(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 1 719 825 A1

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

(43) Date of publication:
08.11.2006 Bulletin 2006/45

(21) Application number: **04801681.0**

(22) Date of filing: **07.12.2004**

(51) Int Cl.:
C25D 5/26 $^{(2006.01)}$ ***C25D 15/02*** $^{(2006.01)}$

(86) International application number:
PCT/JP2004/018535

(87) International publication number:
WO 2005/056883 (23.06.2005 Gazette 2005/25)

(84) Designated Contracting States:
DE FR GB

(30) Priority: **09.12.2003 JP 2003410746**

(71) Applicant: **Kansai Paint Co., Ltd**
Amagasaki-shi,
Hyogo-ken 661-0964 (JP)

(72) Inventors:
- **KUBOTA, Kentaro, c/o KANSAI PAINT CO., LTD.**
  Kanagawa 254-8562 (JP)
- **HARUTA, Yasuhiko, c/o KANSAI PAINT CO., LTD.**
  Kanagawa 254-8562 (JP)
- **HIRAKI, Tadayoshi, c/o KANSAI PAINT CO., LTD.**
  Kanagawa 254-8562 (JP)

(74) Representative: **Zimmermann, Gerd Heinrich**
Zimmermann & Partner,
P.O. Box 33 09 20
80069 München (DE)

(54) ELECTROPLATED COATING OF ZINC ALLOY WITH EXCELLENT CORROSION RESISTANCE AND PLATED METAL MATERIAL HAVING SAME

(57) Objects of the present invention is to provide a zinc-based alloy electroplated film having a high corrosion resistance comparable to Zn-Cr alloy plating without containing chromium which gives a heavy environmental load, and a plated metal material using the same. The present invention relates to a zinc-based alloy electroplated film excellent in corrosion resistance containing (A) 30 to 96% by weight of zinc, (B) 2 to 20% by weight of an iron-group metal, and (C) 2 to 50% by weight of tungsten.

Printed by Jouve, 75001 PARIS (FR)

Description

<Technical Field>

[0001] The present invention relates to a zinc-based alloy electroplated film excellent in corrosion resistance and a plated metal material using the same, which can be utilized in a wide range of fields such as automobiles, home electric appliances, and building materials.

<Background Art>

[0002] In response to the request for high corrosion resistance on metal materials to be used in automobiles, home electric appliances, building materials, and the like, there has been increasingly utilized zinc-based alloy metal materials where iron-based materials are coated with zinc or a zinc-based alloy plated film. Various kinds of methods for coating iron-based materials with zinc are present. As the plating methods, hot dip galvanization where a plated film is formed by dipping a base metal in molten zinc or zinc alloy and electrogalvanization where a plated film is formed by precipitating metallic zinc dissolved in an aqueous solution through electrolysis have been known. Furthermore, baths for the electrogalvanization is classified into an acidic bath and an alkaline bath according to the nature of the plating solution. Examples of the acid bath include a sulfate bath, an ammonium chloride bath, a potassium chloride bath, an ammonium chloride and potassium chloride mixed bath, and the like. Examples of the alkaline bath include a cyan bath, a zincate bath, and the like. They have been used properly according to individual characteristics. However, with regard to the metal materials used in automobiles, home electric appliances, building materials, and the like and exposed under severe conditions, even when these plated metal materials are utilized, a sufficient corrosion resistance cannot be obtained in some cases and thus further improvement of corrosion resistance has been required. Under such circumstances, zinc-based alloy plated metal materials such as Zn-Fe, Zn-Ni, and Zn-Cr have been developed. Of these, it is disclosed that a Zn-Cr alloy plated film has a high corrosion resistance (For example, see Patent Literatures 1, 2, and 3).

[0003] With regard to the Zn-Cr alloy plated film, since a corrosion-inhibiting effect due to Cr present in the film is remarkable and the film is not passivated and retains a relatively low potential, a so-called sacrificial anticorrosive action is also effective over a long period of time and corrosion resistance is excellent even under a situation where the base iron is exposed.

[0004] As mentioned above, the Zn-Cr alloy plated film is practically excellent but it contains a problem of hexavalent chromium mist generated at plating and hence environmental problems of disturbing plating worker's health and inducing air pollution have been closed up. Thus, development and practical application of a highly corrosion-resistant alternative metal material giving a less environmental load have been an urgent necessity.

Patent Literature 1: JP 64-55397 A
Patent Literature 2: JP 2-51996 B
Patent Literature 3: JP 3-240994 B

<Disclosure of the Invention>

[0005] An object of the invention is to provide a zinc-based alloy electroplated film having a high corrosion resistance comparable to Zn-Cr alloy plating without containing chromium which gives a heavy environmental load, and a plated metal material using the same.

[0006] As a result of extensive studies for solving the above-described problems, the present inventors have found that corrosion resistance can be remarkably improved by using a plated film containing zinc as a base material and specific amounts of an iron-group metal and tungsten, and have accomplished the invention.

[0007] Thus, the invention relates to a zinc-based alloy electroplated film containing:

(A) 30 to 96% by weight of zinc,
(B) 2 to 20% by weight of an iron-group metal, and
(C) 2 to 50% by weight of tungsten.

[0008] Further, the invention relates to a plated metal material which has the above-described zinc-based alloy electroplated film.

