



(11) **EP 2 100 986 A1**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
16.09.2009 Bulletin 2009/38

(51) Int Cl.:
C23C 22/34 *(2006.01)* **C23C 22/78** *(2006.01)*
C23C 30/00 *(2006.01)*

(21) Application number: **09002152.8**

(22) Date of filing: **16.02.2009**

(84) Designated Contracting States:
**AT BE BG CH CY CZ DE DK EE ES FI FR GB GR
HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL
PT RO SE SI SK TR**
Designated Extension States:
AL BA RS

(30) Priority: **04.03.2008 JP 2008053227**

(71) Applicant: **Mazda Motor Corporation
Fuchu-cho
Aki-gun
Hiroshima 730-8670 (JP)**

(72) Inventors:
• **Katsura, Daiji
Aki-gun
Hiroshima 730-8670 (JP)**
• **Shigenaga, Tsutomu
Aki-gun
Hiroshima 730-8670 (JP)**

(74) Representative: **Müller-Boré & Partner
Patentanwälte
Grafinger Strasse 2
81671 München (DE)**

(54) **Chemical conversion treatment agent and surface-treated metal material**

(57) Disclosed is a chemical conversion treatment agent, which comprises: a film-forming component to form a chemical conversion film in which the number of local low-resistance areas each having an insulation resistance value of 5000 Ω or less is 20 or less/100 μm^2 ;

and at least one kind of fine particles selected from the group consisting of metal fine particles, semiconductor fine particles and electrically conductive organic fine particles.

EP 2 100 986 A1

Description

[0001] The present invention relates to a chemical conversion treatment agent and a surface-treated metal material.

[0002] A metal material, such as a galvanized steel sheet, is widely used in vehicle bodies and others. In such cases, the metal material is generally subjected to a coating process, such as a cationic electrodeposition coating process. Further, in advance of the cationic electrodeposition coating process, the metal material, i.e., a workpiece to be coated, is subjected to a chemical conversion treatment as a pretreatment. In this chemical conversion treatment, a chemical conversion treatment agent comprising a primary component of zinc phosphate (i.e., zinc phosphate-based treatment agent) is often used as a chemical conversion treatment agent. The workpiece subjected to the chemical conversion treatment using the zinc phosphate-based treatment agent makes it possible to improve the quality of an electrodeposition coating film to be obtained by the cationic electrodeposition coating process (hereinafter also referred to simply as "coating film"). That is, in the cationic electrodeposition coating process, excellent electrodeposition coatability (film thickness characteristic of a coating film) can be obtained.

[0003] However, the zinc phosphate-based treatment agent has a problem that phosphate ions thereof cause eutrophication. Moreover, the chemical conversion treatment using the zinc phosphate-based treatment agent involves a problem about production of sludge to be wasted (i.e., waste sludge). With a view to solving these problems, there has been proposed a metal oxide-type chemical conversion treatment agent which comprises: at least one selected from the group consisting of zirconium, titanium and hafnium; fluorine; and a water-soluble resin (see, for example, JP 2004-218074A (U.S. Patent Application Publication No. 20040163735)).

[0004] A chemical conversion treatment agent comprising a primary component of a zirconium compound is currently under development. This zirconium compound-based treatment agent is not only capable of solving the above problems with the zinc phosphate-based treatment agent, but also relatively excellent in terms of cost and quality.

[0005] However, when a workpiece is subjected to a chemical conversion treatment using the zirconium compound-based treatment agent, a chemical conversion film will be formed in which the number of local low-resistance areas each having an insulation resistance value of $5000\ \Omega$ or less is 20 or less/ $100\ \mu\text{m}^2$. That is, a chemical conversion film having a relatively small number of the local low-resistance areas i.e., a relatively low electrical conductivity, as compared with a chemical conversion film formed using the zinc phosphate-based treatment agent, will be formed on a surface of the workpiece.

[0006] Then, in an electrodeposition coating process, a relatively high voltage will be applied between an anode, and a portion of the workpiece adjacent to the anode (in a vehicle body, an outer panel), whereas a relatively low voltage will be applied between the anode, and a portion of the workpiece far from the anode (in the vehicle body, an inner panel), as a phenomenon specific to the electrodeposition coating process. In this situation, if a chemical conversion film having a relatively low electrical conductivity is formed on the workpiece, a deposition amount of coating film is liable to decrease in the portion of the workpiece far from the anode and belonging to a low voltage-applied region.

[0007] Therefore, a workpiece having a chemical conversion film formed using the zirconium compound-based treatment agent involves a problem that a deposition amount of coating film decreases in a portion of the workpiece far from an anode and belonging to a low voltage-applied region (in a vehicle body, an inner panel), as compared with a workpiece having a chemical conversion film formed using the zinc phosphate-based treatment agent, as will be described later (see FIG. 2).

[0008] In view of the above circumstances, it is an object of the present invention to provide a chemical conversion treatment agent capable of forming a chemical conversion film which allows a high-quality coating film to be formed by a subsequent cationic electrodeposition coating process, even if it contains a film-forming component to form only a relatively small number of local low-resistance areas in the chemical conversion film. That is, it is an object of the present invention to provide a chemical conversion treatment agent capable of improving electrodeposition coatability in a portion of a workpiece belonging to a low voltage-applied region, even if it forms a chemical conversion film having a relatively small number of local low-resistance areas.

[0009] It is another object of the present invention to provide a surface-treated metal material having a chemical conversion film formed using the above chemical conversion treatment agent.

[0010] In order to achieve the above objects, according to one aspect of the present invention, there is provided a chemical conversion treatment agent which comprises: a film-forming component to form a chemical conversion film in which the number of local low-resistance areas each having an insulation resistance value of $5000\ \Omega$ or less is 20 or less/ $100\ \mu\text{m}^2$; and at least one kind of fine particles selected from the group consisting of metal fine particles, semiconductor fine particles and electrically conductive organic fine particles.

[0011] In the first aspect of the present invention, the chemical conversion treatment agent can form a chemical conversion film which allows a high-quality coating film to be formed by a subsequent cationic electrodeposition coating process. Specifically, the chemical conversion treatment agent can form a chemical conversion film which allows a formation (deposition) of a coating film in a subsequent cationic electrodeposition coating process to be accelerated so as to improve electrodeposition coatability in a portion of a workpiece belonging to a low voltage-applied region. The

reason is considered to be that, even if a chemical conversion film having a relatively small number of local low-resistance areas is formed by the chemical conversion treatment agent, the at least one kind of fine particles selected from the group consisting of metal fine particles, semiconductor fine particles and electrically conductive organic fine particles is contained in the chemical conversion film, and the number of local electrical-conductive areas can be increased during voltage application in the electrodeposition coating process, by utilizing a tunneling effect based on the fine particles.

[0012] According to a second aspect of the present invention, there is provided a surface-treated metal material which comprises a chemical conversion film formed using a chemical conversion treatment agent. The chemical conversion treatment agent includes: a film-forming component to form a chemical conversion film in which the number of local low-resistance areas each having an insulation resistance value of $5000\ \Omega$ or less is 20 or less/ $100\ \mu\text{m}^2$; and at least one kind of fine particles selected from the group consisting of metal fine particles, semiconductor fine particles and electrically conductive organic fine particles. In the surface-treated metal material, the chemical conversion film is codeposited with the at least one kind of fine particles selected from the group consisting of metal fine particles, semiconductor fine particles and electrically conductive organic fine particles.

[0013] In the second aspect of the present invention, the surface-treated metal material can have a high-quality coating film formed by a cationic electrodeposition coating process. Specifically, the surface-treated metal material has a coating film excellent in electrodeposition coatability even in a portion of a workpiece belonging to a low voltage-applied region. The reason is considered to be that, even if a chemical conversion film formed on a surface of the surface-treated metal material has a relatively small number of local low-resistance areas, the at least one kind of fine particles selected from the group consisting of metal fine particles, semiconductor fine particles and electrically conductive organic fine particles is contained in the chemical conversion film, and the number of local electrical-conductive areas can be increased during voltage application in an electrodeposition coating process, by utilizing a tunneling effect based on the fine particles.

[0014] These and other objects, features, aspects and advantages of the invention will become more apparent upon reading the following detailed description along with the accompanying drawings.

FIG. 1 is an explanatory diagram schematically showing a cationic electrodeposition coating process.

FIG. 2 is a graph showing a film thickness characteristic of a coating film formed on each of a conventional ZrO_2 film and a zinc phosphate film.

FIG. 3 is an explanatory diagram conceptually showing low-resistance areas of a zinc phosphate film.

FIG. 4 is an explanatory diagram conceptually showing deposition of a coating film on the low-resistance areas of the zinc phosphate film.

FIG. 5 is a top plan view conceptually showing an initial stage of deposition of a coating film on the low-resistance areas of the zinc phosphate film.

FIG. 6 is a top plan view conceptually showing an intermediate stage of the deposition of the coating film on the low-resistance areas of the zinc phosphate film.

FIG. 7 is a front view conceptually showing a last stage of the deposition of the coating film on the low-resistance areas of the zinc phosphate film.

FIG. 8 is an explanatory diagram conceptually showing low-resistance areas of a ZrO_2 film.

FIG. 9 is an explanatory diagram conceptually showing deposition of a coating film on the low-resistance areas of the ZrO_2 film.

FIG. 10 is a top plan view conceptually showing an initial stage of deposition of a coating film on the low-resistance areas of the ZrO_2 film.

FIG. 11 is a top plan view conceptually showing an intermediate stage of the deposition of the coating film on the low-resistance areas of the ZrO_2 film.

FIG. 12 is a front view conceptually showing a last stage of the deposition of the coating film on the low-resistance areas of the ZrO_2 film.

FIG. 13 is a graph showing a film thickness characteristic of a coating film formed on each of a ZrO_2 film codeposited with n-type ZnO, a conventional ZrO_2 film, and a zinc phosphate film.

FIG. 14 is an explanatory diagram conceptually showing deposition of a coating film on the ZrO_2 film codeposited with n-type ZnO.

FIG. 15 is a graph showing a current density distribution during non-voltage application, in each of the conventional ZrO_2 film, and the ZrO_2 film codeposited with n-type ZnO.

FIG. 16 is a graph showing a current density distribution during voltage (1 V) application, in the conventional ZrO_2 film.

FIG. 17 is a graph showing a current density distribution during voltage (1 V) application, in the ZrO_2 film codeposited with n-type ZnO.

