treatment of the prior art.

**[0241]** Non-electrolytic treatment baths consist primarily of "an electrolytic reaction between an article to be treated (solid) and a treating bath (liquid) on the same metal surface". A summary of the differences (contents) between the present invention and non-electrolytic treatment is shown in Table 6.

Table 6

Differences Between Electrolytic Reactions			
		Non-electrolytic Treatment	Electrolytic Treatment (Present Invention)
Reaction contents	Electrolytic reaction system	Electrochemical reaction between an article to be treated (solid) and a treating bath (liquid) on the same metal surface	Consists primarily of an electrochemical reaction between electrodes in a treatment bath
	Electrolysis reaction of solvent (water)	Absent	Present



Table 6 (continued)

Differences Between Electrolytic Reactions			
		Non-electrolytic Treatment	Electrolytic Treatment (Present Invention)
Effects on film	Formation mechanism of phosphate crystals	Phosphate precipitates (oxidation, anodic reaction) corresponding to reduction reaction (cathodic reaction) of promoter (NO <sub>2</sub> -)	Precipitation due to interelectrode electrochemical reaction
	Metal precipitation accompanying change in charge	None as a general rule. However, in the case of film formation on iron, slight reduction and precipitation (cathodic reaction) of nickel that dissolves accompanying dissolution of iron (anodic reaction) is observed at the iron interface.	Yes. Precipitation can occur throughout the film formation period by an interelectrode electrochemical reaction. This precipitation reaction may also not occur.

**[0242]** The characteristic of the film of the present invention can be said to be a film resulting primarily from an interelectrode electrochemical reaction. Namely, this film is formed by obtaining a large amount of electrochemical energy as compared with films obtained from non-electrolytic treatment.

**[0243]** The following indicates examples of the present invention. The processes of the examples and comparative examples are shown in Table 7.

**[0244]** The degreasing process consists of immersing for 4-5 minutes in an alkaline degreaser at a prescribed concentration and temperature. The acid washing process consists of immersing for 5-10 minutes in a 10% hydrochloric acid solution. Surface conditioning consists of immersing in 0.2% PL-ZT manufactured by Nihon Parkerizing Co., Ltd. The rinsing process is performed until degreaser and other chemicals are completely removed from the article to be treated. Electrodeposition coating is performed, so that a coated film thickness after baking is 20-25  $\mu\text{m}$ , using Power Top U-56 manufactured by Nippon Paint Co., Ltd.

Table 7

Processes of Examples and Comparative Examples (○ indicates processes that were performed, while - indicates processes that were not performed)								
Process	Degreasing →	Rinsing →	Acid washing →	Rinsing →	Surface conditioning →	Phosphate chemical treatment →	Rinsing →	Processes after chemical treatment
Exm. 1	○	○	-	-	-	○	○	Pure water rinsing →
Comp Ex. 1.	○	○	-	-	○	○	○	electrodeposition coating → pure water rinsing → baking (190°C, 25 min.)

Table 7 (continued)

Processes of Examples and Comparative Examples (○ indicates processes that were performed, while - indicates processes that were not performed)								
Process	Degreas- ing →	Rinsing →	Acid wash- ing →	Rinsing →	Surface condition- ing →	Phos- phate chemical treatment →	Rinsing →	Pro- cesses after chemical treatment
Exm. 2	○	○	-	-	○	○	○	Immer- sion in 5% sodium stearate solution (85°C, 5 mm.) → Cold-forg- ing press- ing
Comp Ex. 2	○	○	○	○	○	○	○	
Exm. 3	○	○	-	-	-	○	○	Pure water rinsing → elec- trodeposi- tion coating → pure water rins- ing → bak- ing (190°C, 25 min.)
Comp Ex. 3	○	○	-	-	-	○	○	
Exm. 4	○	○	-	-	-	○	○	Pure water rinsing → elec- trodeposi- tion coating → pure water rins- ing → bak- ing (190°C, 25 min.)
Exm. 5	○	○	-	-	-	○	○	

[0245] Table 8 shows the composition of the phosphate chemical treatment bath and the electrochemical conditions of the examples and comparative examples.

Table 8

Phosphate Chemical Treatment Bath Composition and Electrochemical Conditions											
	Treatment Bath Composition (g/l)					Treatment Bath Chemical Analysis Values		Treatment Bath Electrochemical Conditions			
	phosphate ion	Nitrate ion	Nickel ion	Zinc ion	Sodium ion	Total acidity (Pt)	Promoter conc. (Pt)	pH	ORP (mV) Ag/AgCl electrode potential	EC (mS)	Temp. (° C)
Exm.1	7.6	12	5.5	0.4	0	20	0	0.5	270	15.3	27.6
Comp. Ex. 1	7	20	0.5	3	6.4	12	5	3.05	520	-	28
Exm.2	21.2	20.2	0.25	17.1	0	44	0	2.17	399	21	32.4
Comp. Ex. 2	Nihon Parker Ltd. Palbond 3500 Bath, non-electrolytic treatment bath (80°C), immersed for 15 minutes					50	2.5	-	-	-	80
Exm.3	4.3	17.1	6	0.8	0	28	0	1.2	275	20.9	30.4
Comp. Ex. 3	7	19	4.5	2.5	0.6	21	0	2.77	356	24.5	36.4
Exm.4	2.8	10.1	3.8	0.4	0	18	0	2.09	338	9.1	28.7
Exm.5	2.9	11	3.9	0.4	0	18	0	2.18	318	8.7	27.7

**[0246]** Table 9 shows the electrolysis treatment conditions of the examples and comparative examples. With the exception of Comparative Example 2, the phosphate chemical treatment baths were filtered and circulated so that the treatment baths did not decompose and there was no clouding due to formation of sludge. The film of Comparative Example 2 is of the thick film type used for cold forging lubrication treatment. In order to obtain a thick film by non-electrolytic treatment, it was necessary to heat the bath, and the bath was maintained at 80°C.

Table 9 Electrolytic Treatment Conditions of  
Examples and Comparative Examples

	No. of treatments (pieces/lot)	Volume of treatment tank (L)	Electrolysis Conditions			
			Anodic treatment	Cathodic Treatment		
				Ni electrode	Fe electrode	Zn electrode
Exm. 1	8	200	9.6 V x 28 A x rising for 4 sec., holding for 6 sec. (electrode surface area = 380 cm <sup>2</sup> /piece)	---	17.7 V x 51 A x rising for 4 sec., holding for 105 sec. (electrode surface area = 380 cm <sup>2</sup> /piece)	---
Comp. Ex. 1	---	25	No electrolysis (non-electrolytic treatment: 3 minutes)			
Exm. 2	5	25	2.9 V x 0.01 A x rising for 30 sec. (electrode surface area = 20 cm <sup>2</sup> /piece)	---	2.9 V x 0.01 A x rising for 2 min., dormant for 11 min. (electrode surface area = 20 cm <sup>2</sup> /piece)	5.5 V x 2.5 A x rising for 3 min., holding for 10 min. (electrode surface area = 20 cm <sup>2</sup> /piece)
Comp. Ex. 2	---	1000	No electrolysis (non-electrolytic treatment: 15 minutes)			
Exm. 3	8	200	20 V x 20 A x rising for 4 sec., holding for 6 sec. (electrode surface area = 75 cm <sup>2</sup> /piece)	---	17.7 V x 51 A x rising for 4 sec., holding for 105 sec. (electrode surface area = 75 cm <sup>2</sup> /piece)	---
Comp. Ex. 3	1	25	2.5 V x 1.2 A x rising for 10 sec., dormant for 2 sec. (electrode surface area = 100 cm <sup>2</sup> /piece)	---	3 V x 1.3 A x rising for 10 sec., holding for 10 sec. x 8 dormant (electrode surface area = 100 cm <sup>2</sup> /piece)	---
			Above anodic treatment → cathodic treatment is repeated three times			

Exm. 4	8	200	18 V x 19 A x rising for 1 sec., holding for 6 sec.	(1) (18 V x 31 A x (dormant for 1 sec. → rising for 2 sec.) x 13 times (2) 9 V x 8 A x rising for 15 sec., holding for 58 sec. (electrode surface area = 90 cm <sup>2</sup> /piece)	(1) Dormant for 42 sec. (2) 11 V x 8 A x rising for 20 sec., holding for 50 sec. (electrode surface area = 40 cm <sup>2</sup> /piece)	---
Exm. 5	8	200	18 V x 19 A x rising for 1 sec., holding for 6 sec.	(1) (18 V x 30 A x (dormant for 1 sec. → rising for 2 sec.) x 13 times (2) 7 V x 0.4 A x rising for 15 sec., holding for 58 sec. (electrode surface area = 90 cm <sup>2</sup> /piece)	(1) Dormant for 2 sec. (2) 15 V x 16 A x rising for 20 sec., holding for 50 sec. (electrode surface area = 40 cm <sup>2</sup> /piece)	---

#### Example 1

[0247] The automobile air-conditioner part (clutch, stator housing) shown in the drawing was used as the article to be treated. The stator housing of Fig. 4 consists of a plate in the form of flat surface portion 20 (press stamped part) and a housing in the form of outer peripheral portion 21 (press formed part) welded and joined in a coating evaluation test. The housing in the form of the outer peripheral portion is made by deforming a plate in an irregular way by press forming. For this reason, the housing outer periphery is a surface that is greatly deformed in the press forming. A lubricating oil portion is strongly adhered to the greatly deformed surface simultaneously with being greatly deformed during press forming. As a result, during surface treatment, phenomena occur such as the lubricating oil portion being adhered to the surface due to it being greatly deformed. Consequently, that portion has a tendency to resist (obstruct) the chemical action of the metal surface, causing the performance of surface treatment to decrease. The corrosion resistance of the coating decreases in the example of Fig. 4.

[0248] The article to be treated was subjected to phosphate chemical treatment according to the process of Table 7 and under the conditions of Tables 8 and 9. Furthermore, the values indicated for ORP in Table 8 are the potentials (mV) indicated using an Ag/AgCl electrode for the reference. The values are converted to the hydrogen standard electrode potential when the value indicated using an Ag/AgCl electrode for the reference is taken to be +210 mV.

[0249] Electrodeposition coating was performed on the article to be treated according to the process starting with the chemical treatment of Table 7. Following electrodeposition coating, a coating corrosion resistance evaluation test was performed on the article to be treated. The coating corrosion resistance evaluation test was performed by making

scratches in the coating extending to the substrate with a knife in the flat surface portion and outer peripheral portion of the article to be treated and immersing it, for 240 hours, in a 5% sodium chloride solution at 55°C. After 240 hours of immersion had elapsed, the article to be treated was rinsed with water. After drying by allowing to stand for at least 2 hours, adhesive tape was affixed to the coated surface that was scratched with the knife and then peeled off with considerable force. The width of the coating film that was peeled off as a result of peeling off the tape was measured and used to evaluate coating corrosion resistance. The smaller the peeled width, the better the corrosion resistance. The results of evaluation of corrosion resistance were compared with Comparative Example 1 and are shown in Table 10.

#### Comparative Example 1

**[0250]** The same article to be treated was used as that in Example 1. With the exception of adding a surface conditioning step and performing phosphate chemical treatment by non-electrolytic process, the process was the same as that of Example 1. Phosphate chemical treatment was performed by non-electrolytic treatment using the method indicated in Tables 8 and 9. Evaluation of coating corrosion resistance was performed in the same manner as Example 1. The results of evaluation of coating corrosion resistance were compared with Example 1 and are shown in Table 10.

#### [Results of Evaluation of Coating Corrosion Resistance]

**[0251]** The results of evaluation of coating corrosion resistance are shown in Table 10. In a comparison between Example 1 and Comparative Example 1, Example 1 clearly has better corrosion resistance. In addition, although the flat surface portion demonstrates better corrosion resistance when comparing the flat surface portion with the outer peripheral portion, there is very little difference observed in Example 1. In Comparative Example 1, however, there is a large difference in corrosion resistance between the flat surface portion and outer peripheral portion. As was previously mentioned, this difference is the result of the effect of press forming decreasing the chemical treatment reaction of the metal surface in a non-electrolytic treatment. Since Example 1 is an example of electrolytic treatment, a large amount of electrochemical energy can be used for the electrolytic reaction. Consequently, there are no effects of press forming and a phosphate chemical film is formed resulting in satisfactory corrosion resistance.

Table 10

Results of Evaluation of Corrosion Resistance (Maximum Peeled Width)		
	Peeled width after salt water immersion test (mm)	
	Flat surface	Outer periphery
Example 1 (electrolytic treatment)	0	1 or less
comparative Example 1 (non-electrolytic treatment)	5	Entire surface peeled

#### [Analysis of Formed Phosphate Chemical Treatment Film]

**[0252]** Analysis was performed to confirm differences in films between electrolytic treatment and non-electrolytic treatment.

**[0253]** The phosphate chemical films of Example 1 and Comparative Example 1 were analyzed by an energy dispersed X-ray analyzer (EDX) and glow discharge analyzer (GDS). Analyses were performed on the flat surface portion and outer peripheral portion. The results are shown in Table 11.

