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(54) Zincate type zinc-iron alloy electroplating bath.

(57) A zincate type Zn-Fe alloy electroplating bath is disclosed which comprises a Zn compound, an alkali hydroxide, a Fe(II, III) salt, a complexing agent for dissolving the Fe(II, III) salt and a brightening agent. The brightening agent comprises a compound obtainable by quaternizing a derivative of thiourea with an alkylating agent bearing C_1-C_4 alkyl groups, and an alkylated polyalkylene polyamine obtainable by alkylating one or more of the basic nitrogen atoms of a polyalkylene polyamine with an alkylating agent bearing C_1-C_3 alkyl groups.

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The present invention relates to a zincate type zinciron alloy electroplating bath.

It is well known that an electroplated or deposited zinc (Zn) film can be codeposited with iron (Fe) or nickel (Ni) to enhance the corrosion resistance of the deposited Zn film. Therefore, many types of Zn alloy electroplating baths have been developed heretofore for forming a Zn film into which Fe or Ni is codeposited.

In many types of Zn alloy electroplating baths reported by the present time, a typical electroplating bath which may deposit a Zn-Fe alloy or a Zn-Ni alloy is a zincate type Zn alloy electroplating bath which contains a Fe salt or a Ni salt solubilized with the aid of a complexing agent.

Such a Zn alloy electroplating bath is disclosed in, for example, Japanese Patent Publication No. 60-181293.

A Zn film deposited on a work is generally treated by chromating for the purpose of enhancement of corrosion resistance of the Zn film. Similarly, a Zn alloy film deposited on a work may be treated by chromating for the same purpose. However, higher deposition ratio of Fe or Ni to Zn in the Zn film generally prevents formation of a good chromating film. On the contrary, lower deposition ratio of Fe or Ni to Zn in the Zn film generally prevents formation of a chromating film which may exhibit an enhanced corrosion resistance. Therefore, the deposition ratio of Fe or Ni to Zn has to be significantly closely controlled. Many investigations have been made to define preferable deposition ratio of Fe and Ni to Zn in the Zn film which may permit formation of a preferable chromating film. As a result, it has been known that the deposition ratio of Fe and Ni to Zn is preferably 0.1 - 5% for Fe and 2 - 20% for Ni.

The deposited Zn alloy film is desired to have a bright ,or glossy surface in appearance, since the quality of the surface of the Zn alloy film finished by post-treatment such as chromating highly depends on the brightness or glossiness of the surface of the Zn alloy film before applying such post-treatment.

In electroplating processes, it is technically difficult to maintain a uniform current density over the whole surface of a work to be plated. For example, when the work has projected portions and recessed portions, the current density on the projected portions becomes higher than that on the recessed portions. However, it is difficult to obtain a substantially equal current density on these two portions. Therefore, the important condition required for a practical Zn alloy electroplating bath is to assure provision of a Zn alloy film having a substantially constant alloy composition ratio and excellent glossiness in a wide range of current density.

As a result of examination of the conventional Zn alloy electroplating baths, it has been found that these baths do not sufficiently satisfy the condition required for the alloy electroplating baths as described above.

In order to avoid the disadvantages of the conventional Zn alloy electroplating baths, the inventors of the present invention have developed a Zn-Fe alloy electroplating bath as follows. The Zn-Fe alloy electroplating bath is a zincate type electroplating bath containing a Zn compound, an alkali hydroxide, a Fe(II, III) salt, a complexing agent for dissolving the Fe salt, and a brightening agent. The brightening agent used here is an alkylated polyalkylene polyamine produced by alkylating some of basic nitrogen atoms of polyalkylene polyamine with an alkylating agent having C1-C3 alkyl groups.

This Zn-Fe alloy electroplating bath is disclosed in Japanese Laid-Open Patent Publication No. 62-238387. It has been found that such a Zn-Fe alloy electroplating bath may provide a glossy film in a relatively wide range of current density and may reduce variation in deposition ratio of Fe to Zn in accordance with the level of the current density. The Zn-Fe alloy electroplating bath may form a good film in the range of the current density of 0.2 to 15 A/dm^2.

The inventors of the present invention have further improved the Zn-Fe alloy electroplating bath disclosed in the above Japanese Laid-Open Patent Publication No. 62-238387 to develop a new Zn-Fe alloy electroplating bath. The new Zn-Fe alloy electroplating bath is a zincate type electroplating bath containing a Zn compound, an alkali hydroxide, a Fe(II, III) salt, a complexing agent for dissolving the Fe salt, and brightening agents. The brightening agents used here are an alkylated polyalkylene polyamine produced by alkylating some of basic nitrogen atoms of polyalkylene polyamine with an alkylating agent having C1-C3 alkyl groups, and a compound selected from the group consisting of reaction products of imidazole or its derivative with epihalohydrin and reaction products of imidazole or its derivative with epihalohydrin in the presence of aliphatic amine.