FIG. 18 is a table showing an influence of a content ratio of n-type ZnO (semiconductor fine particles) to the ZrO_2 film codeposited with n-type ZnO, on a film thickness characteristic (electrodeposition coatability) and corrosion resistance.

FIG. 19 is an explanatory graph showing a technique of determining an upper limit of an amount (mass%) of n-type

ZnO in view of corrosion resistance.

[0015] With reference to the drawings, the present invention will now be described based on one embodiment thereof.

[0016] Firstly, a cationic electrodeposition coating process will be described.

[0017] Typically, in a coating process for vehicles, a chemical conversion film is formed on a workpiece by a chemical conversion treatment (a surface-treated metal material is formed), and then a cationic electrodeposition coating film (undercoating film) is formed on the surface-treated metal material.

[0018] FIG. 1 is an explanatory diagram schematically showing a cationic electrodeposition coating process. As shown in FIG. 1, in the cationic electrodeposition coating process, a workpiece (e.g., vehicle body) W is firstly immersed in a cationic electrodeposition coating material (cationic electrodeposition paint) contained in a tank T. Then, a voltage is applied between the tank T and the workpiece W under a condition that the tank T and the workpiece W are set as an anode and a cathode, respectively. As a result, a coating film is formed (deposited) on a surface of the workpiece W. The cationic electrodeposition coating film can be improved in terms of electrodeposition coatability and adhesion as well as corrosion resistance by a chemical conversion film formed on a surface of the workpiece W before the cationic electrodeposition coating process.

[0019] The chemical conversion film is formed by a chemical conversion treatment using a chemical conversion treatment agent.

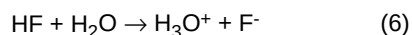
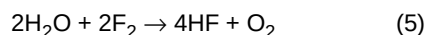
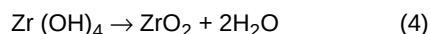
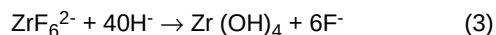
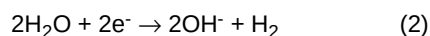
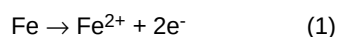
[0020] The chemical conversion treatment agent according to this embodiment of the present invention comprises: a film-forming component to form a chemical conversion film in which the number of local low-resistance areas each having an insulation resistance value of 5000 Ω or less is 20 or less/100 μm^2 ; and at least one kind of fine particles selected from the group consisting of metal fine particles, semiconductor fine particles and electrically conductive organic fine particles.

[0021] Preferably, the film-forming component contains a compound having at least one selected from the group consisting of Zr, Ti, Hf and Si, as a primary component, and further contains an etching agent, such as fluorine, and a water-soluble resin, as a secondary component. Based on this chemical conversion treatment agent, the chemical conversion film will comprise a primary component consisting of an oxide of at least one selected from the group consisting of Zr, Ti, Hf and Si.

[0022] More specifically, in this embodiment, H_2ZrF_6 as a zirconium compound is used as the primary component of the film-forming component, and a chemical conversion film comprising a primary component of a zirconium oxide (hereinafter expressed as " ZrO_2 ") will be formed on a workpiece to be coated (the chemical conversion film will hereinafter be referred to as " ZrO_2 film"). That is, the workpiece is formed as a surface-treated metal material having a ZrO_2 film on a surface thereof.

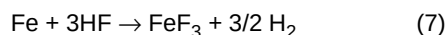
[0023] Through a chemical conversion treatment using the above chemical conversion treatment agent, the workpiece (metal blank (steel sheet)) is dissolved (etched) by acid, so that hydroxide ions will be formed on a surface of the workpiece to increase a pH value of the surface. Along with the increase in pH value, zirconium hydroxide is deposited, and converted to ZrO_2 through dehydration/condensation reactions.

[0024] For example, in the chemical conversion treatment, reactions expressed as the following reaction formulas (1) to (6) are developed:

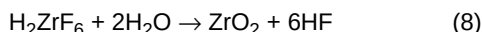


[0025] For example, the above reaction formulas can be collectively expressed as the following formulas (7) and (8):

Etching of steel sheet



Deposition of film



The reason for using the ZrO_2 film as the chemical conversion film is that the ZrO_2 film can prevent eutrophication and suppress the production of waste sludge associated with the chemical conversion treatment while ensuring corrosion resistance, as compared with a zinc phosphate film formed using a zinc phosphate-based treatment agent. More specifically, there has heretofore been known a zinc phosphate film formed using a zinc phosphate-based treatment agent, as a chemical conversion film excellent in corrosion resistance, adhesion of a coating film, etc. However, the use of the zinc phosphate film involves problems that phosphate ions of the zinc phosphate-based treatment agent cause eutrophication, and waste sludge is produced along with the chemical conversion treatment. Therefore, in this embodiment, a chemical conversion treatment agent is selected in such a manner as to form the ZrO_2 film as a chemical conversion film capable of preventing the above problems while ensuring corrosion resistance, etc. In this regard, it is known that the ZrO_2 film has a property of being formed as a continuous noncrystalline (amorphous) film, and thereby the number of local low-resistance areas each having an insulation resistance value of 5000 Ω or less tends to decrease, specifically, become 20 or less/100 μm^2 .

[0026] In this embodiment, the at least one kind of fine particles selected from the group consisting of metal fine particles, semiconductor fine particles and electrically conductive organic fine particles is contained in (codeposited with) the ZrO_2 film as the chemical conversion film formed using the chemical conversion treatment agent. The reason is that there is a need for correcting the following disadvantage of the ZrO_2 film. While the ZrO_2 film can prevent the problems about eutrophication and sludge production, a film thickness characteristic (electrodeposition coatability) of a coating film based on the ZrO_2 film itself is inferior to that of the zinc phosphate film (see FIG. 2), because the ZrO_2 film has a relatively small number of the local low-resistance areas, as mentioned above.

[0027] The present invention will be more specifically described below.

[0028] In a cationic electrodeposition coating process, as one characteristic thereof, a relatively high voltage will be applied between an anode (in FIG. 1, the tank T) and a portion of a workpiece W adjacent to the anode (in a vehicle body, an outer panel), whereas a relatively low voltage will be applied between the anode and a portion of the workpiece W far from the anode (in the vehicle body, an inner panel), as shown in FIG. 1. Thus, formation (deposition) of a cationic electrodeposition coating film is initiated from the portion of the workpiece W adjacent to the anode. The deposited coating film has electrical insulation properties, and therefore an electrical resistance of the deposited coating film becomes higher as an amount of the deposited coating film is increased along with progress of the deposition of the coating film. Consequently, the deposition of the coating film onto the portion having the deposited coating film will be gradually reduced, and instead deposition of the coating film onto a portion having no deposited coating film will be initiated.

[0029] During a course of the cationic electrodeposition coating process, as shown in FIG. 2, if a conventional ZrO_2 devoid of any of metal fine particles, semiconductor fine particles and electrically conductive organic fine particles is formed on a workpiece (e.g., cold-rolled steel sheet), a film thickness of a cationic electrodeposition coating film is liable to become excessively small in a low voltage (about zero to 70 V)-applied region, and to become excessively large in a high voltage (70 V or more)-applied region, as compared with a workpiece having a zinc phosphate film formed thereon. FIG. 2 is a graph showing a relationship between a film thickness of a cationic electrodeposition coating film and an applied voltage, in each of two types of workpieces on which a conventional ZrO_2 film and a zinc phosphate film are formed, respectively, as a chemical conversion film. In FIG 2, the vertical axis represents a film thickness (μm) of a cationic electrodeposition coating film, wherein a larger film thickness indicates a capability to obtain more excellent corrosion resistance, and the horizontal axis represents a voltage (V) to be applied to a surface-treated metal material, wherein a low voltage-applied region, i.e., a region applied with a relatively low voltage may be considered to be a portion of the workpiece (surface-treated metal material) far from an anode, e.g., an inner panel of a vehicle body, and a high voltage-applied region, i.e., a region applied with a relatively low voltage may be considered to be a portion of the workpiece adjacent to the anode, e.g., an outer panel of the vehicle body.

[0030] As seen in FIG. 2, in a portion of a workpiece adjacent to the anode and belonging to the high voltage-applied region (in a vehicle body, an outer panel), a film thickness of a coating film in the workpiece having the conventional ZrO_2 film becomes larger than that of a coating film in the workpiece having the zinc phosphate film. Further, in a portion of a workpiece far from the anode and belonging to the low voltage-applied region (in a vehicle body, an inner panel), the film thickness of the coating film in the workpiece having the conventional ZrO_2 film becomes smaller than that of the coating film in the workpiece having the zinc phosphate film. Thus, the workpiece having the conventional ZrO_2 film is inferior in throwing power of a cationic electrodeposition coating film, to the workpiece having the zinc phosphate film.

[0031] Through various researches on the above controversial phenomenon, the inventors have formulated the following hypothesis.

(1) When a surface of a steel sheet S (a surface of a workpiece W) is treated with a zinc phosphate-based treatment agent, a crystalline zinc phosphate film 1 having a large number of pointed-shaped portions lying side-by-side is formed

to define a large number of low-resistance areas (lower regions of boundary spaces between respective adjacent ones of the pointed portions) 2, as shown in FIG. 3 which is an explanatory diagram conceptually showing a configuration, etc., of the low-resistance areas of the zinc phosphate film.

[0032] Thus, electrons transfer to each of the low-resistance areas 2, so that electrolysis occurs on the surface of the steel sheet S to generate hydroxide ions, and acid giving water solubility to a coating material is neutralized by the hydroxide ions. During this process, H_2 is generated.

[0033] Based on the neutralization of the acid, a coating film F is deposited on the surface of the steel sheet S, as shown in FIG. 4 which is an explanatory diagram conceptually showing deposition of a cationic electrodeposition coating film in the low voltage-applied region of the workpiece having the zinc phosphate film formed thereon. Thus, formation of the coating film F on the surface of the steel sheet S is promoted even in a portion of the workpiece (steel sheet S) far from the anode and belonging to the low voltage-applied region.

[0034] In contrast, when a steel sheet S is subjected to a chemical conversion treatment using a zirconium compound-based treatment agent, a ZrO_2 film 21 is formed as a flat continuous noncrystalline film, as shown in FIG. 8 which is an explanatory diagram conceptually showing low-resistance areas of the conventional ZrO_2 film. Although a local low-resistance area 22 is formed in the conventional ZrO_2 film 21, the number of the local low-resistance areas 22 is extremely small. Thus, the conventional ZrO_2 film 21 has a relatively low electrical conductivity, and thereby an amount of coating film to be deposited on a portion of the workpiece (steel sheet S) far from the anode and belonging to the low voltage-applied region becomes smaller.