Table 11

List of Film Analysis Results (Charts)				
	Film analysis (EDX)		Film analysis (GDS)	
	Flat surface	Outer periphery	Flat surface	Outer periphery
Example 1	Fig. 5	Fig. 6	Fig. 9	Fig. 10
Comparative Example 1	Fig. 7	Fig. 8	Fig. 11	Fig. 12

[0254] To begin with, the results of EDX were analyzed. EDX yields information relating to the component elements of the film. Film analysis was performed under the same conditions in Fig. 5 through Fig. 8.

[0255] EDX charts were compared between Example 1 (Figs. 5 and 6) and Comparative Example 1 (Figs. 7 and 8) at the same portion of the article to be treated. The flat surface portions were compared. In Fig. 5 (electrolytic treatment), although the nickel peak is higher than the zinc peak, in Fig. 7 (non-electrolytic treatment), the zinc peak is higher than the nickel peak. This trend is also observed in a comparison of the outer peripheral portions (Figs. 6 and 8).

[0256] The results of analyzing the atom number density of the films obtained from the results of EDX analysis performed under the same conditions in Figs. 5 through 8 are shown in Table 12. Although the atom number density obtained from the results of EDX analysis include carbon (C) and gold (Au), the discussion is made after omitting carbon and gold since they are not film components.

[0257] (Carbon is present as a result of washing the film with an organic solvent before analysis, while gold is used during fixation of the test piece in the analyzer.) The ratio of film component elements is determined by calculating the atom number density ratio of each element relative to phosphorus (P) that is always contained in the phosphate film.

[0258] A discussion of the films is provided in the following two sections based on the atom number density ratios of the metal elements.

(1) Ratio of metal that does not become a phosphate (Ni)/phosphorus (P) of the phosphate

(2) Ratio of metal that does not become a phosphate (Ni)/metal that serves as the base material (substrate) and becomes a phosphate (Fe)

**Table 12 Results of Film Analysis by Energy  
Dispersed X-ray Analyzer (EDX)**

Type of Element		Atom number density (%)							Ratio of atom number density vs. P					Atom number density ratio		
		C	O	P	Fe	Ni	Zn	Au	P	O	Fe	Ni	Zn	Ni/ Zn	Ni/ Fe	Zn/ Fe
Exm. 1	Flat	69.4	15.3	2.9	3.3	6.1	1.9	1.2	1	5.3	1.2	2.1	0.64	3.28	1.81	0.56
	Per-iph.	65.6	16.7	3.2	5.3	6.1	1.8	1.4	1	5.3	1.7	1.9	0.56	3.39	1.15	0.34
Co. Ex. 1	Flat	61.6	17.9	3.8	10.4	0.04	4.7	1.5	1	4.7	2.7	0.01	1.24	0.008	0.004	0.46
	Per-iph.	72.4	0.9	1.6	13.3	0.2	3.2	1.3	1	5.5	8.2	0.12	1.38	0.09	0.15	0.17
Exm. 2		76.6	11.7	3.1	0.96	--	5.5	2.1	1	3.8	0.3	--	1.76	0	--	5.68
Co. Ex. 2		70.1	16.5	3.8	5.2	--	3.3	1.1	1	4.4	1.4	--	0.88	0	--	0.63

(1) Ratio of metal that does not become a phosphate (Ni)/phosphorus (P) of the phosphate

[0259] In looking at the atom number density ratio Ni/P, although the density of Ni is larger at 2.1 and 1.9 in both the flat surface and outer peripheral portions of Example 1, the density of P is much larger at 0.01 and 0.12 in the flat surface and outer peripheral portions of Comparative Example 1, respectively. This indicates that films produced with electrolytic treatment contain a large amount of metal that does not become phosphate (Ni). On the other hand, in the case of non-electrolytic treatment, a film consisting primarily of phosphate is formed, and the results of Comparative Example 1 verify this fact. These results indicate that a film containing a large amount of metal that does not form a phosphate (Ni) is suitable for coating surface treatment and improves corrosion resistance.

[0260] Furthermore, in Comparative Example 1, the flat surface portion contains a larger amount of phosphorus than the outer peripheral portion. The reason for this is that it is difficult to form a film on the outer peripheral portion, and since a phosphate chemical film is not reliably formed, this corresponds to a smaller amount of phosphate, which is the main component of the film.

(2) Ratio of metal that does not become a phosphate (Ni)/metal that serves as the base material (substrate) and becomes a phosphate (Fe)

[0261] Fe is an element which, in addition to serving as the base material (substrate), also forms a film with phosphate crystals. If a film is reliably formed, the Ni/Fe ratio indicates the ratio of Ni to Fe in the film, while if a film is not reliably formed, it indicates the ratio of Ni to the base material surface.

**[0262]** Although the Ni/Fe ratio of Example 1 is 1 or more for both the flat surface and outer peripheral portions, the Ni/Fe ratio of Comparative Example 1 is 1 or less for both the flat surface and outer peripheral portions. These results also indicate that the content of Ni affects coating corrosion resistance.

**[0263]** GDS involves analyzing elements that come out of the film following glow discharge of the film, and allows the information to be obtained on the component elements of the film, film strength and so forth. For this reason, GDS provides information on the (1) distribution status of elements in the film, and (2) bonding strength of the film. The "distribution status of elements in the film" can be read directly from the GDS chart. In addition, "film strength" makes it possible to compare the amount of time taken to reach the iron base material when analysis is performed under identical conditions. Namely, the longer the amount of time taken to reach the iron base material, the stronger the film.

**[0264]** Furthermore, the voltage applied in GDS analysis differs depending on the type of element. For this reason, analysis results of each film do not yield information on "the existence ratios between elements within the film". However, the analyses of Figs. 9 through 12 were performed under identical conditions. Thus, the status of the presence of the elements in the film can be compared between each sample (film).

**[0265]** GDS was also used to compare Example (Figs. 9 and 10) and Comparative Example (Figs. 11 and 12) at the same portion of the article to be treated.

**[0266]** First, the (1) distribution status of elements in the film was compared.

**[0267]** For the flat surface portions, the manner in which nickel and so forth are contained in the film can be analyzed by looking at the charts of Fig. 9 (electrolytic treatment) and Fig. 11 (non-electrolytic treatment). Fig. 9 (electrolytic treatment) shows that nickel is distributed throughout in the direction that penetrates the film. On the other hand, Fig. 11 (non-electrolytic treatment) shows that hardly any nickel is contained. In addition, Fig. 9 (electrolytic treatment) shows that iron atoms are gradually increasing in the film, suggesting that the iron electrode (anode) used in electrolytic treatment is dissolving and forming a film. Since the behavior of iron differs from that of phosphorus (P), a phenomenon can be predicted by which iron atoms (metal) are incorporated in the film in the same manner as nickel. Furthermore, this phenomenon is similar for the outer peripheral portion as well.

**[0268]** Subsequently, a discussion of film bonding strength is provided. Film bonding strength is obtained by comparing the amount of time (A) in GDS analysis until the iron base material is reached after the film is penetrated. Those results are shown in Table 13.

Table 13

Film Depth in GDS Analysis (Film Strength)		
	A: Time of GDS analysis until iron base material is reached (sec.)	
	Flat surface portion	Outer peripheral portion
Example 1	100 (Fig. 9)	95 (Fig. 10)
Comparative Example 1	25 (Fig. 11)	30 (Fig. 12)

**[0269]** This evaluation indicates that although the chemical treatment time of the article to be treated is nearly the same, Example 1 has film strength that is three times that of Comparative Example 1.

**[0270]** The above results support the fact that the phosphate chemical film that includes precipitation of metal (Ni) accompanying a change in charge caused by electrolytic treatment, which is a characteristic of the present invention, is effective for performing its function, namely providing coating corrosion resistance.

**[0271]** In addition, as shown in Table 8, the nitrate ion concentration in the treatment bath of Example 1 is roughly 1/2 that of the treatment bath of Comparative Example 1. This is only possible by performing electrolytic treatment in a bath that does not contain sodium ion. Since the concentration of nitric acid has been lowered, the present invention is an environmentally-friendly technology.

## Example 2

**[0272]** A part used in an automobile starter shown in Fig. 13 was used for the article to be treated. This part (a pipe-shaped part having a diameter of 23 mm and length of 80 mm) is formed by cold-forging press working and forming spline-shaped grooves for meshing with gear teeth on the inside of a pipe-shaped form. It is made of an alloy material containing about 1% chromium. Phosphate chemical treatment is performed in the form of a cold-forging press lubrication substrate. Thus, the object of the phosphate chemical treatment film is to decrease the load during cold forging working. Thus, the evaluation of the film is also performed based on the load during cold forging working.



**[0273]** Electrolytic treatment of the article to be treated was performed by electrolytic phosphate chemical treatment using the process of Table 7 and under the conditions of Tables 8 and 9. Sodium stearate is reacted with the phosphate chemical treatment film in the step following chemical treatment of Table 6 to form a metallic soap film (zinc stearate). This is followed by cold-forging press working.

#### Comparative Example 2

**[0274]** The same part as Example 2 was used for the article to be treated. The process was the same as that of Example 2 with the exception of omitting the surface conditioning step by performing acid washing, and using different phosphate chemical treatment. Phosphate chemical treatment was performed by non-electrolytic treatment (80°C) according to the method shown in Tables 8 and 9. Comparative Example 2 is the treatment processing method of production equipment currently in use.

[Evaluation of Cold-Forging Press Working Load, etc.]

**[0275]** Evaluation of cold-forging press working load and film analysis are summarized in Table 14.

**[0276]** The "Cold-forging press working load" of Table 14 is the load to which the press is subjected during cold-forging press working. The lower the value of the cold-forging press working load, the better the lubrication performance. In addition, analysis of film weight was performed according to the following method. The "water dissolved portion" indicates the value resulting from measuring the weight of the article to be treated before and after immersing in water at 100°C for 10 minutes, and then dividing the resulting weight by the surface area of the article to be treated. The "metallic soap portion" indicates the value resulting from measuring the weight of the article to be treated before and after immersing for 20 minutes in isopropyl alcohol (IPA) at 75°C, and dividing the resulting weight by the surface area of the article to be treated. The "phosphate film portion" indicates the value resulting from measuring the weight of the article to be treated before and after immersing for 20 minutes in 5% chromic acid (CrO<sub>3</sub>) at 50-70°C, and dividing the resulting weight by the surface area of the article to be treated.

**[0277]** In addition, the results of analyzing atom number density (%) by EDX are also shown in Table 14.

Table 14

Evaluation of Cold-Forging Press Working Load and Film Analysis					
	Performance evaluation (cold-forging press working load)	Film analysis (EDX charts)	Film Layer and Weight Analysis (g/m <sup>2</sup> )		
			Water dissolved portion	Metallic soap portion	Phosphate film portion
Example 2	67 Kg/cm <sup>2</sup> (mean value)	Fig. 14	10.2	11.8	14.4
Comparative Example 2	82 Kg/cm <sup>2</sup> (mean value)	Fig. 15	2.4	1.8	6.7

**[0278]** Evaluation of the cold-forging press working load showed that Example 2 is superior to Comparative Example 2. The reason for this can be made clear from the "Results of Film Layer and Weight Analysis" of Table 14. According to the "Results of Film Layer and Weight Analysis" of Table 14, the film of Example 2 contains approximately 5 times as much metallic soap as the film of Comparative Example 2. Metallic soap contributes greatly to cold-forging press working lubrication. Thus, it is clear that the higher the content of this component, the greater the decrease in the cold-forging press working load.

**[0279]** Since the metallic soap portion is zinc stearate, it is necessary for the film to contain a large amount of zinc. The amount of zinc in the film can be determined from the results of EDX analysis. When comparing the charts of Figs. 14 and 15, in addition to Example 2 (Fig. 14), which is an electrolytic treatment film, containing a smaller amount of iron, it can also be confirmed to contain a larger amount of zinc. In addition, this is quantitatively compared and confirmed in the results of analysis of EDX atom number density (%) of Table 12. If the chemical structure of the phosphate chemical film is assumed to be Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, then the atom number density ratio of Zn to P (Zn/P) becomes 1.5. When the atom number density ratio of Zn/P is calculated in Table 12, it becomes 1.76 in Example 2, thus indicating an excess amount

of zinc relative to  $\text{Zn}_3(\text{PO}_4)_2$ . In Comparative Example 2, however, the ratio becomes 0.88, thus indicating an amount of zinc that is less than the corresponding  $\text{Zn}_3(\text{PO}_4)_2$ .

[0280] These findings indicate that electrolytic treatment is able to change the composition of the film. Namely, they suggest that an excess amount of zinc relative to the chemical structure of  $\text{Zn}_3(\text{PO}_4)_2$  becomes a film in the form of zinc metal accompanying a change in charge. This is only possible as a result of the electrolytic treatment of the present invention. This also contributes greatly to lowering the cold-forging press working load.