<Best Mode for Carrying Out the Invention>

[0009] The zinc-based alloy electroplated film of the invention contains zinc (A), an iron-group metal (B), and tungsten

(C) as essential components.

[0010] The composition of the plated film falls within the following range of each component in view of corrosion resistance: 30 to 96% by weight, preferably 50 to 90% by weight of zinc (A), 2 to 20% by weight, preferably 5 to 15% by weight of an iron-group metal (B), and 2 to 50% by weight, 3 to 20% by weight of tungsten (C).

[0011] The iron-group element (B) herein means nickel, cobalt, or iron. A plated film of an alloy of zinc and iron-group metal is generally known but corrosion resistance of the resulting alloy plated film is remarkably improved by further combining tungsten therewith. In particular, since the effect is large when iron is used as the iron-group metal (B), it is preferred to use it but corrosion resistance is also good in the system where iron is combined with cobalt and/or nickel.

[0012] The zinc-based alloy electroplated film of the invention is formed by subjecting primary molded articles such as steel strip in coil to continuous electroplating and by subjecting small parts such as bolts and secondary molded articles including press molded articles to electroplating with placing them in rotatable perforated vessels such as barrels or cages.

"Zn ion (a)"

[0013] The Zn ion as component (a) of the plating solution constitutes a main component of the plated layer.

[0014] The Zn ion is added to the plating bath in the form of chloride, sulfate, fluoride, cyanide, oxide, an organic acid salt, a phosphate salt, or elementary metal. "Iron-group-metal ion (b)"

[0015] The iron-group-metal ion as component (b) of the above-described plating solution is selected from an Ni ion, a Co ion, and an Fe ion.

[0016] The iron-group-element ion (b) is added to the plating bath in the form of chloride, sulfate, fluoride, cyanide, oxide, an organic acid salt, a phosphate salt, or elementary metal.

"W ion (c)"

[0017] The W ion as component (c) of the above-described plating solution is added to the plating bath in the form of tungstic acid-based compound.

[0018] Examples of the tungstic acid-based compound include tungstic acid, tungstate salts, phosphotungustic acid, and phosphotungstate salts. Examples of the salts include ammonium salts, potassium salts, calcium salts, sodium salts, and the like. Of these, sodium tungstate and ammonium tungstate are particularly preferred in view of corrosion resistance.

"Plating solution"

[0019] Ions of metals other than the above-described (a), (b), and (c), e.g., Mg, Mn, Ti, Pb, Al, P, or the like may be added to the above-described plating solution.

[0020] Further, it is preferred to add a complexing agent to the plating solution for the purpose of stabilizing the metal ions in the plating solution. The complexing agent can be selected from the group consisting of oxycarboxylate salts such as citrate salts, tartrate salts, and gluconate salts, aminoalcohols such as monoethanolamine, diethanolamine, and triethanolamine, polyamines such as ethylenediamine (EDA), diethylenetriamine, and triethylenetetramine, amino-carboxylate salts such as ethylenediamine tetraacetate salts and nitroacetate salts, polyhydric alcohols such as sorbit and pentaerythritol, and mixtures thereof.

[0021] In the invention, functions of high corrosion resistance, coating adhesiveness, and the like can be imparted by combining a corrosion-inhibiting pigment and/or ceramic particles capable of being precipitated as discontinuous particles from the electroplating solution.

[0022] As the above-described corrosion-inhibiting pigment, generally known one can be used and preferred examples thereof include phosphate salts, molybdate salts, metaborate salts, silicate salts, and the like.

[0023] Further, examples of the ceramic particles include particles of oxides such as Al_2O_3, SiO_2, TiO_2, ZrO_2, Y_2O_2, ThO_2, CeO_2, and Fe_2O_3; carbides such as B_4C, SiC, WC, ZrC, TiC, graphite, and graphite fluoride; nitrides such as BN, Si_3N_4, and TiN; borates such as Cr_3B_2, and ZrB_2; silicate salts such as $2MgO{\cdot}SiO_2$, $MgO{\cdot}SiO_2$, and $ZrO_2{\cdot}SiO_2$, and the like. The blending amount of the corrosion-inhibiting pigment and/or ceramic particles into the plating bath is desirably within the range of 5 to 500 g per liter. Further, the smaller the particle size is, the more excellent dispersion stability is. Therefore, ultrafine particles having a size of 1 μm or less are preferred. Furthermore, it is desirable to control co-precipitated amount in the plating matrix to the range of 1 to 30% by weight, particularly 1 to 10% by weight per total precipitated amount. When the co-precipitated amount is small, an effect of improving corrosion resistance is not exhibited and, when it exceeds 30% by weight, the plated film becomes brittle and also adhesiveness with the base material decreases, so that the cases are problematic.

[0024] In order to improve corrosion resistance, a corrosion-inhibiting organic compound may be further added to the plating bath. Examples of preferable corrosion-inhibiting organic compound include alkynes, alkynols, amines or salts thereof, thio compounds, aromatic carboxylic acid compounds or salts thereof, and heterocyclic compounds, and the like.

[0025] Of these, the alkynes mean organic compounds containing a carbon-carbon triple bond and examples thereof include pentyne, hexyne, heptyne, octyne, and the like.