(2) A resistance in each of the few local low-resistance areas of the conventional ZrO_2 film 21 is greater than that in each of the low-resistance areas of the zinc phosphate film 1. Therefore, no current flows through the conventional ZrO_2 film 21 unless a certain level or more of voltage is applied thereto. Thus, as shown in FIG. 9 which is an explanatory diagram conceptually showing deposition of a cationic electrodeposition coating film in the low voltage-applied region of the workpiece (steel sheet S) having the conventional ZrO_2 film formed thereon, it is more difficult to deposit a coating film F on a portion of the workpiece far from the anode and belonging to the low voltage-applied region, as compared with the workpiece having the zinc phosphate film 1 (see FIG. 4 for comparison). That is, in the workpiece having the conventional ZrO_2 film 21, a cationic electrodeposition coating film is unlikely to be deposited on a portion of the workpiece other than the local low-resistance areas 22, as shown in FIG. 9.

(3) Further, a resistance in a maximum-resistance area (an area having a maximum film thickness of about 50 nm: see FIG 8) 23 of the conventional ZrO_2 film 21 is less than that in a maximum-resistance area (a pointed area having a maximum film thickness of about 1 to 2 nm:

see FIG. 3) 3. Therefore, in the high voltage-applied region, a coating film F is more widely deposited on the conventional ZrO_2 film 21 than on the zinc phosphate film 1. Thus, in a portion of a workpiece adjacent to the anode and belonging to the high voltage-applied region (in a vehicle body, an outer panel), a film thickness of the coating film F in the workpiece having the conventional ZrO_2 film 21 becomes fairly greater than that of a coating film in the workpiece having the zinc phosphate film 1.

[0035] FIGS. 5, 6, 10 and 11 conceptually show the above hypothesis. Specifically, FIG. 5 is an explanatory diagram conceptually showing an initial stage of deposition of a cationic electrodeposition coating film in the high voltage-applied region of the workpiece having the zinc phosphate film formed thereon, and FIG. 6 is an explanatory diagram conceptually showing an intermediate stage of the deposition of the cationic electrodeposition coating film in the high voltage-applied region of the workpiece having the zinc phosphate film formed thereon. FIG. 10 is an explanatory diagram conceptually showing an initial stage of deposition of a cationic electrodeposition coating film in the high voltage-applied region of the workpiece having the conventional ZrO_2 film formed thereon, and FIG. 11 is an explanatory diagram conceptually showing an intermediate stage of the deposition of the cationic electrodeposition coating film in the high voltage-applied region of the workpiece having the conventional ZrO_2 film formed thereon.

[0036] (4) A size (spatial size) of each of the low-resistance areas 2 of the zinc phosphate film is relatively small. Thus, electrolysis occurs in each of the low-resistance areas 2 to generate hydroxide ions, and acid giving water solubility to paint is neutralized by the hydroxide ions. During this process, H_2 is generated. That is, H_2 is continuously generated from the initial stage. Then, when a coating film F is deposited, (the space of) each of the low-resistance areas 2 is easily filled with the coating film F, as shown in FIG. 7 which is an explanatory diagram conceptually showing a last stage of the deposition of the cationic electrodeposition coating film in the high voltage-applied region of the workpiece having the zinc phosphate film formed thereon.

[0037] In contrast, each of the few low-resistance areas 22 of the conventional ZrO_2 film 21 is thinner and larger (wider) than the low-resistance area 2 of the zinc phosphate film 1. Thus, although a coating film F is deposited through concentration of electric charges in the large low-resistance area 22, generation of hydroxide ions and neutralization of acid giving water solubility to paint by the hydroxide ions (a process of generating H_2), the large low-resistance area 22 is not easily filled with the coating film F, as shown in FIG. 12 which is an explanatory diagram conceptually showing a last stage of the deposition of the cationic electrodeposition coating film in the high voltage-applied region of the workpiece having the conventional ZrO_2 film formed thereon. Therefore, a resistance is not increased along with the deposition of

the coating film on the workpiece (steel sheet S) to allow the coating film F to be continuously deposited, so that a film thickness of the coating film F becomes fairly greater than that of a coating film in the workpiece having the zinc phosphate film 1. This makes it difficult to allow electrons to transfer to a portion of the workpiece far from the anode (in a vehicle body, an inner panel) to which electrons essentially hardly transfer, and thereby no coating film is deposited thereon.

[0038] Based on the above hypothesis, the inventors have formed a chemical conversion film using the chemical conversion treatment agent according to this embodiment, in such a manner that a ZrO_2 film 21 is employed as a matrix, and at least one kind of fine particles selected from the group consisting of metal fine particles, semiconductor fine particles and electrically conductive organic fine particles is codeposited within the ZrO_2 film 21.

[0039] The reason for employing the ZrO_2 film 21 as a matrix is to ensure basic functions, such as corrosion resistance. Further, the reason for codepositing the at least one kind of fine particles selected from the group consisting of metal fine particles, semiconductor fine particles and electrically conductive organic fine particles within the ZrO_2 film 21 is to reduce a rate of ZrO_2 so as to reduce an amount of coating film F to be deposited on a portion of a workpiece adjacent to an anode (in a vehicle body, an outer panel), and increase the number of electrical-conductive areas each capable of conducting a current therethrough only when a given value or more of voltage is applied thereto, with a focus on an electron tunneling effect. Based on reducing a rate of ZrO_2 , an amount of coating film F to be deposited on a portion of a workpiece adjacent to an anode (in a vehicle body, an outer panel) can be reduced to prevent excessive deposition of the coating film F. Further, based on electrical conductivity (tunneling effect) of the at least one kind of fine particles selected from the group consisting of metal fine particles, semiconductor fine particles and electrically conductive organic fine particles, deposition of the coating film F can be promoted in a portion of the workpiece far from the anode (in a vehicle body, an inner panel). This makes it possible to allow the ZrO_2 film 21 to have a film thickness characteristic (electrodeposition coatability) of a coating film close to that based on a zinc phosphate film 1. In addition, the ZrO_2 film 21 codeposited with the at least one kind of fine particles can achieve satisfactory corrosion resistance and electrodeposition coatability, as well as being able to prevent the problems about eutrophication and sludge production.

[0040] As a specific example of the fine particles, the metal fine particles may be fine particles of at least one of Mg, Al, Ca, Co, Ni, Cu and Zn. Preferably, the semiconductor fine particles may be fine particles of an oxide semiconductor, such as ZnO or TiO_2 . Further, an oxide of Ti, Zn, etc., which exhibits semiconductor properties, may be used in the form of ions. The electrically conductive organic fine particles may be polyaniline fine particles or fine particles of a metal protected by an organic matter. The fine particles preferably have an average particle size of 40 nm or less, more preferably 20 to 40 nm.

[0041] As for the problem with the conventional ZrO_2 film that a film thickness of a coating film in a workpiece having the conventional ZrO_2 film becomes fairly larger than that of a coating film in a workpiece having the zinc phosphate film, in a portion of the workpiece adjacent to the anode and belonging to the high voltage-applied region, and becomes fairly smaller than that of the coating film in the workpiece having the zinc phosphate film, in a portion of the workpiece far from the anode and belonging to the low voltage-applied region, it is contemplated that a size of each of the low-resistance areas 22 of the conventional ZrO_2 film devoid of any of metal fine particles, semiconductor fine particles and electrically conductive organic fine particles is reduced in some way to prevent electric charges from concentrating in the low-resistance area 22.

[0042] However, if the size of each of the low-resistance areas 22 is reduced in the above manner, a thickness of the ZrO_2 film will be increased, and no coating film will be deposited unless a voltage for initiating deposition of a coating film is set at a higher value. In contrast, in the ZrO_2 film 21 codeposited with the at least one kind of fine particles selected from the group consisting of metal fine particles, semiconductor fine particles and electrically conductive organic fine particles, it is considered that, although each of the low-resistance areas 22 is relatively large, the number of electrical-conductive areas is increased during voltage application by a tunneling effect based on the at least one kind of fine particles, so as to avoid concentration of electric charges in the large low-resistance area 22. In this respect, the ZrO_2 film 21 can have a film thickness characteristic of a coating film close to that based on a zinc phosphate film 1, while preventing the aforementioned problems.

[0043] In order to verify the above hypothesis, a chemical conversion film formed using the chemical conversion treatment agent according to this embodiment, i.e., a ZrO_2 film codeposited with the at least one kind of fine particles selected from the group consisting of metal fine particles, semiconductor fine particles and electrically conductive organic fine particles, is compared with the conventional ZrO_2 film and the zinc phosphate. The following description will be made based on one example where the chemical conversion film formed using the chemical conversion treatment agent according to this embodiment is a ZrO_2 film codeposited with n-type ZnO which is semiconductor fine particles.

[0044] FIG. 13 shows a film thickness characteristic of a coating film formed on the ZrO_2 film codeposited with n-type ZnO (semiconductor fine particles), as chemical conversion film, for the purpose of supporting the above hypothesis. Specifically, FIG. 13 is a graph showing a relationship between a film thickness of a cationic electrodeposition coating film and an applied voltage, in each of three types of workpieces on which the ZrO_2 film codeposited with n-type ZnO, the conventional ZrO_2 film and the zinc phosphate film are formed, respectively, as a chemical conversion film. In FIG. 13, the vertical axis and the horizontal axis are the same as those in FIG. 2.

[0045] In this example, a content ratio of the n-type ZnO to the chemical conversion film was 5.6 mass%, and the n-type ZnO had the following composition and characteristics.

Composition: Ga-doped ZnO

Volume resistivity: 20 to 100 ($\Omega \cdot \text{cm}$)

Specific surface area: 30 to 50 (m^2/g)

Average particle size (primary particle size): 20 to 40 (nm)

[0046] The chemical conversion film containing the n-type ZnO in an amount of 5.6 mass% was formed using a chemical conversion treatment agent which has a composition consisting of 100 ppm of H_2ZrF_6 as a metal equivalent to Zr, 7 of fluorine in a mole ratio to Zr, and 50 ppm of amino group-containing alkoxysilane as a water-soluble resin, in solid concentration, with the remainder being a solvent (consisting primarily of water). Each of the conventional ZrO_2 film and the zinc phosphate film was formed using a conventional chemical conversion treatment agent.