[0281] In addition, the analysis results of Table 12 indicate that the film of Example 2 is a film that is completely free of Ni, which is a metal that does form a phosphate. Electrolytic phosphate chemical treatment also makes it possible to not contain metals that do not form phosphate in this manner.

#### Example 3 and Comparative Example 3

[0282] Example 3 and Comparative Example 3 serve to confirm the differences in films formed by electrolytic treatment.

[0283] The automobile air-conditioner part used in Example 1 and Comparative Example 1 was used for the article to be treated in Example 3 and Comparative Example 3, and phosphate chemical treatment and electrodeposition coating were performed according to the process of Table 7. Electrolytic phosphate chemical treatment was performed under the conditions of Tables 8 and 9. The main difference between Example 3 and Comparative Example 3 lies in the phosphate chemical treatment bath. Although the bath of Example 3 does not contain Na ions, the bath of Comparative Example 3 contains Na ions. Evaluation of the coating corrosion resistance of Example 3 and Comparative Example 3 was performed by the same method as in Example 1 and Comparative Example 1. Those results are shown in Table 15.

Table 15

Results of Evaluation of Coating Corrosion Resistance (Maximum Peeled Width)			
	Difference in treatment bath	Peeled width after salt water immersion test (mm)	
		Flat surface	Outer periphery
Example 3	Free of Na ions	0	5
Comparative Example 3	Na ions present	1	10

[0284] The results of Table 15 indicate that Example 3 demonstrates better coating corrosion resistance than Comparative Example 3.

[0285] That difference is considered to be due to the difference in the phosphate chemical films that are formed. Table 16 shows the results of X-ray diffraction patterns of the phosphate chemical films of Example 3 and Comparative Example 3.

Table 16

Film X-Ray Diffraction Results		
	Flat surface portion	Outer peripheral portion
Example 3	No peak for phosphate crystal (see Fig. 16)	No peak for phosphate crystal, Ni peak present (small) (see Fig. 17)
Comparative Example 3	Phosphate crystal peak present (see Fig. 18)	Phosphate crystal peak present (see Fig. 19)

[0286] Differences relating to the phosphate chemical films of Example 3 and Comparative Example 3 consist of the following:

- (1) Presence or absence of phosphate crystal peak
- (2) Presence or absence of Ni peak

**[0287]** The results of Table 16 do not indicate that the film of Example 3 does not contain phosphate crystals. It indicates that the phosphate crystals are extremely minute. It also indicates that as a result of this, compounding of Ni metal and phosphate crystals is proceeding.

**[0288]** Table 17 summarizes that compounding of Ni metal and phosphate crystals is proceeding for the film of Example 3.

Table 17

Micrographs of Elementary Analysis by EPMA (Electro Probe Micro Analysis) in the Direction of the Film Cross-Section					
	SEM photo (4000X)	Elementary Analysis Photos			
		Phosphorus (P)	Zinc (Zn)	Nickel (Ni)	Iron (Fe)
Flat surface	Fig. 20	Fig. 21	Fig. 22	Fig. 23	Fig. 24
Outer periphery	Fig. 25	Fig. 26	Fig. 27	Fig. 28	Fig. 29

**[0289]** The distribution status of each element in cross-sections of the film as observed in the SEM photographs of Figs. 20 and 25 magnified to 4000X is shown in the analysis photos (Figs. 21 through 24 and Figs. 26 through 29) for each element. The results of these photos show that each element is uniformly distributed in the film. The photos also visually indicate that although the film contains phosphate, its crystals are microscopic (results of Table 16).

**[0290]** In addition, these results correspond, although indirectly, with the GDS analysis results shown in Example 1 (Table 12 and Figs. 9 and 10).

**[0291]** The results of Table 15 show that the film obtained from the bath not containing Na ion of Example 3 in which phosphate crystals are minutely dispersed in Ni has effective coating corrosion resistance.

**[0292]** Furthermore, the X-ray diffraction pattern indicated in Japanese Unexamined Patent Publication (Saikohyo) No. 5-822481, which is an example of the prior art of electrolytic phosphate chemical treatment, shows all phosphate peaks.

#### Examples 4 and 5

**[0293]** Examples 4 and 5 are examples of reliably forming Ni for a coating substrate in the presence of phosphate, reducing the amount of electrolyzed Fe and reducing as much as possible the tendency for the treatment bath to deteriorate. Thus, only electrolysis of Ni is performed in the first stage of cathodic electrolytic treatment, and this is followed by simultaneous electrolysis of Ni and Fe. At that time, the amount of electrolyzed Fe is 1/3-1/8 less than that of Example 3.

**[0294]** The automobile air-conditioner part used in Example 3 was used for the article to be treated in Examples 4 and 5, and phosphate chemical treatment and electrodeposition coating were performed according to the process of Table 6. Electrolytic phosphate chemical treatment was performed under the conditions of Tables 8 and 9.

**[0295]** Evaluation of the coating corrosion resistance of Examples 4 and 5 was performed using the same method as Example 1. Those results are shown in Table 18.

Table 18

Results of Evaluation of Coating Corrosion Resistance (Maximum Peeled Width)		
	Peeled width after salt water immersion test (mm)	
	Flat surface	Outer periphery
Example 4	0	2
Example 5	2	4

**[0296]** The corrosion resistance of Examples 4 and 5 is better than that of Comparative Example 3. As was stated in the explanation of Example 1, it is difficult to form a film on the outer peripheral portion in the case of non-electrolytic

treatment. If the electrolytic treatment of the present invention is performed in Examples 4 and 5, it becomes possible to form a film even on such surfaces, indicating that corrosion resistance can be secured.

[0297] Next, the results of EDX analysis of the phosphate chemical films obtained in Examples 4 and 5 are shown.

Table 19

Results of Film Analysis by Energy Dispersed X-ray Analyzer (EDX)												
Type of Element		Atom number density (%)				Ratio of atom number density vs. P				Atom number density ratio		
		P	Fe	Ni	Zn	P	Fe	Ni	Zn	Ni/Zn	Ni/Fe	Zn/Fe
Exm.4	Flat surface	19	62.8	9.6	8.61	1	3.31	0.51	0.45	1.13	0.15	0.13
	Outer periphery	9.7	77.7	7.3	5.3	1	8.01	0.75	0.55	1.36	0.09	0.07
Exm.5	Flat surface	19.9	51.9	15.4	12.9	1	2.61	0.77	0.64	1.20	0.30	0.24
	Outer periphery	26.8	40	25.1	8.6	1	1.49	0.94	0.32	2.94	0.63	0.21

[0298] According to the results of Table 19, the trend of the composite ratio of an element that is not the base material (Fe) does not change in comparison with Table 12. Although both Ni and P are elements that are contained in the film, the ratio at which they are present (Ni/P) is 0.5 or more in both the results of Table 12 and Table 18, indicating that Ni in the film is present in amount greater than 1/4 the amount of P. The results also indicate that the film is considerably different to a film obtained by non-electrolytic treatment in which the Ni/P ratio is far less than 0.25 (see Table 12).

[0299] The examples of Examples 4 and 5 indicate examples of cathodic electrolytic treatment using two Fe and Ni electrodes. They also indicate that this method is effective.

## Claims

1. An electrolytic phosphate chemical treatment method of forming a film containing at least a phosphate and a metal that does not form said phosphate on the surface of an article to be treated having electrical conductivity by performing electrolytic treatment by contacting said article to be treated with a phosphate chemical treatment bath containing at least phosphate ions and phosphoric acid, nitrate ions, metal ions that form a complex with said phosphate ions in said phosphate chemical treatment bath, and metal ions for which the electrical potential at which the ions dissolved in said phosphate chemical treatment bath are reduced and precipitate as metal is equal to or greater than the anodic electrolysis reaction potential of the solvent in the form of water or equal to or greater than -0.83 V (indicated as the hydrogen standard electrode potential); characterized in that,

said phosphate chemical treatment bath has 0-400 ppm of metal ions other than those which are a component of the film, and is substantially free of solids having an effect on the film formation reaction; and, said article to be treated is treated by electrolysis in said phosphate chemical treatment bath with a metal material that forms a complex with phosphate ions in said phosphate chemical treatment bath, and a metal material for which the electrical potential at which the ions thereof dissolved in said phosphate chemical treatment bath is reduced and precipitates as metal is equal to or greater than the anodic electrolysis reaction potential of the solvent in the form of water or equal to or greater than -0.83 V (indicated as the hydrogen standard electrode potential).

2. The electrolytic phosphate chemical treatment method as set forth in claim 1 characterized in that said phosphate chemical treatment bath contains 0-100 ppm of metal ions other than those which are a component of said film which at least contains the phosphate.
- 5 3. The electrolytic phosphate chemical treatment method as set forth in claim 1 characterized in that said phosphate chemical treatment bath is composed of said nitrate ions at a concentration of 6-140 g/l, said phosphate ions and phosphoric acid at a concentration of 0.5-60 g/l, metal ions that form a complex with phosphate in said phosphate chemical treatment bath at a concentration of 0.5-70 g/l, and metal ions for which the electrical potential at which the ions dissolved in said phosphate chemical treatment bath are reduced and precipitate as metal is equal to or  
10 greater than the anodic electrolysis reaction potential of the solvent in the form of water or equal to or greater than -0.83 V (indicated as the hydrogen standard electrode potential) at a concentration of 0-40 g/l.
- 15 4. The electrolytic phosphate chemical treatment method as set forth in claim 3 characterized in that said phosphate chemical treatment bath does not contain an acid having a degree of acid dissociation larger than the degree of acid dissociation of said phosphate ions.
- 20 5. The electrolytic phosphate chemical treatment method as set forth in claim 4 characterized in that, in said phosphate chemical treatment bath, the acid having a degree of acid dissociation larger than the degree of acid dissociation of said phosphate ion is composed of nitric acid.
- 25 6. The electrolytic phosphate chemical treatment method as set forth in claim 1 characterized in that said metal ions that form a complex with said phosphate ions in said phosphate chemical treatment bath are composed of at least one of metal selected from the group consisting of zinc, iron, manganese and calcium.
- 30 7. The electrolytic phosphate chemical treatment method as set forth in claim 1 characterized in that said metal ions for which the electrical potential at which the ions dissolved in said phosphate chemical treatment bath are reduced and precipitate as metal is equal to or greater than the anodic electrolysis reaction potential of the solvent in the form of water or equal to or greater than -0.83 V (indicated as the hydrogen standard electrode potential) is at least one of metal selected from the group consisting of nickel and copper.
- 35 8. An electrolytic phosphate chemical treatment method of forming a film containing at least phosphate on the surface of an article to be treated having electrical conductivity by electrolytic treatment by contacting said article to be treated in a phosphate chemical treatment bath containing phosphate ions and phosphoric acid, nitrate ions, and metal ions that form a complex with said phosphate ions in said phosphate chemical treatment bath; characterized in that,  
  
said phosphate chemical treatment bath has 0-400 ppm of metal ions other than those which are a component of said film, and is substantially free of solids that have an effect on the film formation reaction; and  
40 that said article to be treated is treated by electrolysis with metal materials that form a complex with phosphate ions in said phosphate chemical treatment bath.
- 45 9. The electrolytic phosphate chemical treatment method as set forth in claim 8 characterized in that said phosphate chemical treatment bath contains 0-100 ppm of metal ions other than those which form said film which at least contains phosphate.
- 50 10. The electrolytic phosphate chemical treatment method as set forth in claim 8 characterized in that said phosphate chemical treatment bath is composed of said nitrate ions at a concentration of 6-140 g/l, said phosphate ions and phosphoric acid at a concentration of 0.5-60 g/l, and metal ions that form a complex with phosphate in said phosphate chemical treatment bath at a concentration of 0.5-70 g/l.
- 55 11. The electrolytic phosphate chemical treatment method as set forth in claim 8 characterized in that said phosphate chemical treatment bath does not contain acid having a degree of acid dissociation larger than the degree of acid dissociation of said phosphate ions.
12. The electrolytic phosphate chemical treatment method as set forth in claim 11 wherein, in said phosphate chemical treatment bath, the acid having a degree of acid dissociation larger than the degree of acid dissociation of said phosphate ions is composed of nitric acid.