This new Zn-Fe alloy electroplating bath is disclosed in Japanese Laid-Open Patent Publication No. 2-141596. It has been found that the new Zn-Fe alloy electroplating bath may form a good film in the wider range of the current density of 0.1 to 20 A/dm^2.

As described above, the Zn-Fe alloy electroplating bath has been improved by the inventors of the present invention so as to be put to practical use. However, the Zn-Fe alloy electroplating bath still requires improvements.

As described above, a deposited Zn-Fe alloy film is generally treated by chromating for the purpose of enhancement of corrosion resistance thereof. The chromating commonly used includes yellow chromating, black chromating which provide a silver containing black chromating film (hereinafter referred to as "silver black chromating"), black chromating which provide a silver free black chromating film (hereinafter referred to as

"nonsilver black chromating") and the like.

In these chromating, it is known that the nonsilver black chromating may form the silver free black chromating film only when applied to the Zn-Fe alloy film having the deposition ratio of Fe to Zn is 0.3 - 0.6%. The nonsilver black chromating provides a significant advantage that the formed silver free black chromating film exhibits increased corrosion resistance for a long time because of excellent water repellency thereof. The corrosion resistance of the silver free black chromating film is substantially twice that of the yellow chromating film formed by the yellow chromating. Furthermore, the nonsilver black chromating contributes to lower cost because it does not employ expensive silver.

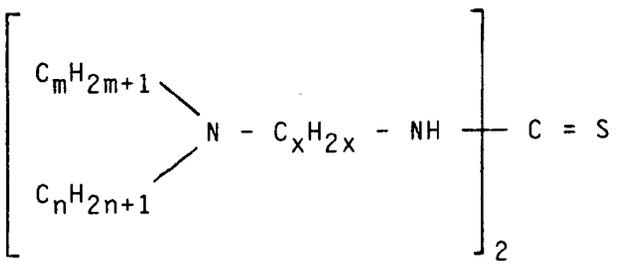
The conventional Zn-Fe alloy electroplating bath, even when operated in high current density near the upper limit of 20 A/dm^2, may deposit a Zn-Fe alloy film which permits formation of a good chromating film by the yellow chromating and the silver black chromating. However, the conventional Zn-Fe alloy electroplating bath, only when operated in current density lower than 10 A/dm^2, may deposit a Zn-Fe alloy film which permits formation of a good chromating film by the nonsilver black chromating.

Therefore, it is strongly required to develop a new Zn-Fe alloy electroplating bath which may deposit a Zn-Fe alloy film permitting formation of a good black chromating film by the nonsilver black chromating even when operated in high current density near 20 A/dm^2.

It is an object of the invention to further improve the Zn-Fe alloy electroplating bath as disclosed in Japanse Laid-Open Patent Publication No. 2-141596.

It is another object of the invention to provide a Zn-Fe alloy electroplating bath which may deposit a Zn-Fe alloy film permitting formation of a good chromating film, more particularly, a good silver free black chromating film even when operated in higher current density.

According to the present invention, there is provided a zincate type Zn-Fe alloy electroplating bath containing a Zn compound, an alkali hydroxide, a Fe(II, III) salt, a complexing agent for dissolving said Fe(II, III) salt, and brightening agents comprising a compound produced by quaternizing a derivative of thiourea with an alkylating agent having C1-C4 alkyl groups, said derivative of thiourea having the following general formula:



wherein x, m and n are integers from 0 to 5, x, m and n are equal to each other or not, and an alkylated polyalkylene polyamine produced by alkylating some of basic nitrogen atoms of polyalkylene polyamine with an alkylating agent having C1 to C3 alkyl groups.

An important feature of the Zn-Fe alloy electroplating bath according to the the present invention is that a good glossy film may be deposited in the wide range of the current density of 0.1 to 30 A/dm^2.

Another feature of the Zn-Fe alloy electroplating bath according to the present invention is that the deposition ratio of Fe to Zn in a deposited Fe-Zn alloy film is not practically varied even if the current density is varied in the wide range of 0.1 to 30 A/dm^2.

A further feature of the Zn-Fe alloy electroplating bath according to the present invention is that a Zn-Fe alloy film permitting formation of a good chromating film by chromating except for the nonsilver black chromating may be deposited in the wide range of the current density of 0.1 to 30 A/dm^2.

A still further feature of the Zn-Fe alloy electroplating bath according to the present invention is that a Zn-Fe alloy film permitting formation of a good black chromating film by the nonsilver black chromating may be deposited in the range of the current density of 0.1 to 20 A/dm^2.

The present invention will become more fully apparent from the claims and the following description.

Now, the present invention will be more fully described with reference to preferred embodiments.