[0047] As seen in FIG. 13, the ZrO_2 film codeposited with the n-type ZnO as the semiconductor fine particles had a film thickness characteristic (electrodeposition coatability) of a coating film close to that based on the zinc phosphate film 1. Specifically, in the case where the ZrO_2 film 21 codeposited with the n-type ZnO as the semiconductor fine particles is used as a chemical conversion film, it is considered that the number of local electrical-conductive areas are increased during voltage application (only one local electrical-conductive area is shown in FIG. 14) to promote deposition of a coating film (resin) F on a surface of a steel sheet S, as shown in FIG. 14 which is an explanatory diagram conceptually showing deposition of a cationic electrodeposition coating film in a low voltage-applied region of a workpiece (steel sheet S) having the ZrO_2 film codeposited with the n-type ZnO. In this case, an applied voltage is preferably set at a value greater than a corrosion potential (e.g., about 1 V), to increase the number of electrical-conductive areas. In FIG. 14, the reference code P indicates a coating material having water solubility given by acid.

[0048] In order to support the above hypothesis, a current density distribution on a surface of each of the conventional ZrO_2 film devoid of any of metal fine particles, semiconductor fine particles and electrically conductive organic fine particles, and the ZrO_2 film codeposited with the n-type ZnO, was measured using a scanning vibrating electrode technique (SVET). FIG. 15 is a graph showing a current density distribution during non-voltage application, in the ZrO_2 film codeposited with the n-type ZnO. In the measurement on the conventional ZrO_2 film, the same result as that in FIG. 15 was obtained. That is, in either measurement, no current was detected during non-voltage application.

[0049] FIG. 16 is a graph showing a current density distribution during voltage (1 V) application, in the conventional ZrO_2 film, and FIG. 17 is a graph showing a current density distribution during voltage (1 V) application, in the ZrO_2 film codeposited with the n-type ZnO. As seen in FIG. 16, even if a voltage of 1V was applied, no current was detected in the conventional ZrO_2 film. In contrast, as seen in FIG. 17, in response to applying a voltage of 1V, a current was detected in the ZrO_2 film codeposited with the n-type ZnO. This verified that the n-type ZnO contributes to an increase in the number of local electrical-conductive areas, so as to promote deposition of a coating film F.

[0050] Further, an influence of a content ratio of the semiconductor fine particles was checked.

[0051] FIG. 18 is a table showing an influence of a content ratio of the n-type ZnO (semiconductor fine particles) to the ZrO_2 film codeposited with the n-type ZnO, on a film thickness (electrodeposition coatability) of a coating film and corrosion resistance. As seen in FIG. 18, a film thickness (electrodeposition coatability) of a coating film becomes larger (better) along with an increase in amount (mass%) of the n-type ZnO, and a problem about corrosion resistance occurs when the amount (mass%) of the n-type ZnO is increased up to a given value or more although the corrosion resistance is in an allowable range when the amount is less than the given value. The corrosion resistance was evaluated based on measurement of a swelling rate (%) of a coating film F after 60 cycles of cyclic corrosion tests (CCTs) (1 cycle of the CCT ~ JIS K5600-7-9 cycle A x 3). Specifically, a smaller swelling rate (%) of the coating film F after 60 cycles of the CCTs indicates more excellent corrosion resistance.

[0052] Five types of chemical conversion treatment agents were used in this measurement to form chemical conversion films containing the n-type ZnO in respective amounts of zero mass%, 3.2 mass%, 5.6 mass%, 7.7 mass% and 11.3 mass%. Specifically, for example, a content of H_2ZrF_6 in the aforementioned chemical conversion treatment agent for forming the chemical conversion film containing the n-type ZnO in an amount of 5.6 mass% was changed to allow a content of the n-type ZnO to be set at each of the above values.

[0053] FIG. 19 is a graph showing a content ratio of the semiconductor fine particles and a coating-film swelling rate, in a workpiece on which the ZrO_2 film codeposited with the n-type ZnO as the semiconductor fine particles is formed. In FIG. 19, the vertical axis represents a coating-film swelling rate (%) after 60 cycles of the CCTs (1 cycle of the CCT ~ JIS K5600-7-9 cycle A x 3), and horizontal axis represents a content ratio (mass%) of the n-type ZnO to the ZrO_2 film codeposited with the n-type ZnO. That is, FIG. 19 shows a technique of determining an upper limit of an amount (mass%) of the n-type ZnO in view of corrosion resistance. Specifically, the relationship between the amount (mass%) of the n-type ZnO and the coating-film swelling rate (%) after 60 cycles of the CCTs in FIG. 18 is plotted in FIG. 19, and an upper limit of the amount (mass%) of the n-type ZnO is determined based on a coating-film swelling rate of 30 (%) which is used as an allowable limit (reference value) of corrosion resistance. In this case, a coating-film swelling rate of 30 (%) is used as an allowable limit (reference value) of corrosion resistance. This is based on the following reason. A 12-year

warranty against a rust hole of an outer panel of a vehicle body becomes mainstream, and it has been confirmed by past records that the warranty is satisfied when the coating-film swelling rate is less than 30 (%). As seen in FIG. 19, the amount (mass%) of the n-type ZnO at the allowable limit of corrosion resistance is 8.2 mass%. That is, it is necessary to set the amount of the n-type ZnO at 8.2 mass% or less in order to ensure corrosion resistance.

[0054] Although the above description has been made based on one example where the fine particles are the semiconductor fine particles, the same effects could be obtained using metal fine particles or electrically conductive organic fine particles. Specifically, as with the ZrO_2 film codeposited with the n-type ZnO as the semiconductor fine particles, a workpiece having a ZrO_2 film codeposited with the metal fine particles or electrically conductive organic fine particles allowed a high-quality coating film to be formed by a subsequent cationic electrodeposition coating process. That is, a formation (deposition) of a coating film in a subsequent cationic electrodeposition coating process can be accelerated to improve electrodeposition coatability in a portion of a workpiece belonging to the low voltage-applied region. Further, the metal fine particles or the electrically conductive organic fine particles had the same desirable range of the content ratio as that of the semiconductor fine particles. Specifically, when an amount of the metal fine particles or the electrically conductive organic fine particles is set at 8.2 mass% or less, a content ratio (volume%) of the metal fine particles or the electrically conductive organic fine particles to a chemical conversion film can be set to be equal to or less than a content ratio (volume%) of the n-type ZnO to the chemical conversion film, so as to ensure corrosion resistance.

[0055] As mentioned above in detail, according to a first aspect of the present invention, there is provided a chemical conversion treatment agent which comprises: a film-forming component to form a chemical conversion film in which the number of local low-resistance areas each having an insulation resistance value of $5000\ \Omega$ or less is 20 or less/100 μm^2 ; and at least one kind of fine particles selected from the group consisting of metal fine particles, semiconductor fine particles and electrically conductive organic fine particles.

[0056] In the first aspect of the present invention, the chemical conversion treatment agent can form a chemical conversion film which allows a high-quality coating film to be formed by a subsequent cationic electrodeposition coating process. Specifically, the chemical conversion treatment agent can form a chemical conversion film which allows a formation (deposition) of a coating film in a subsequent cationic electrodeposition coating process to be accelerated so as to improve electrodeposition coatability in a portion of a workpiece belonging to a low voltage-applied region. The reason is considered to be that, even if a chemical conversion film having a relatively small number of local low-resistance areas is formed by the chemical conversion treatment agent, the at least one kind of fine particles selected from the group consisting of metal fine particles, semiconductor fine particles and electrically conductive organic fine particles is contained in the chemical conversion film, and the number of local electrical-conductive areas can be increased during voltage application in the electrodeposition coating process, by utilizing a tunneling effect based on the fine particles.

[0057] Preferably, in the chemical conversion treatment agent of the present invention, the film-forming component contains, as a primary component, a compound having at least one selected from the group consisting of Zr, Ti, Hf and Si. Although a chemical conversion film formed using this film-forming component has a relatively small number of the local low-resistance areas, the film-forming component allows the chemical conversion film to have properties capable of preventing eutrophication and suppressing sludge production associated with the chemical conversion treatment while ensuring corrosion resistance. More preferably, the film-forming component contains H_2ZrF_6 .

[0058] Preferably, in the chemical conversion treatment agent of the present invention, the fine particles have an average primary particle size of 20 to 40 nm. In this case, the above advantages can be effectively obtained.

[0059] According to a second aspect of the present invention, there is provided a surface-treated metal material which comprises a chemical conversion film formed using a chemical conversion treatment agent. The chemical conversion treatment agent includes: a film-forming component to form a chemical conversion film in which the number of local low-resistance areas each having an insulation resistance value of $5000\ \Omega$ or less is 20 or less/100 μm^2 ; and at least one kind of fine particles selected from the group consisting of metal fine particles, semiconductor fine particles and electrically conductive organic fine particles. In the surface-treated metal material, the chemical conversion film is codeposited with the at least one kind of fine particles selected from the group consisting of metal fine particles, semiconductor fine particles and electrically conductive organic fine particles.

[0060] In the second aspect of the present invention, the surface-treated metal material can have a high-quality coating film formed by a cationic electrodeposition coating process. Specifically, the surface-treated metal material has a coating film excellent in electrodeposition coatability even in a portion of a workpiece belonging to a low voltage-applied region. The reason is considered to be that, even if a chemical conversion film formed on a surface of the surface-treated metal material has a relatively small number of local low-resistance areas, the at least one kind of fine particles selected from the group consisting of metal fine particles, semiconductor fine particles and electrically conductive organic fine particles is contained in the chemical conversion film, and the number of local electrical-conductive areas can be increased during voltage application in an electrodeposition coating process, by utilizing a tunneling effect based on the fine particles.

[0061] Preferably, in the surface-treated metal material of the present invention, the chemical conversion film includes an oxide which has, as a primary component, at least one element selected from the group consisting of Zr, Ti, Hf and Si. Although the chemical conversion film has a relatively small number of the local low-resistance areas, the above

component allows the chemical conversion film to have properties capable of preventing eutrophication and suppressing sludge production associated with the chemical conversion treatment while ensuring corrosion resistance.

[0062] Preferably, in the surface-treated metal material of the present invention, the fine particles are contained in the chemical conversion film in an amount of 8.2 mass% or less with respect to 100 mass% of the chemical conversion film.