13. The electrolytic phosphate chemical treatment method as set forth in claim 8 wherein said metal ions that form a complex with said phosphate ion in said phosphate chemical treatment bath are composed of at least one of metal selected from the group consisting of zinc, iron, manganese and calcium.
- 5 14. The electrolytic phosphate chemical treatment method as set forth in claim 1 or 8 characterized by performing electrolysis using said article to be treated as the anode.
- 15 15. The electrolytic phosphate chemical treatment method as set forth in claim 1 or 8 characterized by performing electrolysis using said article to be treated as the cathode.
- 10 16. The electrolytic phosphate chemical treatment method as set forth in claim 1 or 8 characterized by performing electrolysis using said article to be treated as the anode followed by performing electrolysis using said article to be treated as the cathode.
- 15 17. The electrolytic phosphate chemical treatment method as set forth in claim 1 or 8 wherein cathodic electrolytic treatment, in which electrolysis of said phosphate chemical treatment method is performed using said article to be treated as the cathode, is composed of at least one of either electrolysis in which a metal material identical to a metal for which ions dissolved in said phosphate chemical treatment bath are reduced and precipitated, and/or an electrically conductive material that is insoluble in said phosphate chemical treatment bath, is used as the anode, and electrolysis in which a metal material that forms a complex in said phosphate chemical treatment bath is used as the anode.
- 20 18. The electrolytic phosphate chemical treatment method as set forth in claim 1 wherein a cathodic electrolytic treatment of said phosphate chemical treatment method, in which electrolysis is performed using said article to be treated as the anode, characterized by comprising one cycle consisting of performing electrolysis in which a metal material identical to a metal for which ions dissolved in said phosphate chemical treatment bath are reduced and precipitated, and/or an electrically conductive material that is insoluble in said phosphate chemical treatment bath, is used as the anode, followed by performing electrolysis in which a metal material that forms a complex in said phosphate chemical treatment bath is used as the anode, and this cycle being performed at least once.
- 25 19. The electrolytic phosphate chemical treatment method as set forth in claim 1 wherein a cathodic electric treatment of said phosphate chemical treatment method is carried out, in which electrolysis is performed using said article to be treated as the anode, characterized in that an electrolytic treatment is performed by separating it into an electrolysis tank in which electrolysis is performed using an electrically conductive material insoluble in the phosphate chemical treatment bath as the anode, and an electrolysis tank in which electrolysis is performed using a metal material that forms a complex in said phosphate chemical treatment bath as the anode.
- 30 20. The electrolytic phosphate chemical treatment method as set forth in any of claims 17 through 19 characterized in that said metal material identical to a metal dissolved in said phosphate chemical treatment bath that is reduced and precipitated is at least one of metal selected from the group consisting of nickel and copper.
- 35 21. The electrolytic phosphate chemical treatment method as set forth in any of claims 17 through 19 characterized in that said metal material that forms a complex in said phosphate chemical treatment bath is at least one of metal selected from the group consisting of zinc, iron, manganese and calcium.
- 40 22. The electrolytic phosphate chemical treatment method as set forth in claim 1 or 8 characterized in that, in the case that said article to be treated is not in contact with said phosphate chemical treatment bath, the metal material, which is used as the anode in electrolytic treatment in which said article to be treated is used as the cathode, is used as a cathode, a material that is insoluble in said phosphate chemical treatment bath is used as an anode, and a voltage of 5 V or less is applied between said anode and said cathode.
- 45 23. The electrolytic phosphate chemical treatment method as Set forth in either of claims 1 or 8 characterized in that, in the case that said article to be treated is not in contact with said phosphate chemical treatment bath, the metal material, which is used as the anode in electrolytic treatment in which said article to be treated is used as the cathode, is used as a cathode, a material that is insoluble in said phosphate chemical treatment bath is used as an anode, and voltage is applied, to a degree at which said cathode does not substantially dissolve, between said anode and said cathode.
- 50 55

24. The electrolytic phosphate chemical treatment method as set forth in claim 1 or 8 characterized by removing a portion of said phosphate chemical treatment bath from a tank having said phosphate chemical treatment bath, thermodynamically stabilizing the energy state of the portion as a liquid of said phosphate chemical treatment bath and said portion being later returned to said tank.
25. The electrolytic phosphate chemical treatment method as set forth in claim 24, characterized by removing a portion of said phosphate chemical treatment bath from said tank having said phosphate chemical treatment bath, and removing solids that have precipitated in said phosphate chemical treatment bath during the course of the film formation reaction, and said portion being returned to said tank.
26. The electrolytic phosphate chemical treatment method as set forth in claim 24 characterized in that, when replenishing components of said phosphate chemical treatment bath, a portion of said phosphate chemical treatment bath is removed, and that a replenishing liquid is added to said removed bath that contains treatment bath components having a concentration higher than the concentration of at least one component among the components that compose said phosphate chemical treatment bath.
27. An electrolytic phosphate chemical treatment method in which electrolytic treatment is performed using an article to be treated as the cathode characterized by comprising a reaction in which a metal, for which the electrical potential at which the ions of the metal dissolved in a phosphate chemical treatment bath are reduced and precipitate as a metal is equal to or greater than the anodic electrolysis reaction potential of solvent in the form of water or equal to or greater than -0.83 V (indicated as the hydrogen standard electrode potential), is dissolved in the phosphate chemical treatment bath, is reduced by electrolytic treatment from a cationic state and precipitates on the surface of said article to be treated, and a reaction in which metal ions that complex with phosphate ions in said phosphate chemical treatment bath precipitate as phosphate crystal in said phosphate chemical treatment bath corresponding to dehydrogenation of phosphate ions.
28. The electrolytic phosphate chemical treatment method as set forth in claim 27 characterized in that said metal ions that complex with phosphate ions are at least one of metal selected from the group consisting of Fe, Zn, Mn, Ca and Mg.
29. The electrolytic phosphate chemical treatment method as set forth in claim 27 characterized in that said metal for which the electrical potential at which the ions thereof dissolved in said phosphate chemical treatment bath are reduced and precipitate as a metal is equal to or greater than the anodic electrolysis reaction potential of solvent in the form of water or equal to or greater than -0.83 V (indicated as the hydrogen standard electrode potential) is at least one of metal selected from the group consisting of Ni, Cu, Fe and Zn.
30. The electrolytic phosphate chemical treatment method as set forth in at least one of claims 1, 8 and 27 characterized in that the composition of the treatment bath when electrolytic treatment is performed is such that the ratio of the concentration of metal ions that complex with phosphate ions (g/l) to the concentration of phosphate ions and phosphoric acid (g/l) is 0.1 or more.
31. The electrolytic phosphate chemical treatment method in which electrolytic treatment is performed using said article to be treated as the cathode as set forth in at least one of claims 1, 8 and 27, characterized in that at the start of said electrolytic treatment, the voltage applied between metal materials that form an anode and a cathode is varied.
32. The electrolytic phosphate chemical treatment method as set forth in claim 31 characterized in that said variation in the voltage applied at the start of said electrolytic treatment is in the form of pulses.
33. A compound film on a steel surface characterized by being composed of a metal that does not form a phosphate and a phosphate compound, wherein said metal and phosphate compound that compose the film are dispersed throughout the entire film.
34. A compound film on a steel surface characterized by being composed of a metal that does not form a phosphate and a phosphate compound, wherein a metal is present on the uppermost surface of the film that at least does not form phosphate.
35. A compound film on a steel surface characterized by being composed of a metal that does not form a phosphate

and a phosphate compound, wherein said film does not demonstrate peaks other than the inevitable unavoidable peak of phosphate in X-ray diffraction analysis.

- 5      **36.** A compound film on a steel surface characterized by being composed of a metal that does not form a phosphate and a phosphate compound, wherein the number of atoms of the metal that does not form a phosphate is 0.25 or more the number of atoms of phosphorus that composes phosphate crystals.
- 10      **37.** The compound film as set forth in at least one of claims 33 through 36 characterized in that said metal that does not form a phosphate is at least one of metal selected from the group consisting of Ni, Cu, Fe and Zn.
- 15      **38.** The compound film as set forth in at least one of claims 33 through 36 characterized in that a metal that forms a phosphate compound is at least one metal selected from the group consisting of Fe, Zn, Mn, Ca and Mg.
- 20      **39.** The compound film as set forth in at least one of claims 33 through 36 characterized in that said steel contains at least 95% by weight of iron (Fe) when the total amount of steel is taken to be 100% by weight.
- 25      **40.** The compound film as set forth in claim 35 characterized in that said X-ray diffraction analysis is performed by ESCA or EDX analysis.
- 30
- 35
- 40
- 45
- 50
- 55