[0026] The alkynols mean organic compounds having one or more hydroxyl groups in the alkynes and examples thereof include propargyl alcohol, 1-hexyn-3-ol, 1-heptyn-3-ol, and the like.

[0027] The amines mean organic compounds containing one or more nitrogen atoms in the molecule, which include any of aliphatic or aromatic compounds. Examples of such amines include octylamine, nonylamine, decylamine, laurylamine, tridecylamine, cetylamine, and the like.

[0028] The thio compounds mean organic compounds containing one or more sulfur atoms in the molecule and examples of such thio compounds include decyl mercaptan, cetyl mercaptan, thiourea, and the like.

[0029] The heterocyclic compounds mean organic compounds containing atom(s) other than a carbon atom as ring-constituting atoms in a cyclic molecule and examples of such heterocyclic compounds include pyridine, benzothiazole, benzotriazole, quinoline, indole, and the like.

[0030] Further, examples of the aromatic carboxylic acid compounds include benzoic acid, salicylic acid, toluic acid, naphthalenecarboxylic acid, and the like.

[0031] With regard to the amines or carboxylic acid compounds, it is possible to use a salt thereof, and an equivalent effect can also be obtained thereby. Salts that can be used include, for the case of amines, acid addition salts such as sulfates and hydrochlorides, and for the case of the aromatic carboxylic acid compounds, metal salts such as alkali metal salts and zinc salts, and ammonium salts.

[0032] The amount of the corrosion-inhibiting organic compound to be added to the plating bath is desirably regulated to 0.1 to 10% by weight in the case of the alkynes or alkynols, 3 to 10% by weight in the case of the amines or salts thereof, 0.2 to 5% by weight in the case of the thio compounds, 1 to 10% by weight in the case of the heterocyclic compounds, and 3 to 8% by weight in the case of the aromatic carboxylic acid compounds or salts thereof. A plated film having a co-precipitated amount in terms of C (carbon) content of 0.001 to 10% by weight can be formed on the metal material by using a plating bath to which such a corrosion-inhibiting organic compound. It is possible to determine the carbon content in the plated film according to a combustion method, for example, by measurement on a "C-S analyzing apparatus" where an organic substance is burned and absorbance in an infrared absorption band of CO_2 formed is measured.

[0033] Further, it is possible to incorporate, into the above-described plating solution, additive(s) usually used for the purpose of improving burnt deposit at a high current density or throwing power at a low current density. Examples thereof include a reaction product of an amine with an epihalohydrin, a polyethylenepolyamine, the other quaternary amine polymer, urea, thiourea, gelatin, polyvinyl alcohol, an aldehyde, and the like.

[0034] The above-described plating bath composition can form a plated film excellent in corrosion resistance and coated film adhesiveness by electroplating in a similar manner to a conventional method.

[0035] As bath conditions for electroplating, it is preferable that pH is about 1 to 3 and a bath temperature is about 30 to 80°C in the case that the plating bath is a sulfate bath, pH is about 4 to 7 and a bath temperature is about 10 to 50°C in the case that the plating bath is a chloride bath, and pH is 12 or higher and a bath temperature is about 10 to 50°C in the case that the plating bath is an alkaline bath, and the thickness of the plated film is suitably from about 0.5 to 10 μm in all cases.

"Electroplated metal material"

[0036] The electroplated metal material of the present invention is obtained by electroplating a metal raw material using the above-described electroplating solution composition to form a plated film. The metal raw material includes materials mainly comprising iron, e.g., materials for automobiles, home electric appliances, and building materials, processed into a shape of a plate, tube, joint, clamp, bolt, nut or the like.

[0037] The electroplating conditions are as described above.

[0038] Further, the advantages of the invention can be further enhanced by post-treatment with an acidic aqueous solution of a compound containing at least one element selected from the group consisting of cobalt, nickel, titanium and zirconium, after the formation of the electroplated film. As the compound containing at least one element selected from the group consisting of cobalt, nickel, titanium and zirconium, usable examples include oxides, hydroxides, fluorides, complex fluorides, chlorides, nitrates, sulfates, carbonates, etc. of these metals. Specifically, preferred examples thereof include cobalt nitrate, zirconium oxynitrate, titanium hydrofluoride, zirconium hydrofluoride, ammonium titanium hydrofluoride, and ammonium zirconium hydrofluoride.

[0039] The acidic aqueous solutions of the compounds containing these metal elements preferably has a pH falling within the range of from 1 to less than 7, preferably from 3 to 6. The pH can be adjusted by an acid such as hydrochloric acid, nitric acid, sulfuric acid and hydrofluoric acid, or a base such as sodium hydroxide, potassium hydroxide and amines. Further, a complexing agent, silica particles, etc. may be added to the acidic aqueous solution as needed. The amount of the compound containing the metal element to be added is preferably from 0.001 to 5 mol/liter, and particularly preferably about 0.01 to 1 mol/liter.

[0040] The post-treatment with the acidic aqueous solution can be carried out by bringing the electroplated film into contact with the processing solution, for example by immersing the metal material into the processing solution of a bath temperature of 20 to 80°C, preferably 30 to 60°C, for 5 seconds or longer, preferably about 20 to 90 seconds.