The fine particles contained in the chemical conversion film makes it possible to improve electrodeposition coatability in a portion of a workpiece belonging to a low voltage-applied region, while reliably preventing corrosion resistance from deteriorating beyond an allowable limit.

[0063] Preferably, in the surface-treated metal material of the present invention, the chemical conversion film comprises a primary component consisting of ZrO_2 . This makes it possible to provide a surface-treated metal material having a chemical conversion film comprising a more embodied primary component.

[0064] This application is based on Japanese Patent application No. 2008-053227 filed in Japan Patent Office on March 4, 2008, the contents of which are hereby incorporated by reference.

[0065] Although the present invention has been fully described by way of example with reference to the accompanying drawings, it is to be understood that various changes and modifications will be apparent to those skilled in the art. Therefore, unless otherwise such changes and modifications depart from the scope of the present invention hereinafter defined, they should be construed as being included therein.

Claims

1. A chemical conversion treatment agent comprising:

a film-forming component to form a chemical conversion film in which the number of local low-resistance areas each having an insulation resistance value of $5000\ \Omega$ or less is 20 or less/ $100\ \mu\text{m}^2$; and
at least one kind of fine particles selected from the group consisting of metal fine particles, semiconductor fine particles and electrically conductive organic fine particles.

2. The chemical conversion treatment agent as defined in claim 1, wherein the film-forming component contains, as a primary component, a compound having at least one selected from the group consisting of Zr, Ti, Hf and Si.

3. The chemical conversion treatment agent as defined in claim 1 or 2, wherein the film-forming component contains H_2ZrF_6 .

4. The chemical conversion treatment agent as defined in any one of claims 1 to 3, wherein the fine particles have an average primary particle size of 20 to 40 nm.

5. A surface-treated metal material comprising a chemical conversion film (21) formed using a chemical conversion treatment agent, the chemical conversion treatment agent including: a film-forming component to form a chemical conversion film in which the number of local low-resistance areas each having an insulation resistance value of $5000\ \Omega$ or less is 20 or less/ $100\ \mu\text{m}^2$; and at least one kind of fine particles selected from the group consisting of metal fine particles, semiconductor fine particles and electrically conductive organic fine particles, wherein the chemical conversion film (21) is codeposited with the at least one kind of fine particles selected from the group consisting of metal fine particles, semiconductor fine particles and electrically conductive organic fine particles.

6. The surface-treated metal material as defined in claim 5, wherein the chemical conversion film (21) includes an oxide which has, as a primary component, at least one element selected from the group consisting of Zr, Ti, Hf and Si.

7. The surface-treated metal material as defined in claim 5 or 6, wherein the fine particles are contained in the chemical conversion film in an amount of 8.2 mass% or less with respect to 100 mass% of the chemical conversion film.

8. The surface-treated metal material as defined in any one of claims 5 to 7, wherein the chemical conversion film (21) comprises a primary component consisting of ZrO_2 .