Fig.1

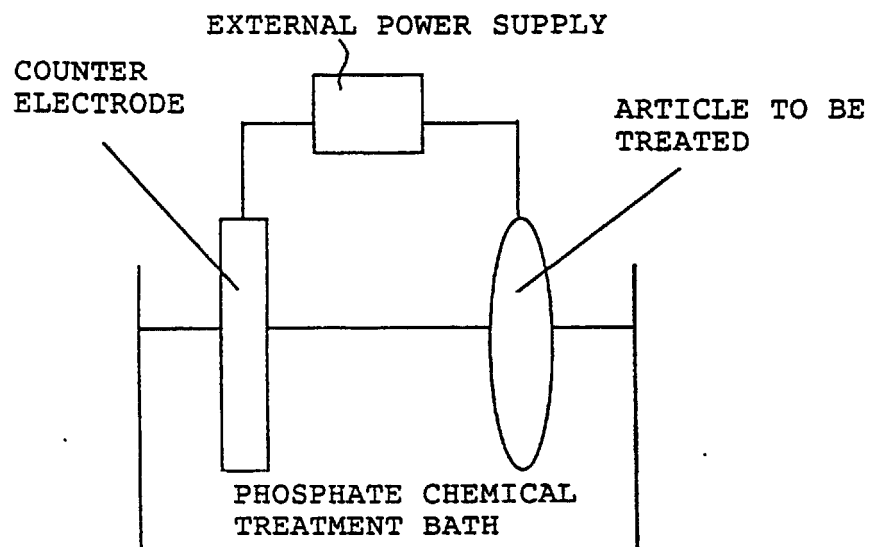


Fig.2

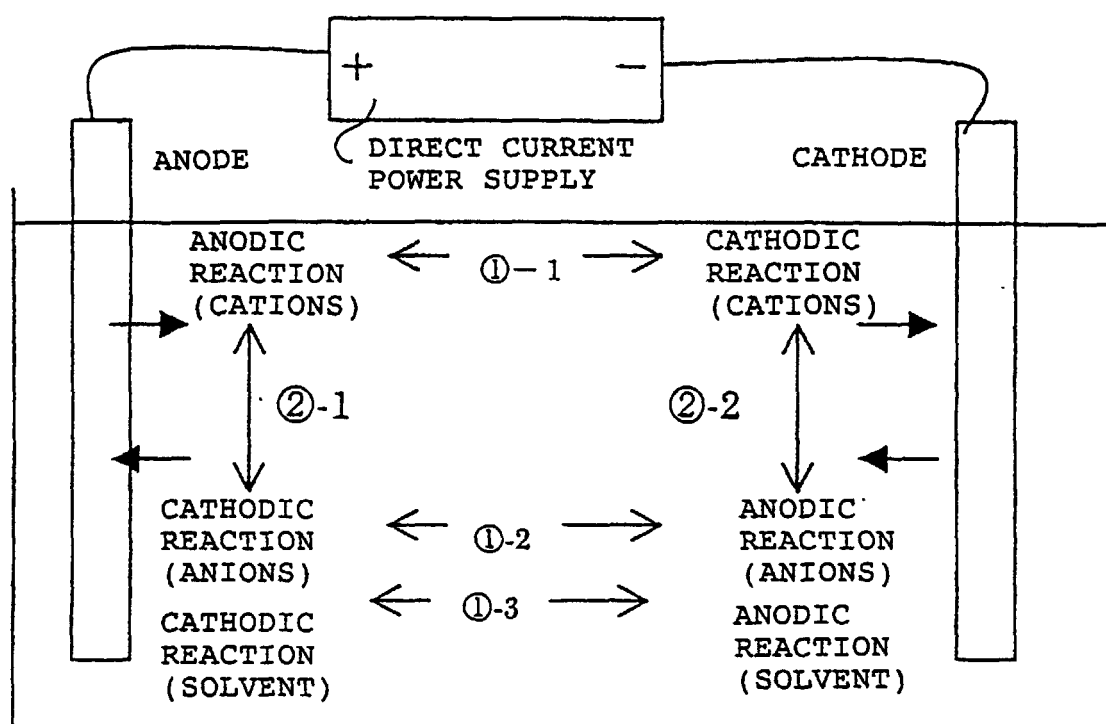


Fig. 3

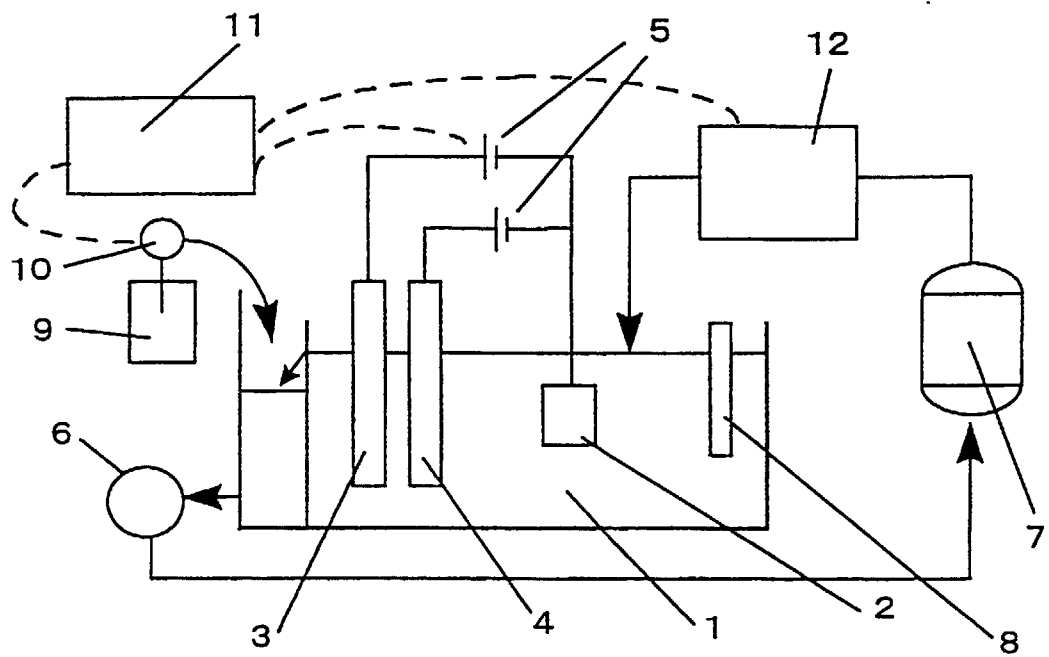


Fig. 4

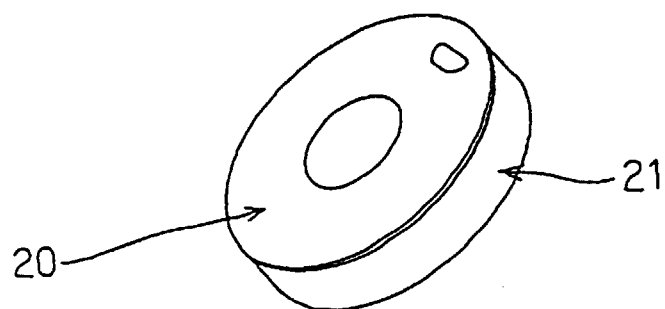


Fig. 5

—: STATOR 1, FLAT SURFACE,  
SPWx1000

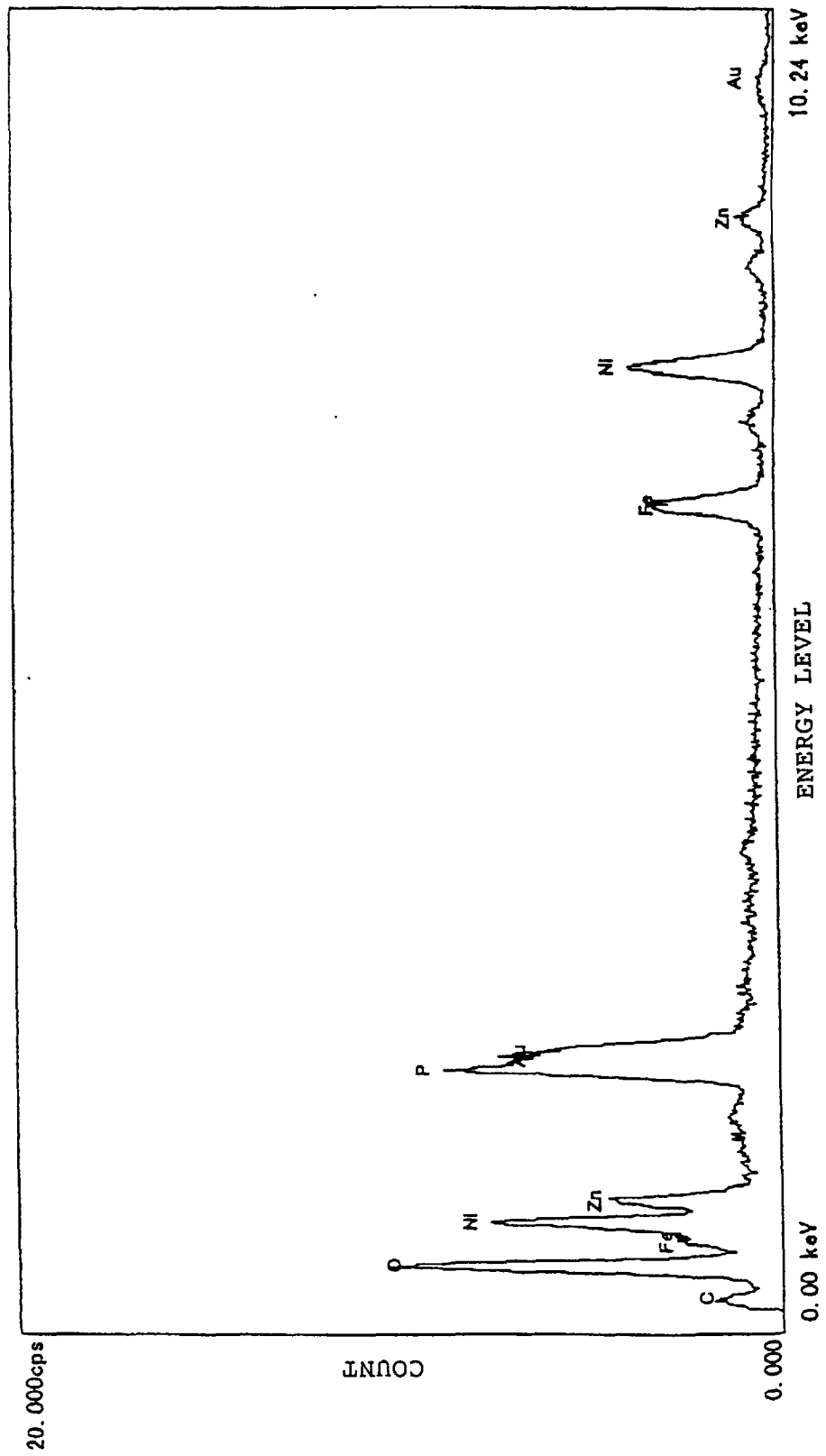


Fig.6

—: STATOR 1, OUTER PERIPHERY,  
SPWX1000

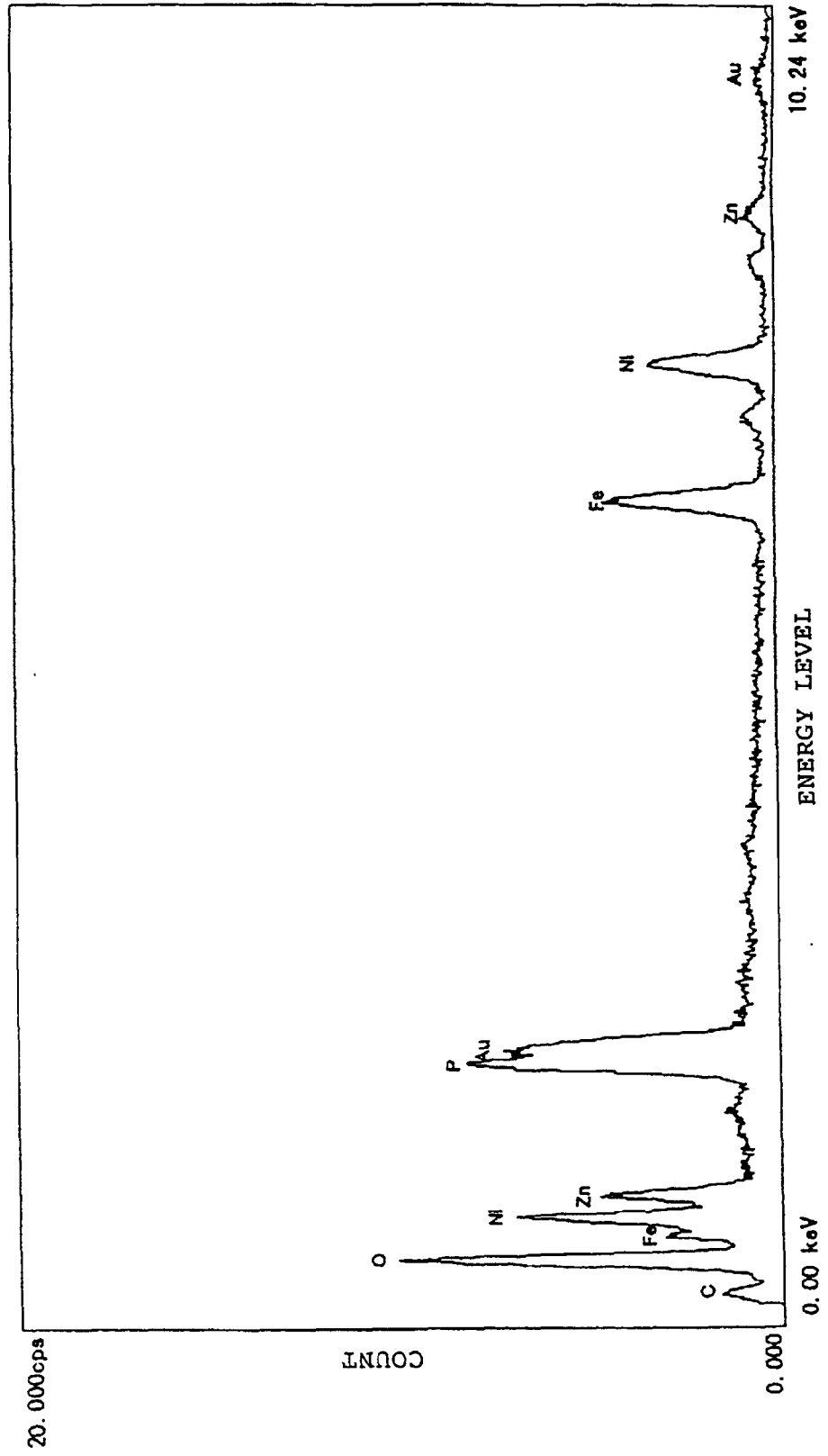


Fig.7

---: STATOR 2, FLAT SURFACE,  
SPWX1000

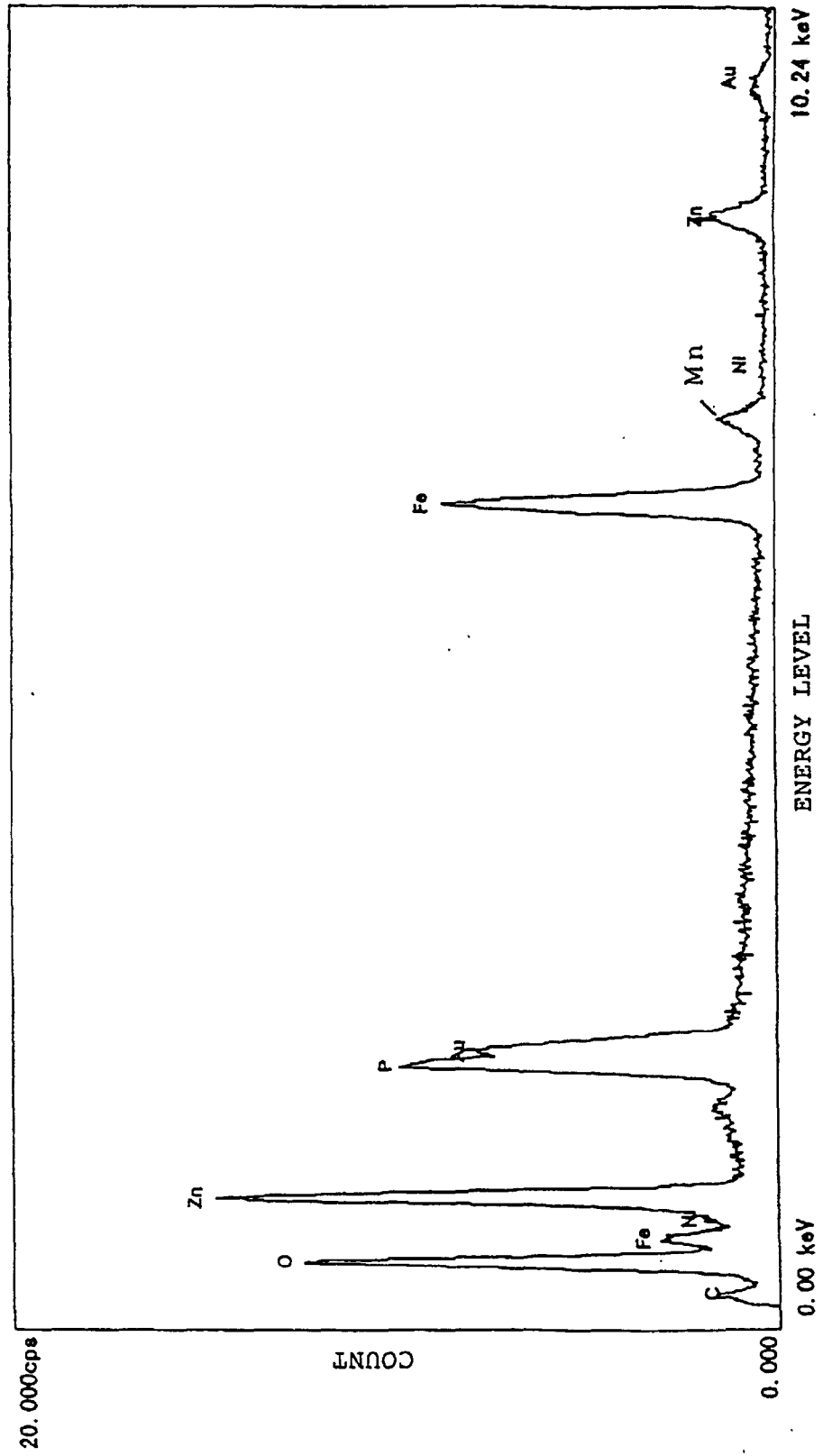


Fig. 8

—: STATOR 2, OUTER PERIPHERY,  
SPWx1000

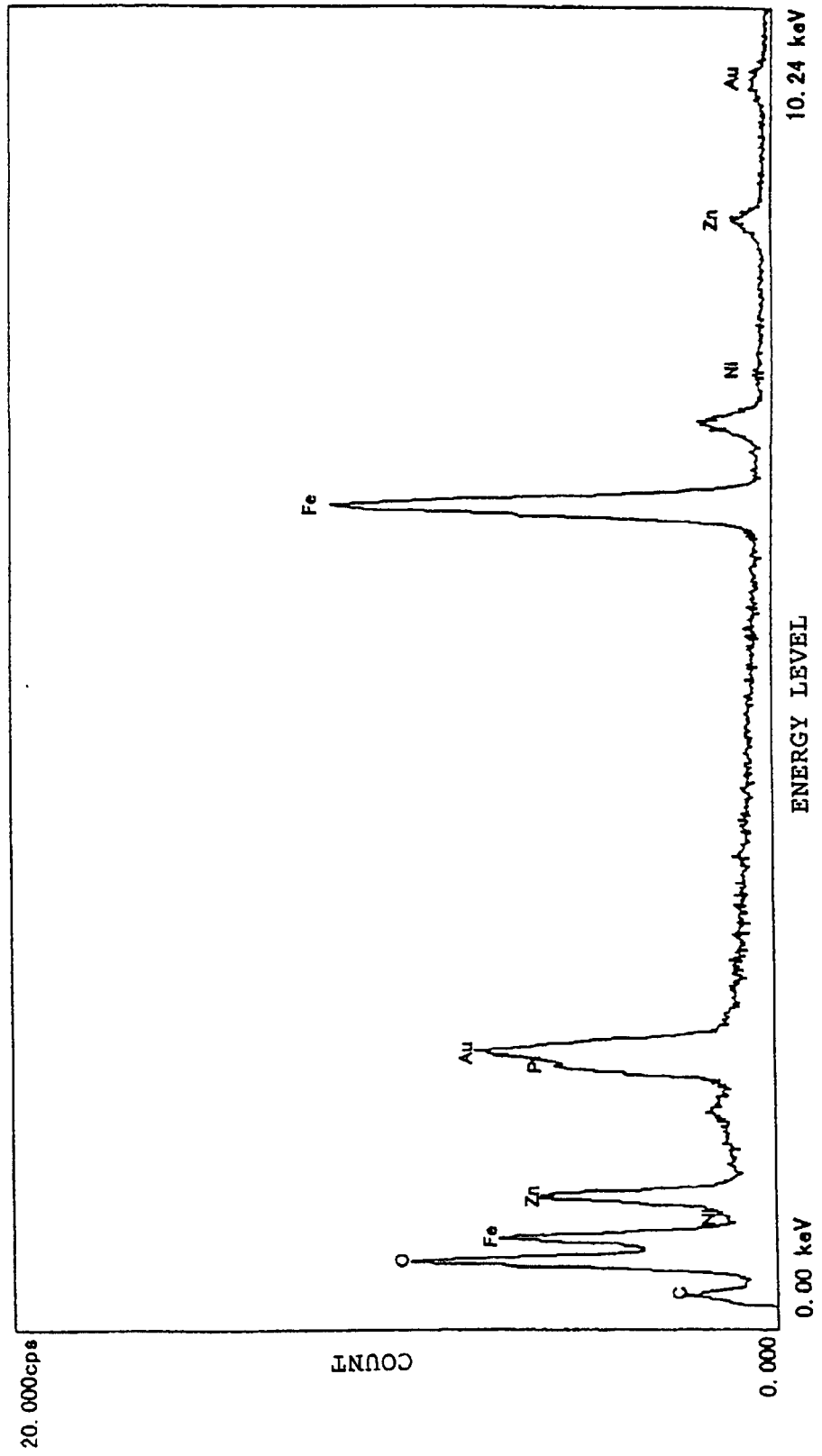


Fig.9

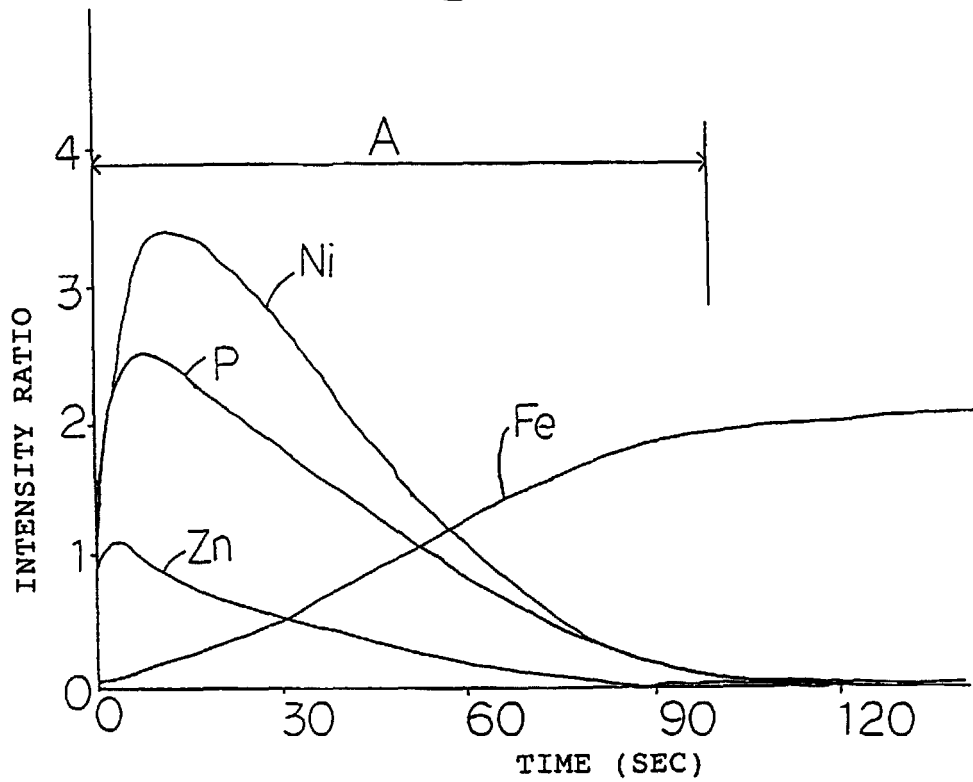


Fig.10