[0041] The electroplated metal material thus obtained is usually subjected to surface treatment and, if necessary, a coating material is further applied thereto. The surface treatment is usually conducted with a chromate-based surface treating agent or phosphate salt-based surface treating agent. However, since the electroplated metal material of the invention is excellent in corrosion resistance, an excellent corrosion resistance is also exhibited even when it is combined with a chromium-free environment-responsive surface-treating agent. In order to reduce an environmental load, it is preferred to combine the material with a chromium-free environment-responsive surface-treating agent.

[0042] The coating material in the case of coating the electroplated metal material of the invention is not particularly limited, any curing mode such as roomtemperature drying, hot curing, or active energy ray-curing can be employed, and any kind of coating materials such as solvent-type coating materials, water-based coating materials, and powdered coating materials may be used. Particularly, in the case that the electroplating metal material of the invention is applied to automobiles, generally, an electrodeposition paint, an intermediate coat, and a top coat are sequentially applied on the plated film and then baked after phosphate salt treatment is applied on the plated film.

<Examples>

[0043] The present invention will be illustrated in greater detail with reference to the following Examples. In this connection, the "part(s)" and "%" used below are each given by weight.

"1. Manufacture of electroplated steel plate"

(Examples 1 to 18 and Comparative Examples 1 to 4)

[0044] A cold-rolled steel plate having a plate thickness of 0.8 mm and a size of 70 mm x 150 mm was subjected to alkaline degreasing and washed with water, and then it was plated in an acidic plating bath containing predetermined metal ions, corrosion-inhibiting pigment, corrosion-inhibiting organic compound, and ceramic particles using an electroplating experimental apparatus. The composition of the film was regulated by changing the concentration ratio of the metal ions in the plating bath, current density, and bath temperature and the thickness of the plated film was controlled by suitably choosing a plating time. The film composition (wt%) and film thickness of each plated layer are shown in Table 1 below. In this connection, the film composition and film thickness of the plated layer were measured on a fluorescent X-ray analyzer SEA5200 (manufactured by Seiko Instruments Inc.).

[0045] Respective metal ions used in the test are supplied from the following compounds.

Zn: $ZnSO_4 \cdot 7H_2O$
Fe: $FeSO_4 \cdot 7H_2O$
Co: $CoSO_4 \cdot 7H_2O$
Ni: $NiSO_4 \cdot 7H_2O$
W : $Na_2WO_4 \cdot 2H_2O$

Table 1

		Metal Composition (% by weight)					Corrosion-inhibiting pigment		Ceramic particles		Corrosion-inhibiting organic compound		Film thickness (μm)
		Zn	Fe	Co	Ni	W	A1(*1)	A2(*2)	B1(*3)	B2(*4)	C1(*5)	C2(*6)	
Example	1	94	3			3							3
	2	92	3			5							5
	3	90	5			5							3
	4	85	5			10							5
	5	80	10			10							3
	6	75	15			10							5
	7	80		10		10							3
	8	80			10	10							3
	9	70	15			15							3
	10	65	20			15							5
	11	65	15			20							3
	12	60	20			20							5
	13	85	5			10	3						3
	14	85	5			10		5					3
	15	85	5			10					0.5		3
	16	85	5			10						0.5	3
	17	85	5			10			5				3
	18	85	5			10				3			3

(continued)

		Metal Composition (% by weight)					Corrosion-inhibiting pigment		Ceramic particles		Corrosion-inhibiting organic compound		Film thickness (μm)
		Zn	Fe	Co	Ni	W	A1(*1)	A2(*2)	B1(*3)	B2(*4)	C1(*5)	C2(*6)	
Comparative example	1	100											5
	2	90	10										5
	3	94	5			1							5
	4	96	1			3							5

The raw materials of Notes (*1) to (*6) in Table 1 are those shown below.
(*1) A1: K-WHITE 840E, manufactured by Tayca Corporation, condensed aluminum phosphate-based one.
(*2) A2: LF Bousei ZP-DL, Kikuchi Color & Chemicals Corporation, zinc phosphate-based one.
(*3) B1: Silica fine particles, average particle diameter of about 0.02 μm.
(*4) B2: Alumina fine particles, average particle diameter of about 0.01 μm.
(*5) C1: 3-Amino-1,2,4-triazole.
(*6) C2: Thiourea.

"2. Coating system 1"

(Examples 19 to 36 and Comparative Examples 5 to 8)

[0046] After each surface of the electroplated steel plates obtained in the above-shown Table 1 was subjected to alkaline degreasing, it was subjected to surface adjustment (spraying treatment using "PREPALEN Z" manufactured by Nihon Parkerizing Co., Ltd.) and further to phosphate salt treatment (spraying treatment using "Palbond 3118" manufactured by Nihon Parkerizing Co., Ltd.), and then was washed with water and dried, whereby a steel plate treated with zinc phosphate (the attached amount of the treated film was 1.5 g/m^2).

[0047] To the thus obtained steel plate treated with zinc phosphate, "MAGICRON 1000 white" (manufactured by Kansai Paint Co., Ltd., an acryl-melamine resin-based coating material, white) was applied so that a dry film thickness became 30 μm, and baked at 160°C for 20 minutes to obtain each test coated plate.

[0048] On respective test coated plates obtained, various tests were carried out in accordance with the following test methods. The results are shown in Table 2 below.