FIG.1

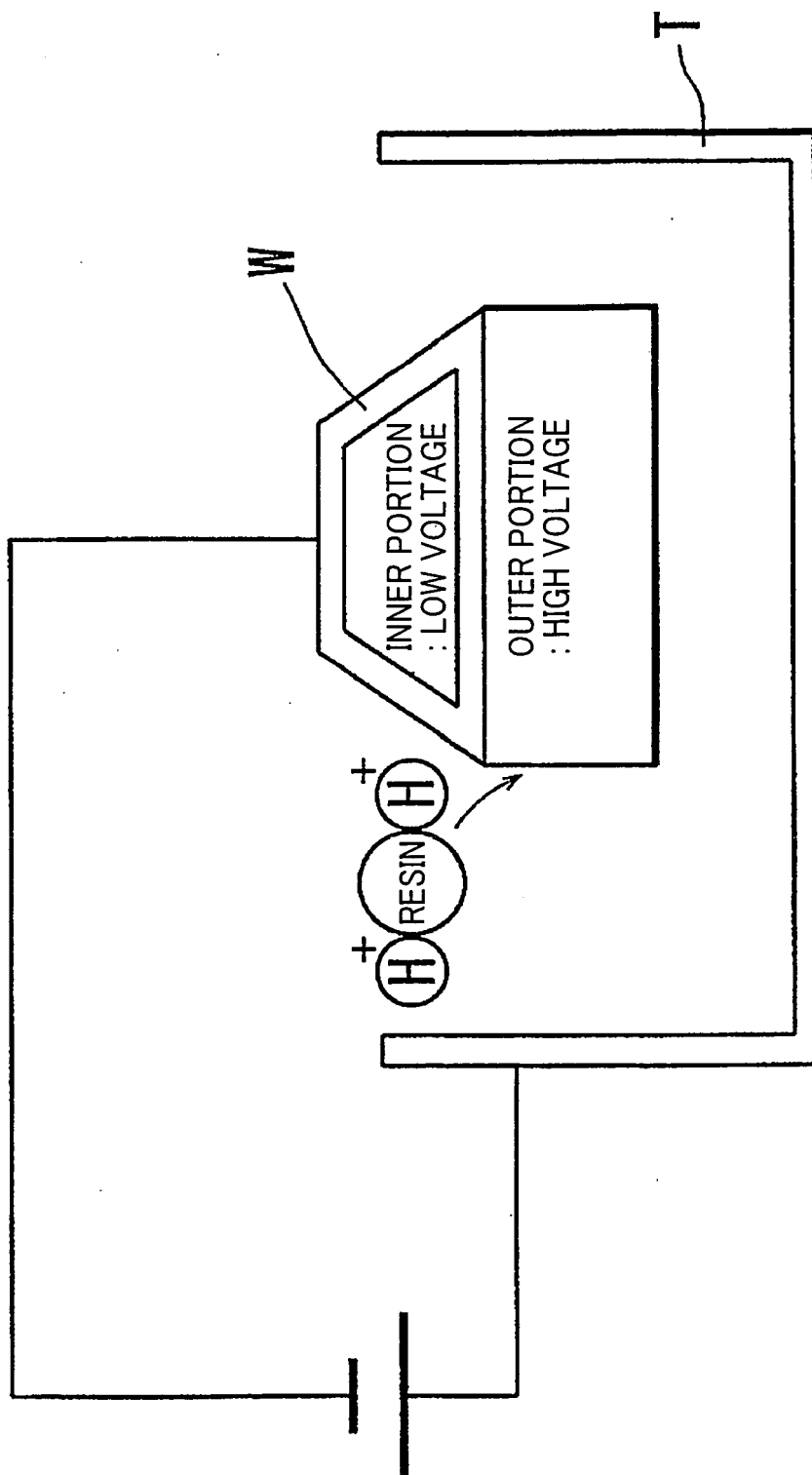


FIG.2

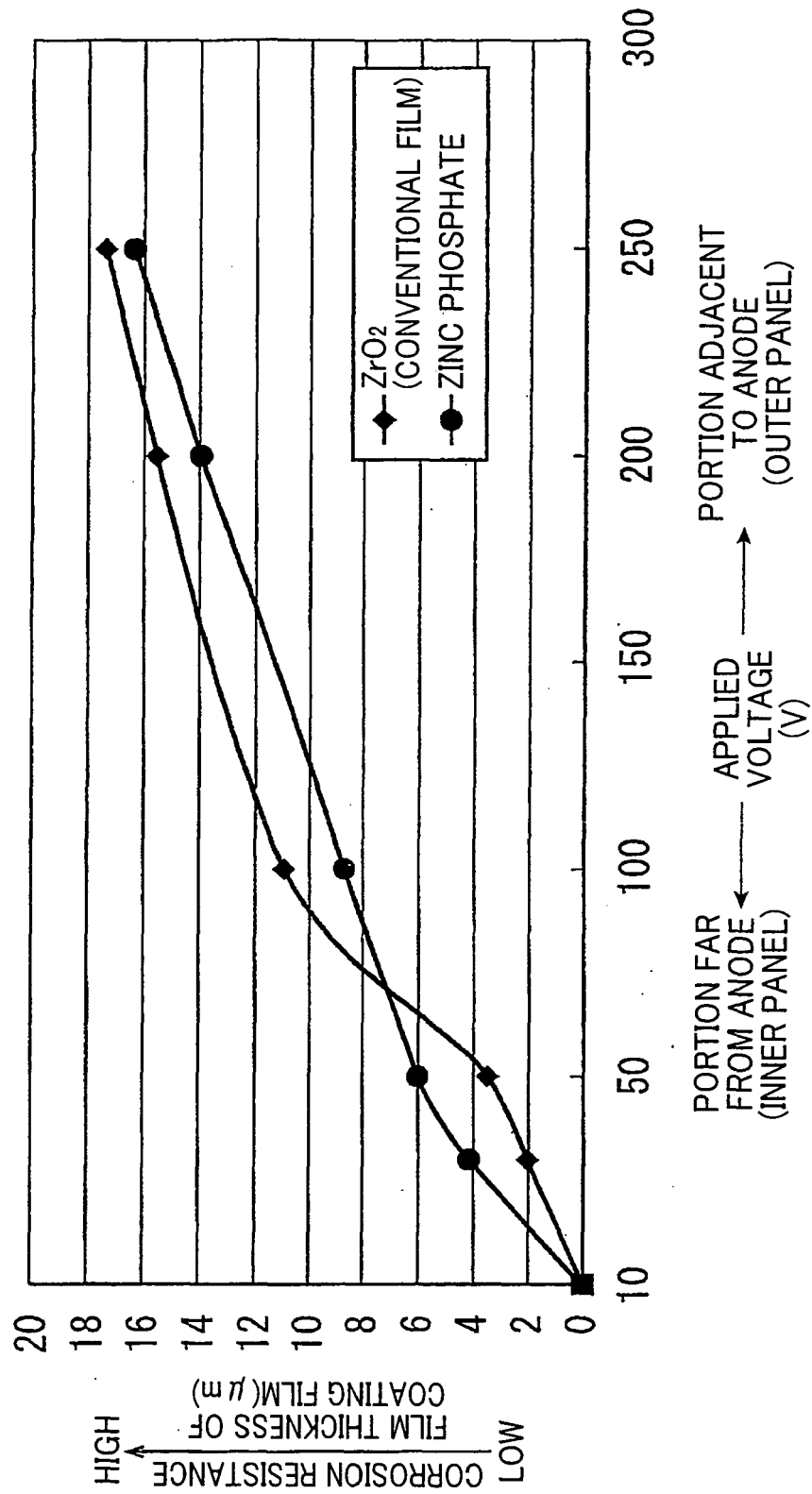


FIG.3

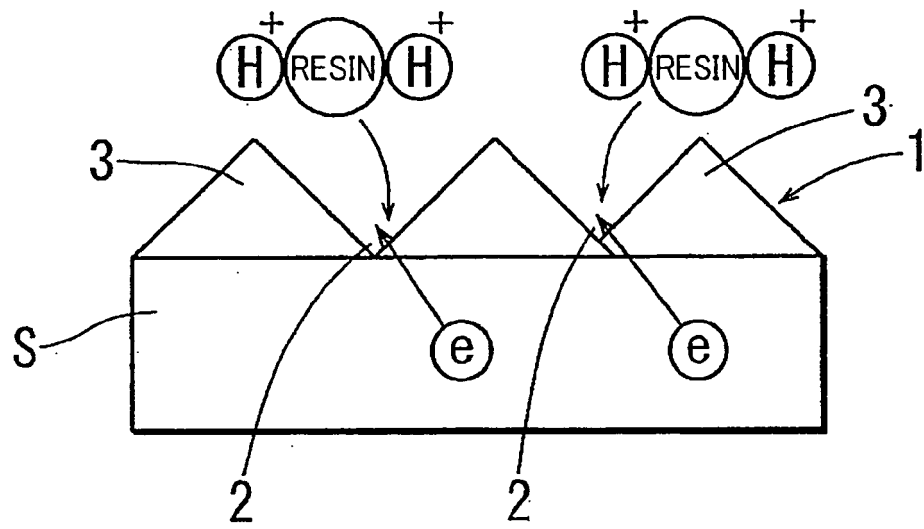


FIG.4

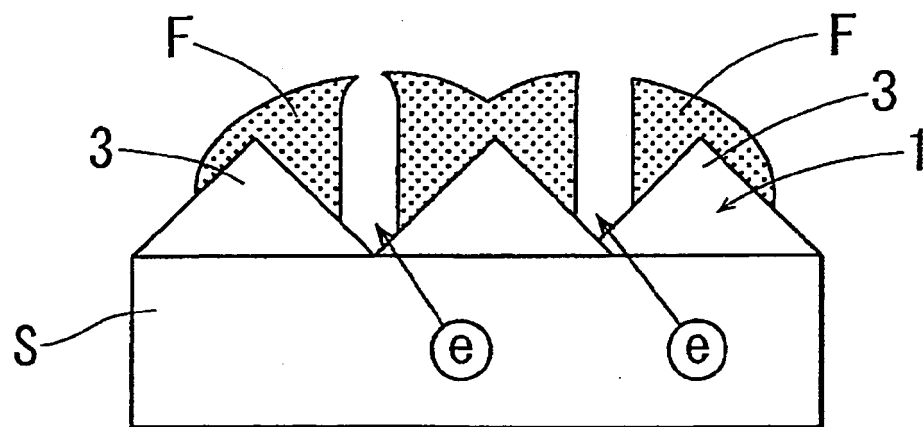


FIG.5

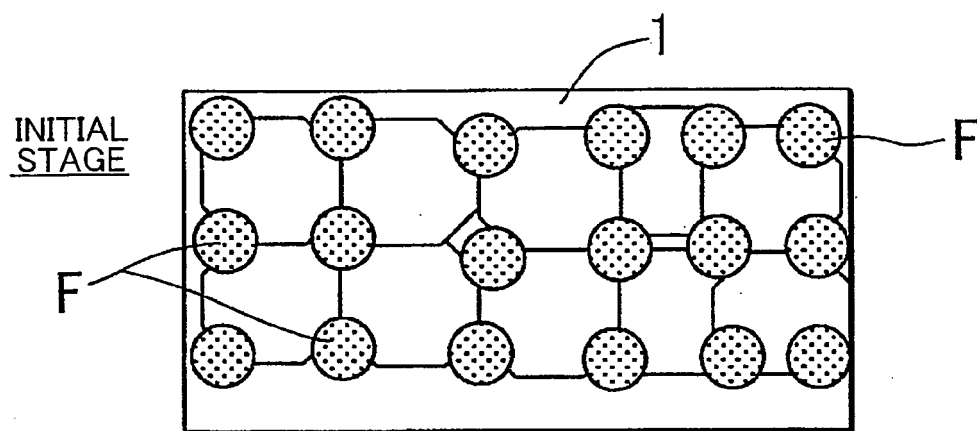


FIG.6

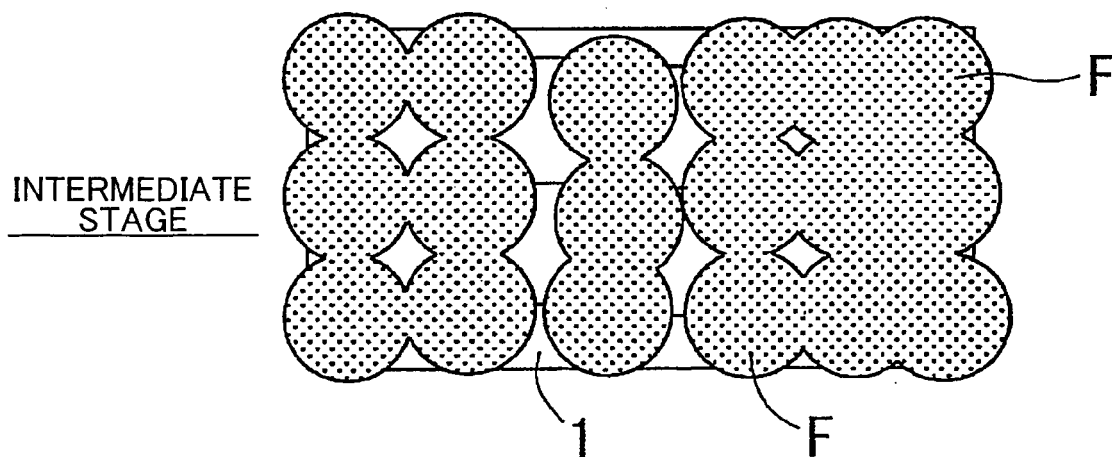


FIG.7

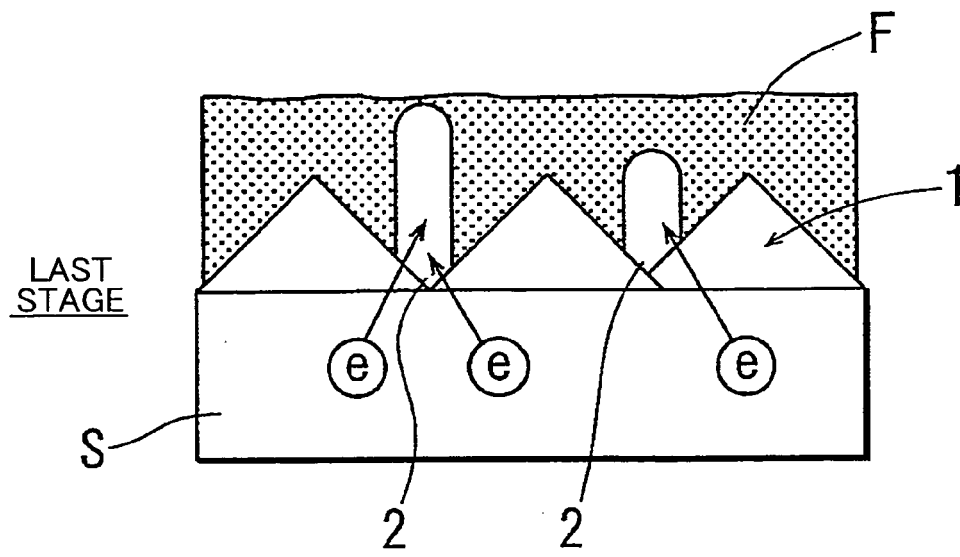


FIG.8

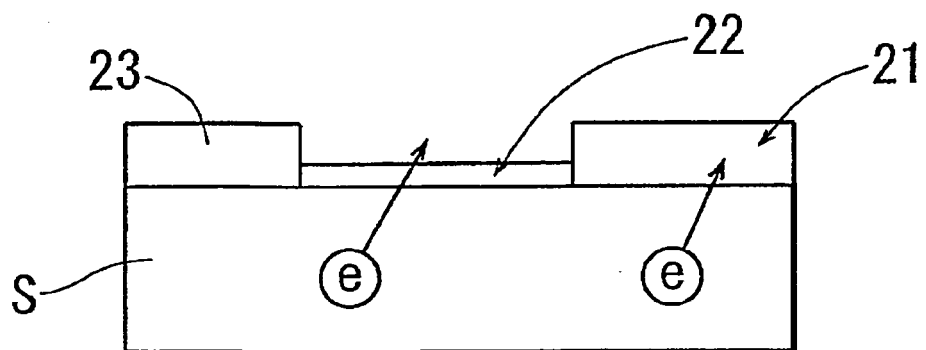


FIG.9

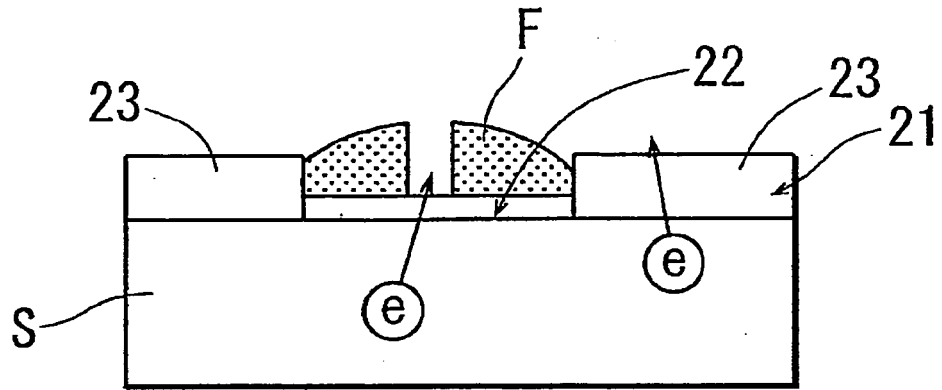


FIG.10

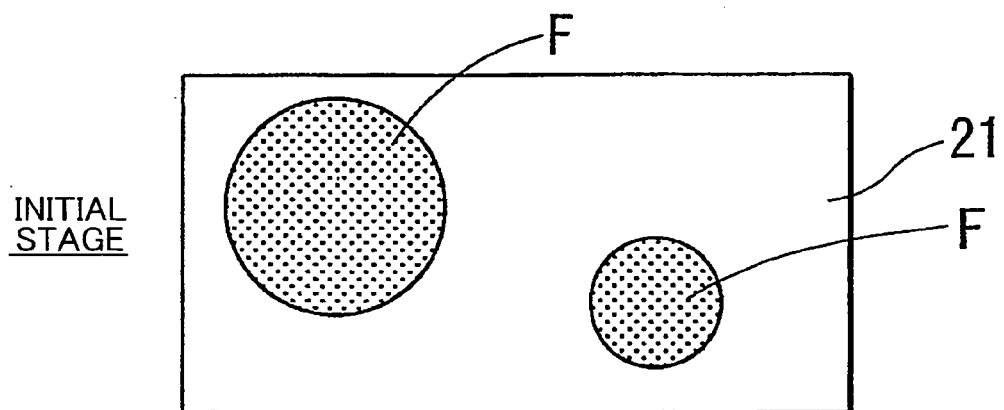


FIG.11

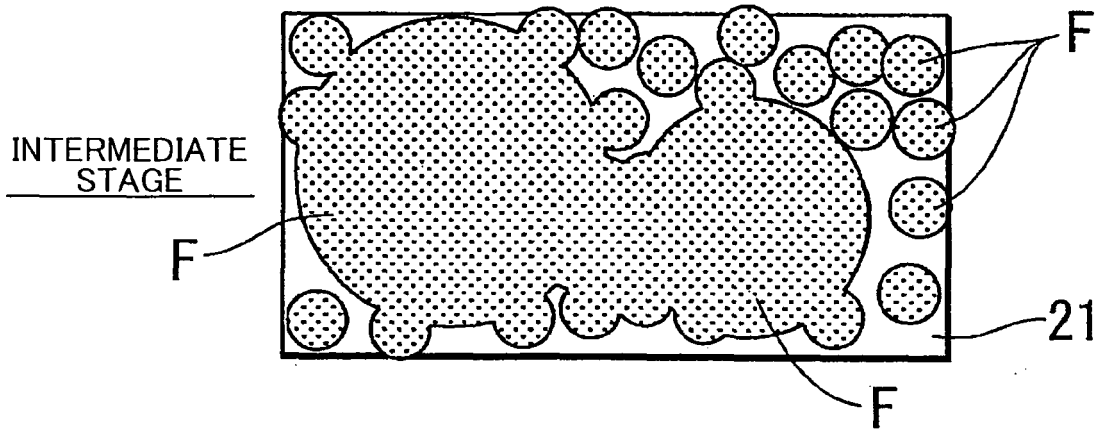


FIG.12

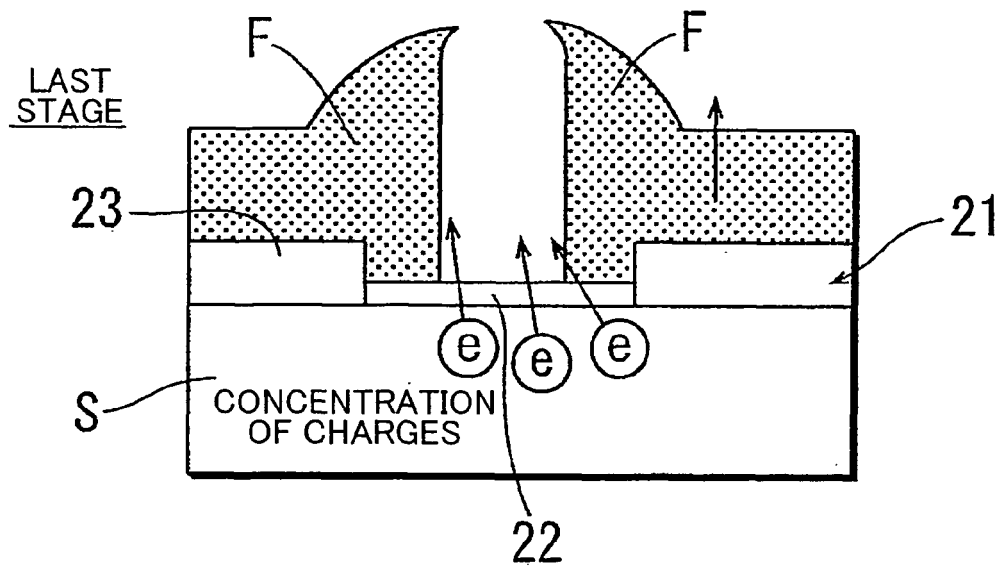


FIG.13

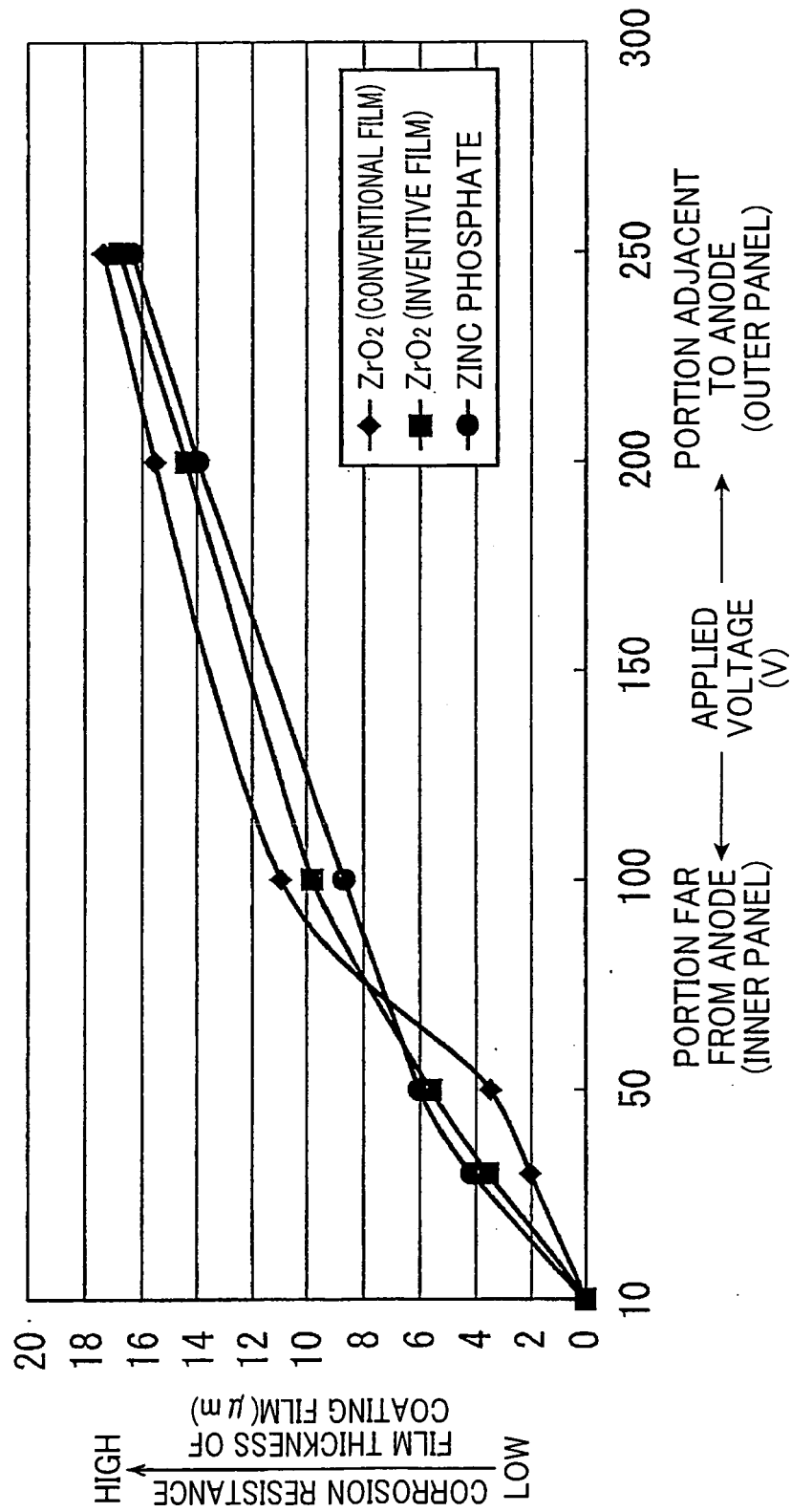


FIG.14

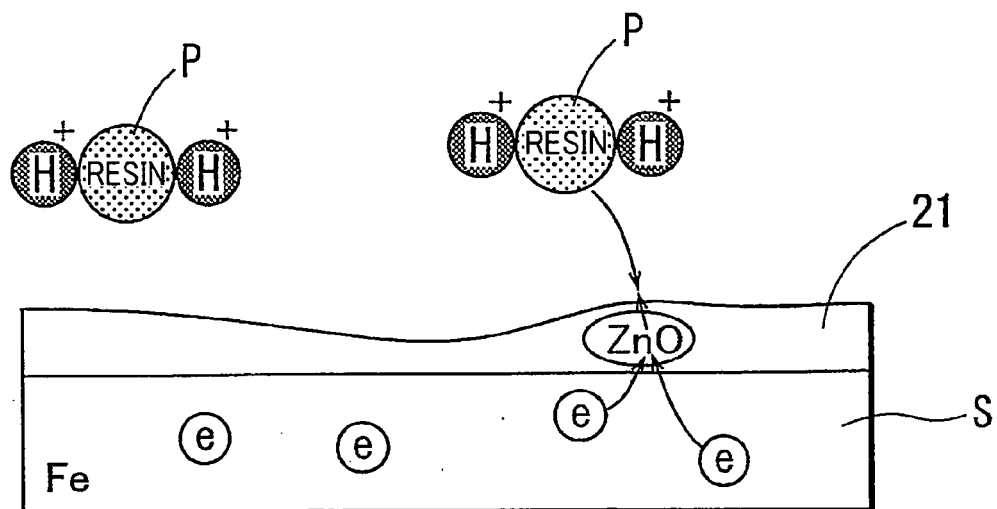


FIG.15

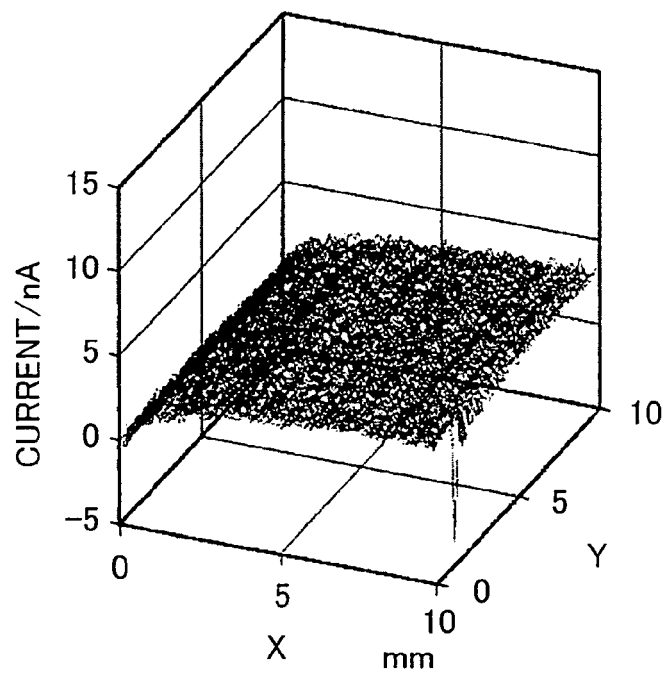


FIG.16

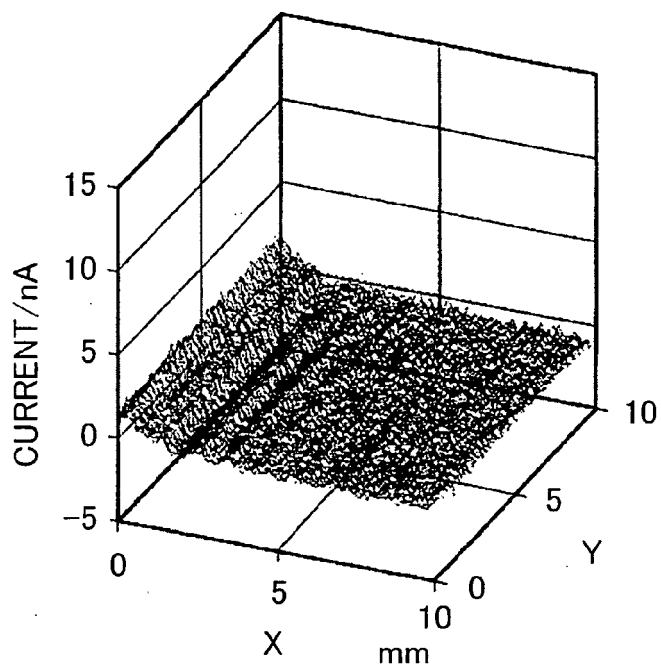


FIG.17

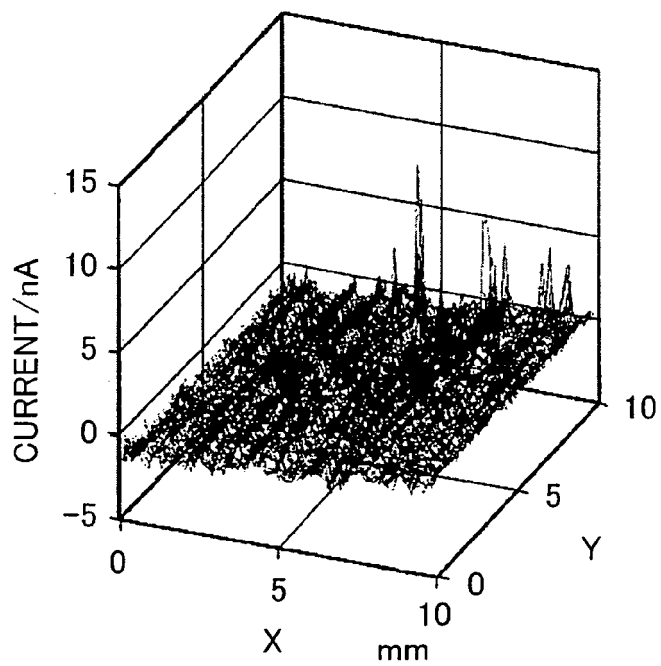
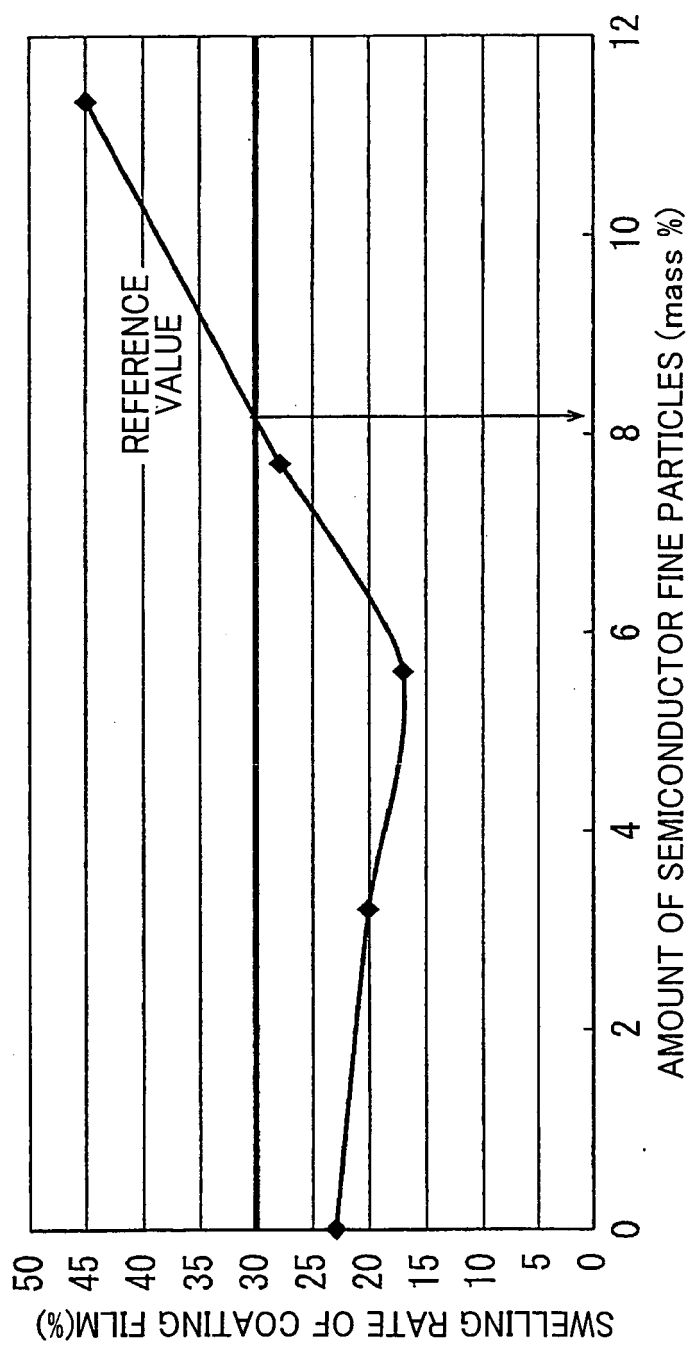


FIG.18

SEMICONDUCTOR FINE PARTICLES (mass %)	FILM THICKNESS OF COATING FILM DURING APPLICATION OF 30V (μ m)	SWELLING RATE OF COATING FILM AFTER 60 CYCLES OF CCTS (%)
0	2	32
3.2	3	20
5.6	3.5	17
7.7	4.5	28
11.3	6	45