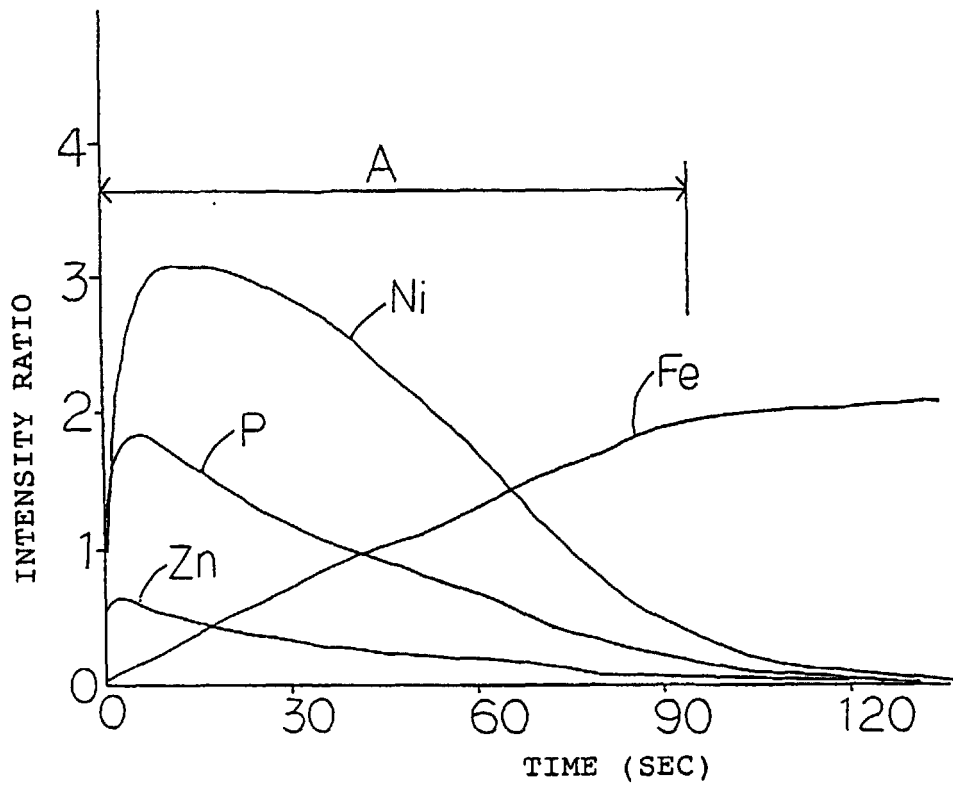




Fig.11

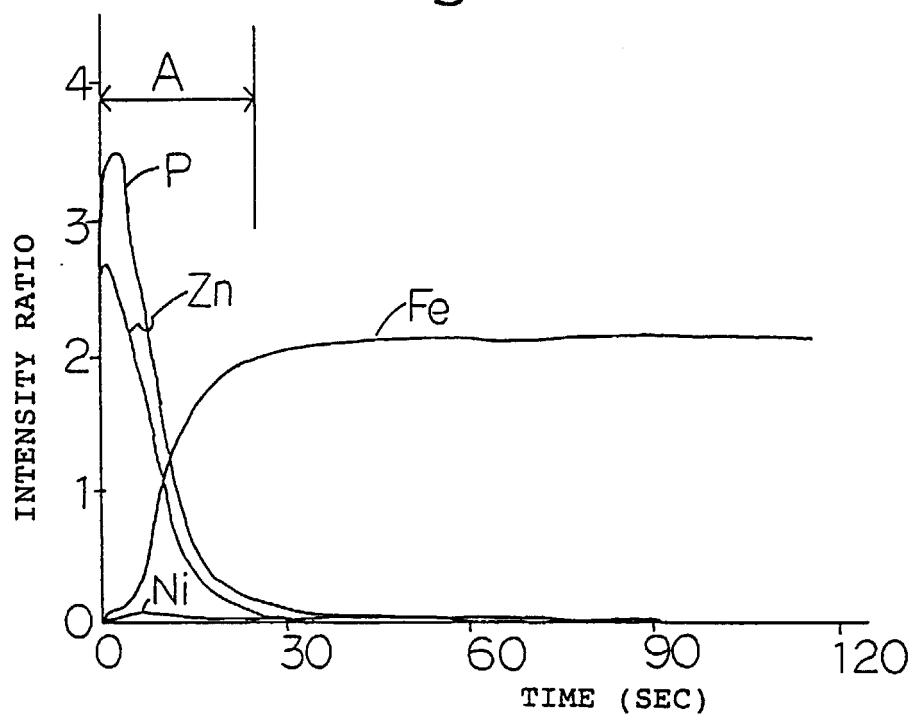


Fig.12

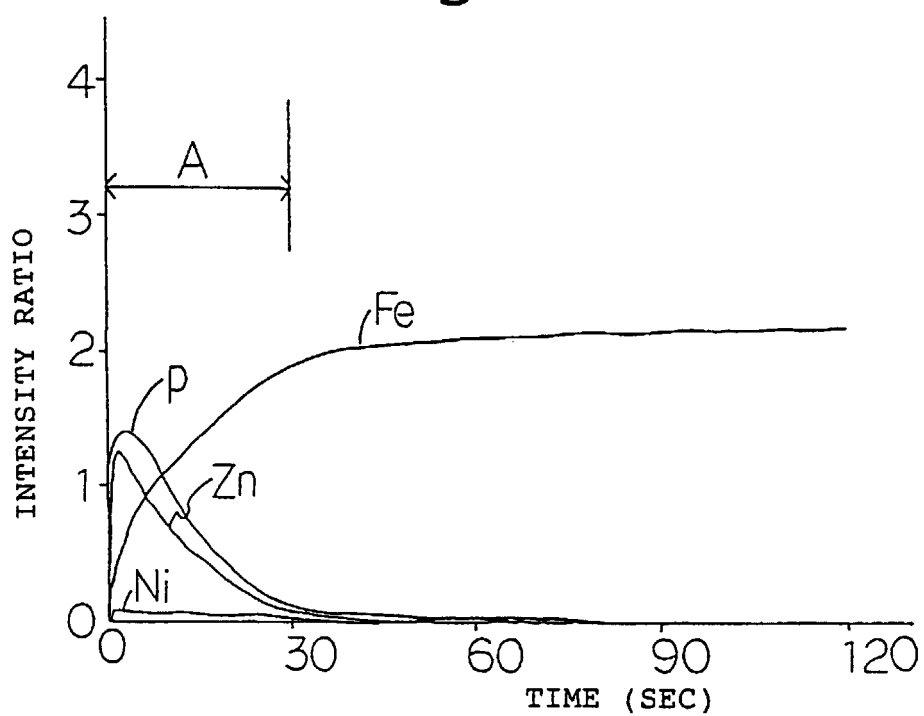


Fig.13

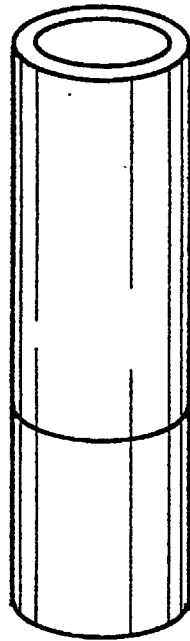


Fig.14

—: TUBE 4, SPWX1000

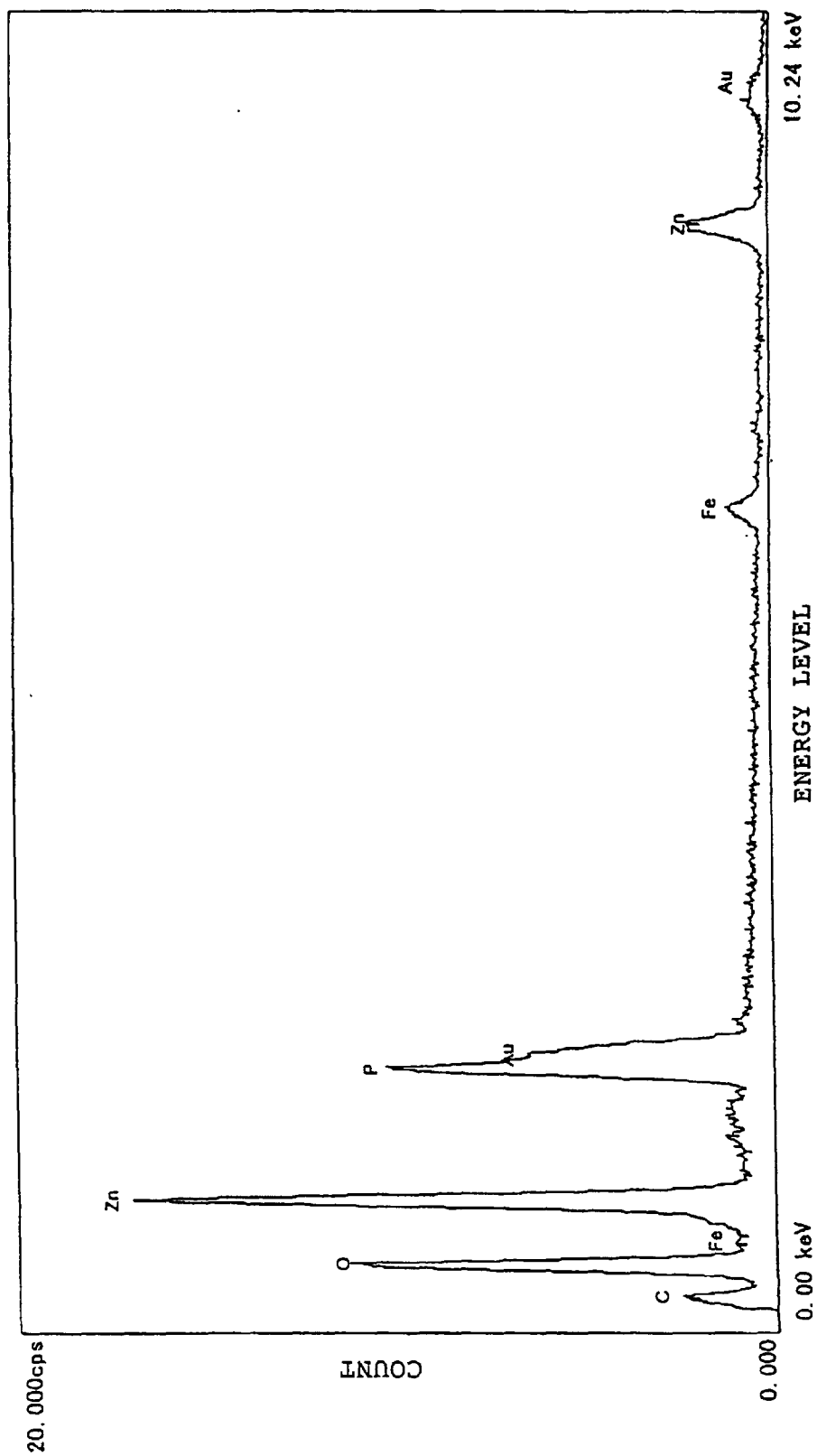


Fig.15

—: TUBE 5, SPW

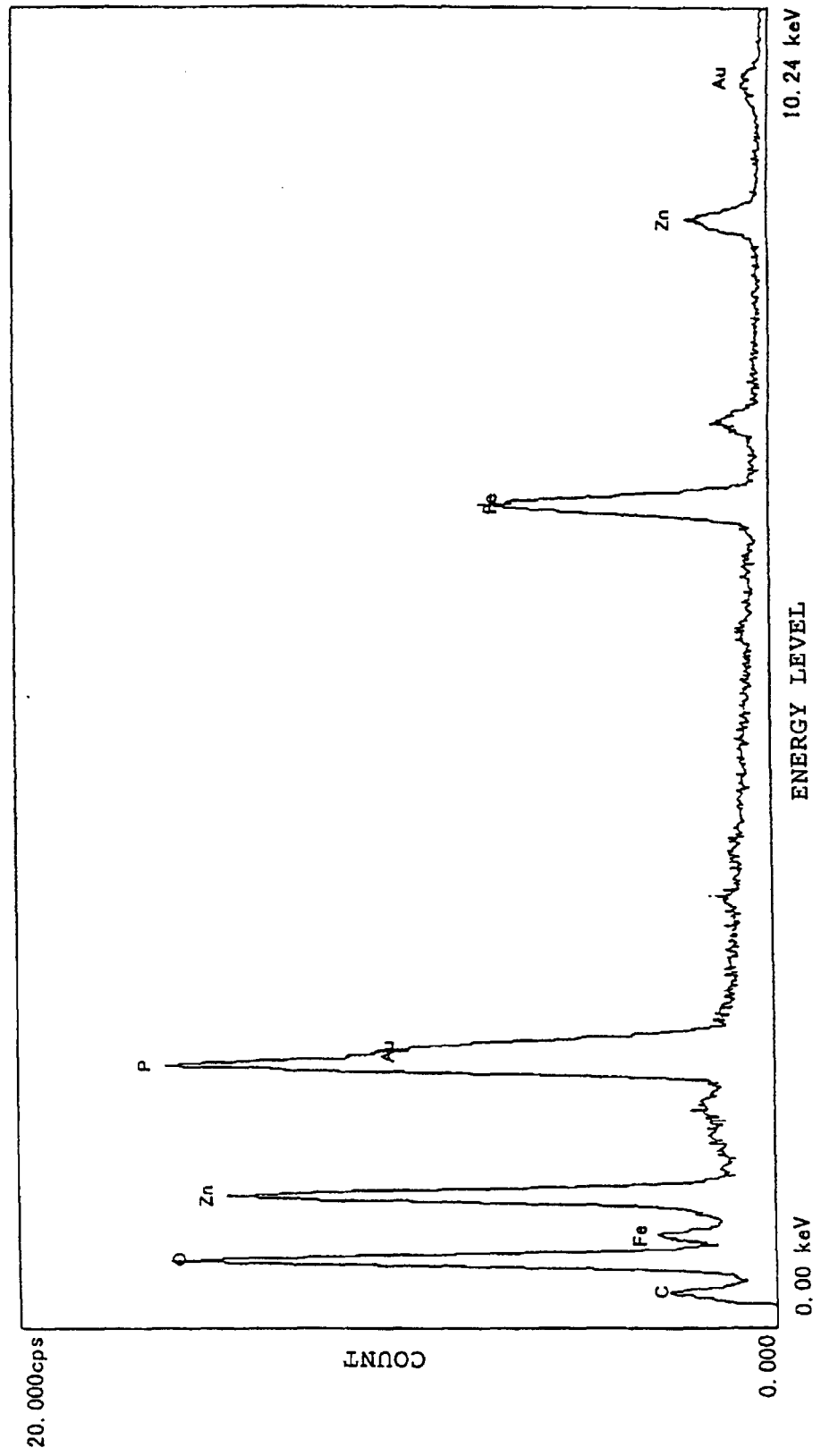


Fig.16

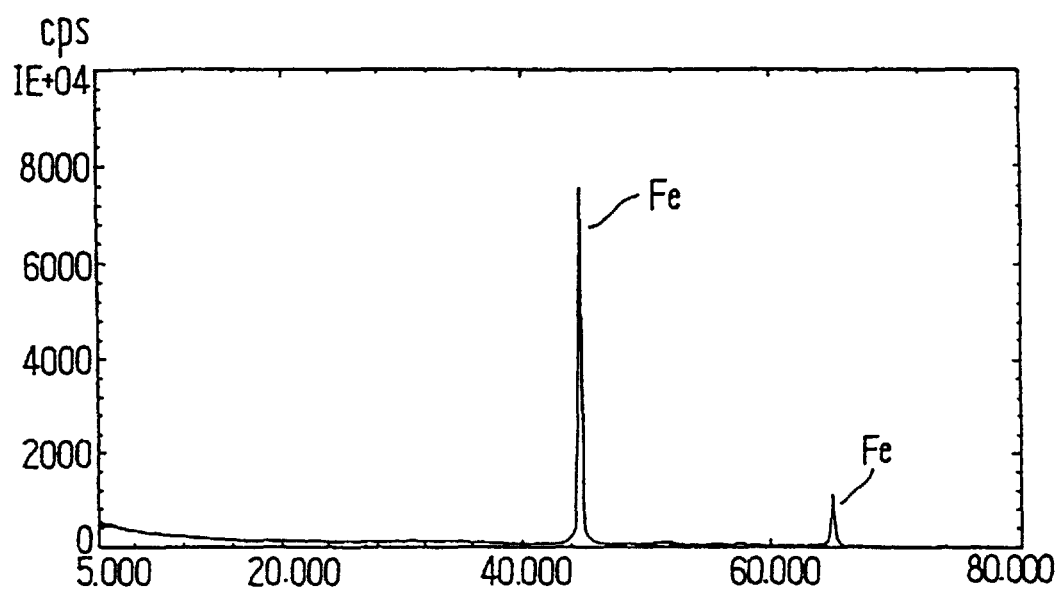


Fig.17

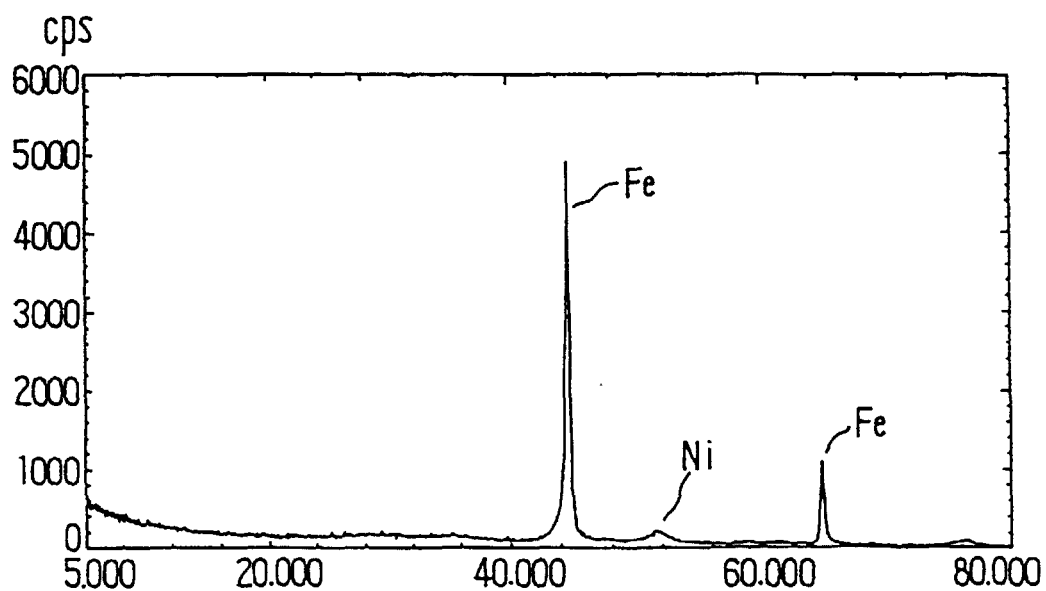


Fig.18

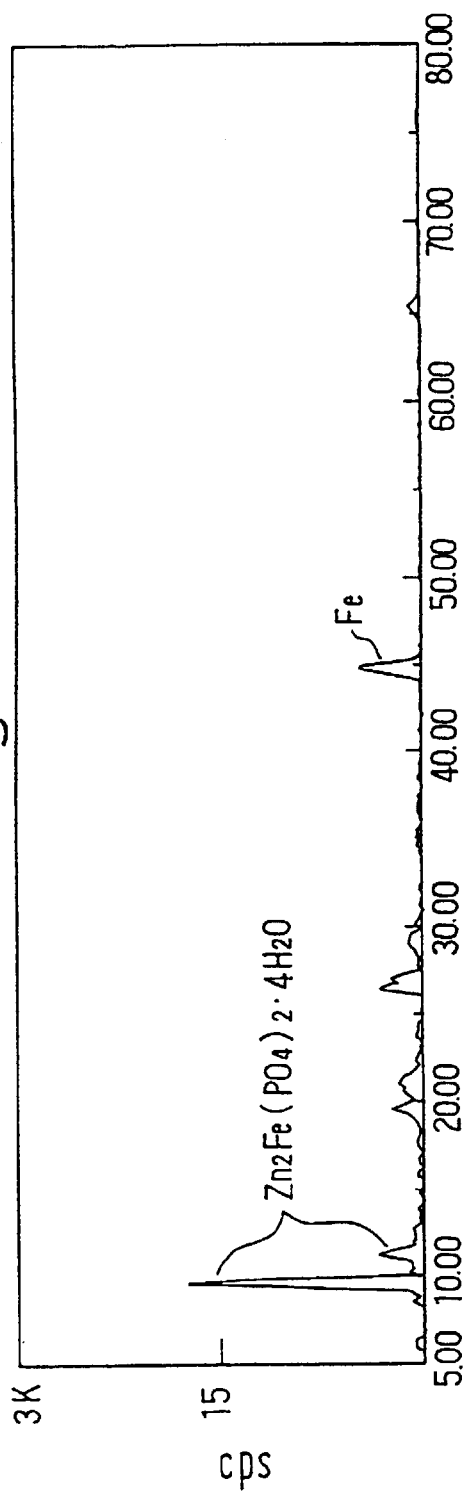


Fig.19

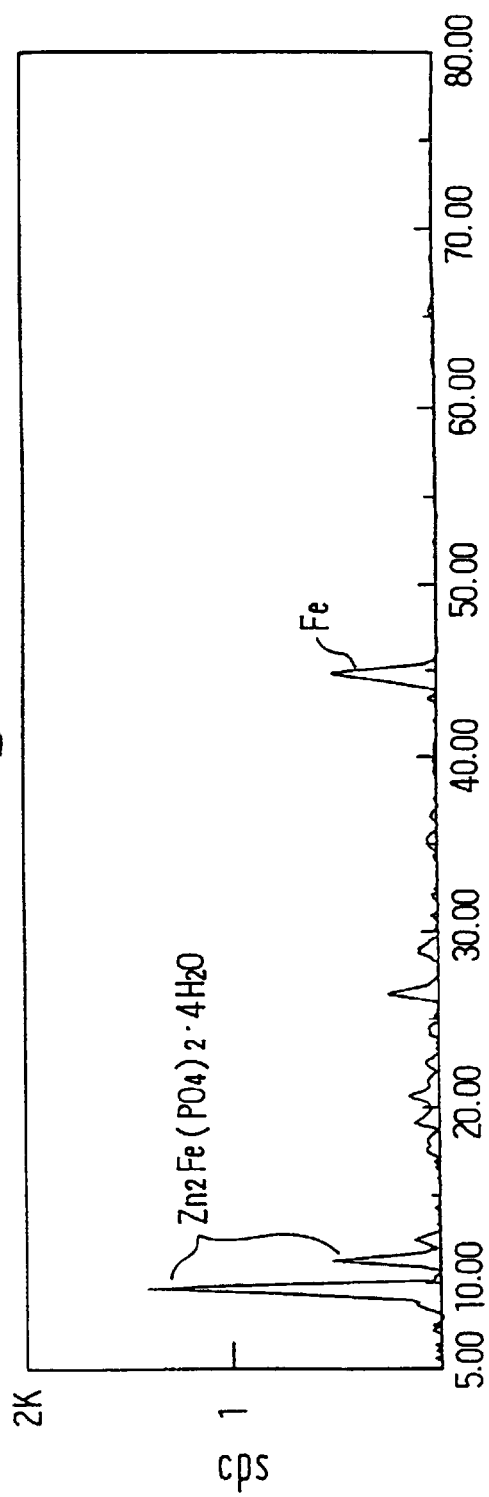


Fig.20

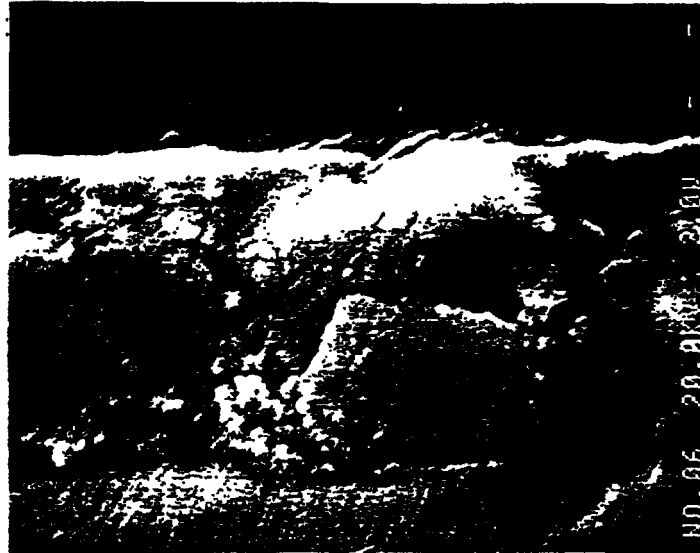


Fig.21

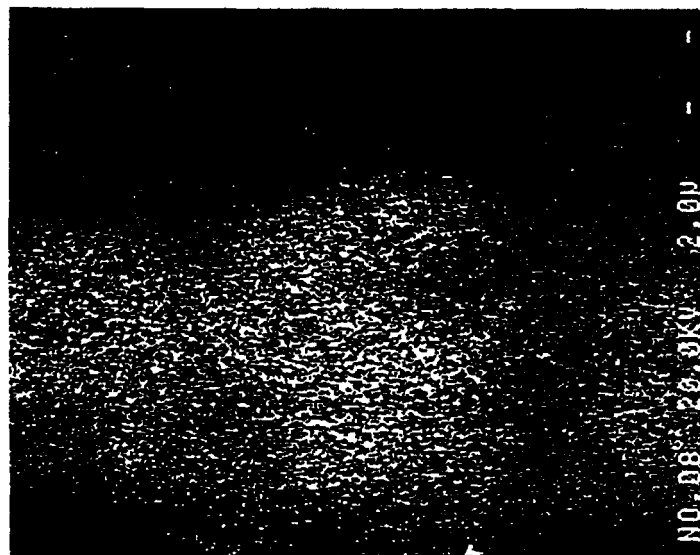