[0049] (Top coat adhesiveness): After each test coated plate was dipped in a boiling water of about 98°C for 2 hours, it was taken out and allowed to stand at room temperature for 2 hours and then the coated surface of the coated plate was cut by a knife so as to result in each of 11 cuts reaching the base metal lengthwise and crosswise in a grid pattern, whereby 100 blocks having 2 mm square were formed. Peeled area of the coated film was evaluated according to the following standards at the time when a cellophane adhesive tape was closely adhered to the grid part and the tape was peeled off instantaneously.

5: No peeling of the coated film is observed.
4: Peeling of the coated film is observed but peeled area is less than 10%.
3: Peeled area is from 10% to less than 25%.
2: Peeled area is from 25% to less than 50%.
1: Peeled area is 50% or more.

[0050] (Corrosion resistance after coating): A crosscut reaching the base metal was incised on each test coated plate. Then, the resulting plate was subjected to salt spray test for 240 hours in accordance with JIS Z-2371, followed by washing with water and drying. Then, a cellophane adhesive tape was closely adhered to the crosscut part and a maximum peeled width (one side, mm) from the crosscut part was measured when the tape was peeled off instantaneously.

Table 2

		Plated film	Test results	
			Top coat adhesiveness	Corrosion resistance after coating
Example	19	Example 1	5	3
	20	Example 2	5	2
	21	Example 3	5	2
	22	Example 4	5	1
	23	Example 5	5	1
	24	Example 6	5	1
	25	Example 7	5	2
	26	Example 8	5	1
	27	Example 9	5	1
	28	Example 10	5	1
	29	Example 11	5	1
	30	Example 12	5	1
	31	Example 13	5	1
	32	Example 14	5	1
	33	Example 15	5	1
	34	Example 16	5	1
	35	Example 17	5	1
	36	Example 18	5	1
Comparative Example	5	Comparative Example 1	4	7
	6	Comparative Example 2	4	5
	7	Comparative Example 3	4	5
	8	Comparative Example 4	4	5

"3. Coating system 2"

(Examples 37 to 54 and Comparative Examples 9 to 12)

[0051] Each of the electroplated steel plates obtained in the above-shown Table 1 was treated with a phosphate salt by subjecting it to washing with hot water, degreasing (spraying at 43°C for 120 seconds using an alkali degreasing agent "FINE L-4460" manufactured by Nihon Parkerizing Co., Ltd.), washing with water, surface adjustment (spraying at ordinary temperature for 30 seconds using a titanium colloid-based surface adjusting agent "PREPALEN ZN" manufactured by Nihon Parkerizing Co., Ltd.), zinc phosphate-based chemical conversion (spraying at 43°C for 120 seconds using a zinc phosphate chemical conversion agent "Palbond L-3020" manufactured by Nihon Parkerizing Co., Ltd.), washing with water, and drying with draining. Thereafter, a cation-type electrodeposition coating "ELECRON GT-10" (manufactured by Kansai Paint Co., Ltd., an epoxypolyester resin-based cation-type electrodeposition coating material) was applied by electrodeposition coating and baked at 170°C for 30 minutes to obtain an electrodeposition plate having a dry film thickness of 20 μm. An intermediate coat "AMILAC TP-65 gray" (manufactured by Kansai Paint Co., Ltd., an aminoalkyd resin-based intermediate coat) was applied to the electrodeposition surface using a spray so that a dry film thickness became 30 μm, and baked at 140°C for 30 minutes. Thereafter, a top coat "NEO AMILAC #6000 white" (manufactured by Kansai Paint Co., Ltd., an aminoalkyd resin-based top coat) was applied using a spray so that a dry film thickness became 30 μm, and baked at 140°C for 20 minutes to obtain each test coated plate.

[0052] On respective test coated plates obtained, various tests were carried out in accordance with the following test methods. The results are shown in Table 3 below.

[0053] (Chipping resistance): A test coated plate was fixed on a test piece holder of a gravel chipping test instrument JA-400 Model (a chipping test apparatus manufactured by Suga Test Instruments Co., Ltd.) at a right angle relative to its gravel spout. Then, the coated surface was blasted with 50 g of crushed granite having a No.7 particle size at -20°C by compressed air of 0.294 MPs (3 kgf/cm^2), and generated chips on the coated film were visually observed and evaluated according to the following standards.

AAAA: The size of chips is considerably small and only the top coat is bruised.
A: The size of chips is small and only the intermediate coat is exposed.
B: The size of chips is small but the steel plate as the base metal is exposed.
C: The size of chips is considerably large and the steel plate as the base metal is exposed to a large extent.

[0054] (Water-resistant secondary adhesiveness): After each test coated plate was dipped in warm water of 40°C for 10 days, it was taken out and dried and then the coated surface of the test coated plate was cut by a knife so as to result in each of 11 cuts reaching the base metal lengthwise and crosswise in a grid pattern, whereby 100 blocks having 2 mm square were formed. Peeled area of the coated film was evaluated according to the following standards at the time when a cellophane adhesive tape was closely adhered to the grid part and the tape was peeled off instantaneously.

5: No peeling of the coated film is observed.
4: Peeling of the coated film is observed but peeled area is less than 10%.
3: Peeled area is from 10% to less than 25%.
2: Peeled area is from 25% to less than 50%.
1: Peeled area is 50% or more.