FIG.19





EUROPEAN SEARCH REPORT

Application Number
EP 09 00 2152

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
P,X	EP 1 978 131 A (ATOTECH DEUTSCHLAND GMBH [DE]) 8 October 2008 (2008-10-08) * page 2, paragraph 8; claims 1,6,7,11,12 * * page 3, paragraph 12 * * page 4, paragraph 26 *	1-6	INV. C23C22/34 C23C22/78 C23C30/00
X	EP 0 358 338 A (ALCAN INT LTD [CA]) 14 March 1990 (1990-03-14) * examples 22,25 *	5-8	
X	EP 0 285 931 A (NIPPON STEEL CORP [JP]) 12 October 1988 (1988-10-12) * page 11, line 32 - line 37; claims 1-4 *	5,7	
A	HOU F ET AL: "Effect of the dispersibility of ZrO ₂ nanoparticles in Ni-ZrO ₂ electroplated nanocomposite coatings on the mechanical properties of nanocomposite coatings" APPLIED SURFACE SCIENCE, ELSEVIER, AMSTERDAM, NL, vol. 252, no. 10, 15 March 2006 (2006-03-15), pages 3812-3817, XP024893504 ISSN: 0169-4332 [retrieved on 2006-03-15] * abstract *	5-8	TECHNICAL FIELDS SEARCHED (IPC) C23C C25D
A	EP 1 612 294 A (ITALTECNO S R L [IT]) 4 January 2006 (2006-01-04) * claims 1-31; examples 1-4 *	1-8	
The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 26 May 2009	Examiner Teppo, Kirsi-Marja