Fig.22



Fig.23

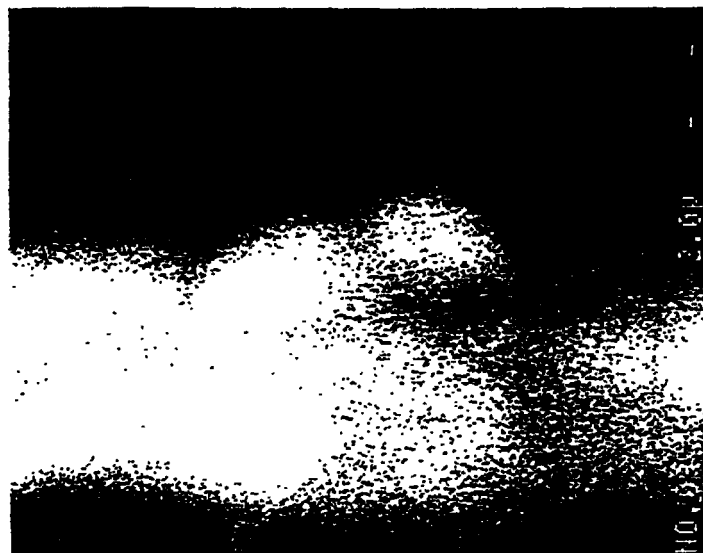




Fig.24



Fig.25



Fig.26

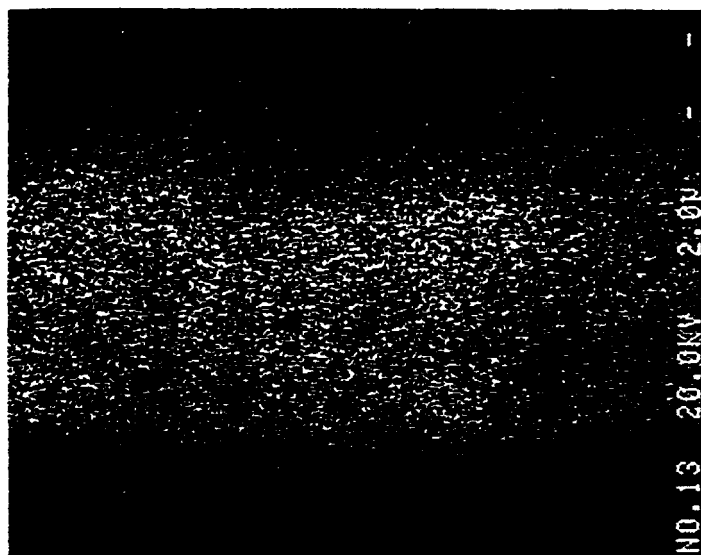


Fig.27



Fig.28

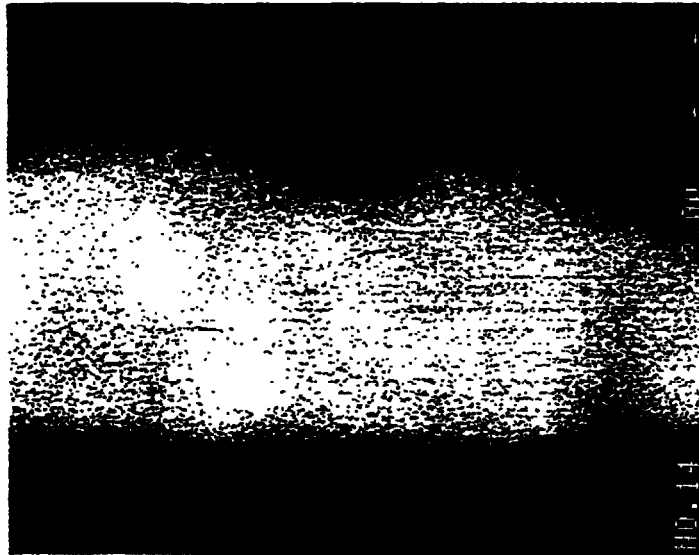
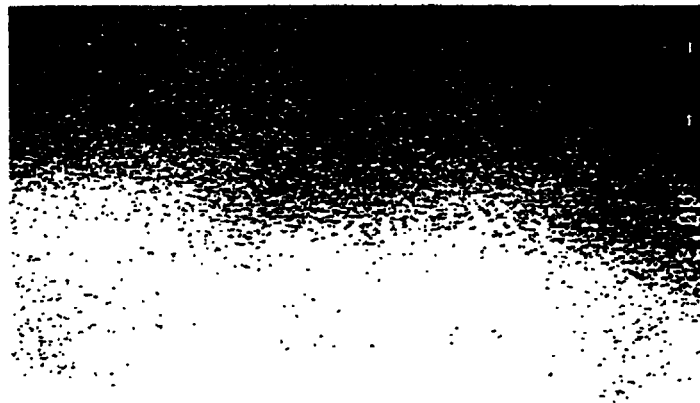


Fig.29



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP99/07124

A. CLASSIFICATION OF SUBJECT MATTER  
Int.Cl<sup>7</sup> C25D11/36

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int.Cl<sup>7</sup> C25D11/36

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho 1926-1996 Toroku Jitsuyo Shinan Koho 1994-2000

Kokai Jitsuyo Shinan Koho 1971-2000 Jitsuyo Shinan Toroku Koho 1996-2000

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO, 93/22481, A1 (Nippon Denso Co., Ltd.), 11 November, 1993 (11.11.93) & AU, 4271993, A & EP, 597131, A & DE, 69316160, C	1-40

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

\* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&amp;" document member of the same patent family

Date of the actual completion of the international search  
14 March, 2000 (14.03.00)Date of mailing of the international search report  
28 March, 2000 (28.03.00)Name and mailing address of the ISA/  
Japanese Patent Office

Authorized officer

Facsimile No.

Telephone No.