[0055] (Corrosion resistance): A crosscut reaching the base metal was incised on each test coated plate and it was subjected to salt spray test for 720 hours in accordance with JIS Z-2371, followed by washing with water and air-drying. Then, rust and swelling at a general part were evaluated according to the following standards as well as a cellophane adhesive tape was closely adhered to the crosscut part and a maximum peeled width (one side, mm) from the crosscut part was measured when the tape was peeled off instantaneously.

A: No generation of rust and swelling on the coated surface is observed.
B: Slight generation of rust and swelling on the coated surface is observed.
C: Remarkable generation of rust and swelling on the coated surface is observed.

[0056] (Salt water resistance): A crosscut reaching the base metal was incised on each test coated plate and it was dipped in 5% saline at 50°C for 10 days, followed by washing with water and air-drying. Then, rust and swelling at a general part were evaluated according to the following standards as well as a cellophane adhesive tape was closely adhered to the crosscut part and a maximum peeled width (one side, mm) from the crosscut part was measured when the tape was peeled off instantaneously.

A: No generation of rust and swelling on the coated surface is observed.
B: Slight generation of rust and swelling on the coated surface is observed.
C: Remarkable generation of rust and swelling on the coated surface is observed.

Table 3

		Plated film	Test results					
			Chipping resistance	Water-resistant secondary adhesiveness	Corrosion resistance		Salt water resistance	
					General part	Maximum peeling width	General part	Maximum peeling width
Example	37	Example 1	AA	5	A	9	A	1
	38	Example 2	AA	5	A	8	A	0
	39	Example 3	AA	5	A	8	A	1
	40	Example 4	AA	5	A	7	A	0
	41	Example 5	A	5	A	6	A	0
	42	Example 6	A	5	A	6	A	0
	43	Example 7	A	5	A	10	A	2
	44	Example 8	A	5	A	9	A	1
	45	Example 9	A	5	A	6	A	0
	46	Example 10	A	5	A	6	A	0
	47	Example 11	A	5	A	5	A	0
	48	Example 12	A	5	A	10	A	2
	49	Example 13	A	5	A	9	A	1
	50	Example 14	A	5	A	3	A	0
	51	Example 15	A	5	A	4	A	0
	52	Example 16	A	5	A	4	A	0
	53	Example 17	A	5	A	5	A	0
	54	Example 18	A	5	A	5	A	0

(continued)

		Plated film	Test results					
			Chipping resistance	Water-resistant secondary adhesiveness	Corrosion resistance		Salt water resistance	
					General part	Maximum peeling width	General part	Maximum peeling width
Comparative Example	9	Comparative Example 1	A	5	A	15	A	4
	10	Comparative Example 2	C	5	’ A	8	A	2
	11	Comparative Example 3	B	5	A	10	A	2
	12	Comparative Example 4	A	5	A	9	A	3

"4. Coating system 3"

(Examples 55 to 72 and Comparative Examples 13 to 16)

[0057] After each surface of the plated steel plates obtained in the above-shown Table 1 was subjected to alkaline degreasing, a titanium-based base-treating agent prepared according to the following formulation was applied thereon by a bar coater so that a dry film thickness became 0.5 μm and the resulting plate was heated for 10 seconds under conditions so that PMT (maximum reaching temperature of steel plate) became 100°C to manufacture a base-treated plate. Thereafter, "KP color 8000 primer" (manufactured by Kansai Paint Co., Ltd., a modified epoxy resin-based coating material) was applied on the treated plate by a bar coater so that a dry film thickness became 5 μm, and the resulting plate was heated for 20 seconds under conditions so that PMT became 210°C to form a coated film. Then, "KP color 1580 white" (manufactured by Kansai Paint Co., Ltd., a polyester resin-based coating material) was applied on the primer film by a bar coater so that a dry film thickness became 15 μm, and the resulting plate was heated for 40 seconds under conditions so that PMT became 215°C to manufacture each test coated plate having an upper-layer coated film.

[0058] On respective test coated plates obtained, tests for adhesiveness, corrosion resistance, and moisture resistance of the coated films were carried out. The results are shown in Table 4 below. Respective tests were carried out in accordance with the following test methods.

<Formulation of titanium-based base-treating agent>

[0059] A mixture of 10 parts of tetra(iso-propoxy)titanium and 10 parts of iso-propanol was added dropwise into a mixture of 10 parts of a 30% hydrogen peroxide solution and 100 parts of deionized water at 20°C under stirring over a period of 1 hour and then the whole was aged at 25°C for 2 hours to obtain a 2% titanium compound aqueous solution. Five parts of 20% zircon hydrofluoric acid and 45 parts of deionized water were blended with 50 parts of the resulting 2% titanium compound aqueous solution to obtain a titanium-based base-treating agent.

[0060] (Coated film adhesiveness): The coated surface of the test coated plate was cut by a knife so as to result in each of 11 cuts reaching the base metal lengthwise and crosswise in a grid pattern, whereby 100 blocks having 1 mm square were formed. Peeled degree of the coated film was evaluated according to the following standards at the time when a cellophane adhesive tape was closely adhered to the grid part and the tape was peeled off instantaneously.