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

3

EPO FORM 1503 03 82 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 09 00 2152

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

26-05-2009

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 1978131	A	08-10-2008	WO 2008119675 A1	09-10-2008

EP 0358338	A	14-03-1990	AT 109217 T	15-08-1994
			AU 625900 B2	16-07-1992
			AU 3951189 A	15-02-1990
			BR 8904061 A	27-03-1990
			CA 1337145 C	03-10-1995
			CN 1040811 A	28-03-1990
			DE 68917059 D1	01-09-1994
			DE 68917059 T2	17-11-1994
			DK 394089 A	13-02-1990
			ES 2059772 T3	16-11-1994
			IN 176027 A1	23-12-1995
			JP 2085373 A	26-03-1990
			NO 893250 A	13-02-1990
			PT 91432 A	08-03-1990

EP 0285931	A	12-10-1988	AU 597163 B2	24-05-1990
			AU 1389788 A	20-10-1988
			CA 1336698 C	15-08-1995
			DE 3882769 D1	09-09-1993
			DE 3882769 T2	11-11-1993
			US 4897317 A	30-01-1990
			US 4877494 A	31-10-1989

EP 1612294	A	04-01-2006	NONE	

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- JP 2004218074 A [0003]
- US 20040163735 A [0003]
- JP 2008053227 20080304 [0064]