5: No peeling of the coated film is observed.
4: Peeling of the coated film is observed but peeled area is less than 10%.
3: Peeled area is from 10% to less than 25%.
2: Peeled area is from 25% to less than 50%.
1: Peeled area is 50% or more.

[0061] (Corrosion resistance): After the edge part and rear surface of the test coated plate, which had been cut into a size of 70 cm x 150 cm, were sealed, there were provided a 4T folded part (a part subjected to a 180° folding, the coated surface being outside and four sheets of a spacer having a thickness of 0.8 mm intervening) at an upper part of the test coated plate and a crosscut part at a lower part of the test coated plate. The coated plate was subjected to salt spray test for 1000 hours in accordance with JIS Z-2371. Then, degree of white rust generation at the 4T folded part, swelling width at the crosscut part, and degree of swelling generation at a general part (a part without processing and cut) were evaluated according to the following standards.

<General part>

[0062]

AA: No generation of swelling is observed.
A: Slight generation of swelling is observed.
B: Considerable generation of swelling is observed.
C: Generation of swelling is remarkable and peeling of the coated film is partly observed.

<Crosscut part>

[0063]

AA: One-surface swelling width from crosscut is less than 1 mm.

A: One-surface swelling width from crosscut is from 1 mm to less than 2 mm.
B: One-surface swelling width from crosscut is from 2 mm to less than 5 mm.
C: One-surface swelling width from crosscut is 5 mm or more.

<4T Folded part>

[0064]

AA: No generation of white rust is observed.
A: Slight generation of white rust is observed.
B: Considerable generation of white rust is observed.
C: Generation of white rust is remarkable and peeling of the coated film is partly observed.

[0065] (Moisture resistance): After the edge part and rear surface of the test coated plate, which had been cut into a size of 70 cm x 150 cm, were sealed, a test was carried out in accordance with JIS K-5400 9.2.2. The test time was 1000 hours under conditions of a temperature in the box of a moisture resistance test instrument of 50°C and a relative humidity of 95 to 100%. The degree of swelling generation of the coated film on the test coated plate after the test was evaluated according to the following standards.

AA: No generation of swelling is observed.
A: Slight generation of swelling is observed.
B: Considerable generation of swelling is observed.
C: Generation of swelling is remarkable and peeling of the coated film is partly observed.

Table 4

		Plated film	Test results				
			Coated film adhesiveness	Corrosion resistance			Moisture resistance
				General part	Crosscut part	Folded part	
Example	55	Example 1	5	AA	A	A	AA
	56	Example 2	5	AA	A	A	AA
	57	Example 3	5	AA	A	A	AA
	58	Example 4	5	AA	A	AA	AA
	59	Example 5	5	AA	A	A	AA
	60	Example 6	5	AA	A	A	AA
	61	Example 7	5	AA	A	A	AA
	62	Example 8	5	AA	A	A	AA
	63	Example 9	5	AA	AA	AA	AA
	64	Example 10	5	AA	AA	AA	AA
	65	Example 11	5	AA	A	AA	AA
	66	Example 12	5	AA	A	A	AA
	67	Example 13	5	AA	A	A	AA
	68	Example 14	5	AA	A	A	AA
	69	Example 15	5	AA	AA	A	AA
	70	Example 16	5	AA	AA	A	AA
	71	Example 17	5	AA	A	A	AA
	72	Example 18	5	AA	AA	A	AA

(continued)

		Plated film	Test results				
			Coated film adhesiveness	Corrosion resistance			Moisture resistance
				General part	Crosscut part	Folded part	
Comparative Example	13	Comparative Example 1	4	AA	C	B	B
	14	Comparative Example 2	5	AA	B	A	AA
	15	Comparative Example 3	4	AA	B	B	AA
	16	Comparative Example 4	4	AA	A	B	AA

"5. Coating system 4"

(Examples 73 to 90 and Comparative Examples 17 to 20)

[0066] A steel bolt was subjected to alkali degreasing and washed with water and then it was dipped in a 1% sulfuric acid solution at room temperature for 30 seconds to effect activation treatment. Thereafter, using a batch-type barrel plating apparatus, plating was conducted in an alkaline plating bath containing predetermined metal ions, corrosion-inhibiting pigment, corrosion-inhibiting organic compound, and ceramic particles shown in Table 7. The composition of the film was regulated by changing the concentration ratio of the metal ions in the plating bath, current density, and bath temperature and the thickness of the plated film was controlled by suitably choosing a plating time. Then, post treatment was carried out by dipping the resulting bolt in an acidic aqueous solution comprising 5g/l of HNO_3 and 15 g/l of $(NH_4)_2ZrF_6$, whereby a bolt for test was manufactured. Corrosion resistance of the resulting bolt for test was evaluated by the following method. The evaluation results are shown in Table 5.

[0067] (Corrosion resistance): A salt spray test (SST) was carried out in accordance with JIS Z2371 and corrosion resistance was evaluated by the time required for generation of white rust 10% or red rust 5%.

Table 5

		Plated film	Corrosion resistance (time required for rust generation)	
			White rust 10%	Red rust 5%
Example	73	Example 1	168	480
	74	Example 2	168	648
	75	Example 3	168	480
	76	Example 4	192	600
	77	Example 5	192	552
	78	Example 6	192	648
	79	Example 7	192	552
	80	Example 8	240	480
	81	Example 9	240	552
	82	Example 10	240	600
	83	Example 11	240	480
	84	Example 12	240	720
	85	Example 13	360	680
	86	Example 14	268	680
	87	Example 15	360	600
	88	Example 16	268	600
	89	Example 17	268	552
	90	Example 18	268	600
Comparative Example	17	Comparative Example 1	8	48
	18	Comparative Example 2	16	72
	19	Comparative Example 3	16	72
	20	Comparative Example 4	16	72

[0068] While the present invention has bee described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

[0069] This application is based on Japanese Patent Application No. 2003-410746 filed December 9, 2003, the contents thereof being herein incorporated by reference.

<Industrial Applciability>

[0070] The zinc-based alloy electroplated film of the invention comprises specific amounts of an iron-group metal and tungsten relative to zinc and has remarkably improved corrosion resistance as compared with the conventional zinc or zinc alloy plated films. The plated metal material having the zinc-based alloy electroplated film is useful as a metal member particularly for automobiles.

Claims

1. A zinc-based alloy electroplated film containing:

(A) 30 to 96% by weight of zinc,
(B) 2 to 20% by weight of an iron-group metal, and
(C) 2 to 50% by weight of tungsten.

2. The zinc-based alloy electroplated film according to claim 1, wherein the iron-group metal (B) is iron.

3. The zinc-based alloy electroplated film according to claim 1 or 2, which further contains 1 to 30% by weight of a corrosion-inhibiting pigment and/or ceramic particles.

4. The zinc-based alloy electroplated film according to claim 3, wherein the corrosion-inhibiting pigment is at least one selected from the group consisting of phosphate salts, molybdate salts, metaborate salts, and silicate salts.

5. The zinc-based alloy electroplated film according to claim 3, wherein the ceramic particles are particles of at least one member selected from the group consisting of Al_2O_3, SiO_2, TiO_2, ZrO_2, Y_2O_2, ThO_2, CeO_2, Fe_2O_3, B_4C, SiC, WC, ZrC, TiC, graphite, graphite fluoride, BN, Si_3N_9, TiN, Cr_3B_2, ZrB_2, $2MgO \cdot SiO_2$, $MgO \cdot SiO_2$, and $ZrO_2 \cdot SiO_2$.

6. The zinc-based alloy electroplated film according to any one of claims 1 to 5, which further contains at least one organic compound selected from the group consisting of alkynes, alkynols, amines or salts thereof, thio compounds, aromatic carboxylic acid compounds or salts thereof, and heterocyclic compounds in the plated film in an amount of 0.001 to 10% by weight in terms of C (carbon) content.

7. A plated metal material, which has the zinc-based alloy electroplated film according to any one of claims 1 to 6.

8. A plated metal material, wherein the zinc-based alloy electroplated film according to any one of claims 1 to 6 is formed on a metal material and then is brought into contact with an acidic aqueous solution containing at least one element selected from the group consisting of cobalt, nickel, titanium, and zirconium.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2004/018535

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl^7 C25D5/26, C25D15/02

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^7 C25D5/26, C25D3/56, C25D15/02

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

Jitsuyo Shinan Koho	1922-1996	Toroku Jitsuyo Shinan Koho	1994-2005
Kokai Jitsuyo Shinan Koho	1971-2005	Jitsuyo Shinan Toroku Koho	1996-2005

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 02/052068 A1 (POSCO CO., LTD.), 04 July, 2002 (04.07.02), Full text & KR 002051273 A & JP 2004-518021 A & EP 1346084 A1 & US 2003-64243 A1 & CN 1404536 A	1-8
X Y	JP 49-11735 A (Toyo Kohan Kabushiki Kaisha), 01 February, 1974 (01.02.74), Full text (Family: none)	1,2,7 3-6,8
Y	JP 2001-254195 A (Nippon Steel Corp.), 18 September, 2001 (18.09.01), Claims; Par. Nos. [0018], [0029] to [0041] (Family: none)	3-6

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

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"&" document member of the same patent family

Date of the actual completion of the international search 07 March, 2005 (07.03.05)	Date of mailing of the international search report 22 March, 2005 (22.03.05)
Name and mailing address of the ISA/ Japanese Patent Office	Authorized officer
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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2004/018535

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 5-195244 A (Nihon Parkerizing Co., Ltd.), 03 August, 1993 (03.08.93), Par. Nos. [0001] to [0033] & WO 93/005198 A1 & US 5342456 A & US 5449414 A & EP 600982 A1 & EP 825280 A2	8
A	JP 3-162598 A (Sumitomo Metal Industries, Ltd.), 12 July, 1991 (12.07.91), (Family: none)	1-8
A	JP 47-16522 B1 (Toyo Kohan Kabushiki Kaisha), 16 May, 1972 (16.05.72), (Family: none)	1-8
A	JP 8-246184 A (ATOTECH USA, INC.), 24 September, 1996 (24.09.96), & EP 727512 A1	1-8
A	JP 2000-309897 A (Sumitomo Metal Industries, Ltd.), 07 November, 2000 (07.11.00), (Family: none)	1-8

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- JP 3240994 B **[0004]**
- JP 2003410746 A **[0069]**