The electroplating bath of the present invention is prepared by adding brightening agents to a basic bath. The basic bath is a zincate type bath containing a Zn compound, an alkali hydroxide, a Fe(II, III) salt and a complexing agent for dissolving the Fe(II, III) salt. The composition of the basic bath used in the present invention is as follows.

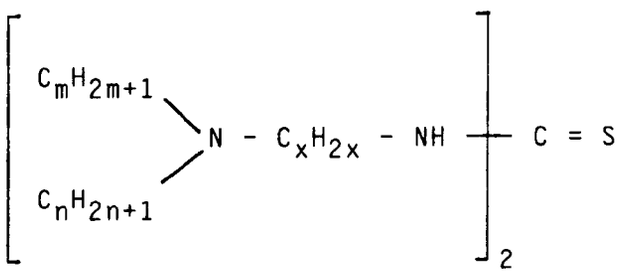
Composition of the basic bath

Zn compound (calculated as Zn^{2+})	:5 - 40 g/l
Alkali hydroxide (such as NaOH)	:30 - 200 g/l
Fe (calculated as Fe^{2+} or Fe^{3+})	:0.02 - 5 g/l
Complexing agent	:1 - 100 mol/1mol of Fe ion

In the above basic bath, the Zn compound may be typically ZnO, and alkali hydroxide may be NaOH, KOH or the like. The Fe salt may be $Fe_2(SO_4)_3 \cdot 7H_2O$, $FeSO_4 \cdot 7H_2O$, $Fe(OH)_3$, $FeCl_3 \cdot 6H_2O$, $FeCl_2 \cdot 4H_2O$ or the like. Furthermore, examples of the complexing agent (chelating agent) suitable for dissolving the Fe salt include hydroxycarboxylates such as citrate, tartrate and gluconate; amino alcohols such as monoethanolamine, diethanolamine and triethanolamine; polyamines such as ethylenediamine (EDA), diethylenetriamine and triethylenetetramine; aminocarboxylates such as ethylenediaminetetraacetate and nitrilotriacetate; polyhydric alcohols such as solbitol and pentaerythritol; and mixtures thereof. Triethanolamine is preferable for the complexing agent.

The following three kinds of brightening agents were used:

(a) a compound produced by alkylating or quaternizing a derivative of thiourea with an alkylating agent having C1-C4 alkyl groups, the derivative of thiourea having the following general formula:



wherein x, m and n are integers from 0 to 5, and x, m and n may be equal to each other or not;

(b) alkylated polyalkylene polyamine produced by alkylating some of basic nitrogen atoms of polyalkylene polyamine with an alkylating agent having C1-C3 alkyl groups; and

(c) one or more compounds selected from the group consisting of reaction products of imidazole or its derivative with epihalohydrin, and reaction products of imidazole or its derivative with epihalohydrin in the presence of aliphatic amine.

The brightening agents (a), (b) and (c) will be hereinafter referred to as brightening agent 1, brightening agent 2 and brightening agent 3, respectively.

The derivatives of thiourea of the above general formula capable of forming the brightening agent 1 are bis(dimethylaminobutyl)thiourea, bis(methylaminopropyl)thiourea, thiocarbazide, bis(aminoethyl)thiourea, N-aminoethyl-N'-methylaminoethylthiourea, bis(dimethylaminopropyl)thiourea, bis(dimethylaminoethyl)thiourea, bis(aminopropyl)thiourea, bis(methylaminoethyl)thiourea and N-methylaminoethyl-N'-dimethylaminoethylthiourea.

Compounds employable as the alkylating agent for forming the brightening agent 1 are those such as CH_3Cl, CH_3Br, CH_3I, C_2H_5Cl, C_2H_5Br, C_2H_5I, $(CH_3)_2SO_4$, $(C_2H_5)_2SO_4$, C_3H_7Cl, C_3H_7Br and C_3H_7I.

The dosage of the brightening agent 1 can range from 0.1 to 50 g/l (preferably from 0.5 to 30 g/l).

Polyalkylene polyamines suitable for forming the brightening agent 2 are those such as polyethyleneimine, polypropyleneimine and polybutyleneimine each of which has a molecular weight of from 300 to 5,000.

Further, compounds suitable as the alkylating agent for forming the brightening agent 2 are C1-C3 compounds, such as CH_3Cl, CH_3Br, CH_3I, C_2H_5Br, C_2H_5I, $(CH_3)_2SO_4$, $(C_2H_5)_2SO_4$, C_3H_7I, C_3H_7Cl and C_3H_7Br.

The dosage of the brightening agent 2 can range from 0.1 to 50 g/l (preferably from 0.5 to 10 g/l).

The derivatives of imidazole capable of forming the brightening agent 3 are 1-methylimidazole, 1-ethylimidazole, 2-methylimidazole, 1,2-dimethylimidazole, 1-ethyl-2-methylimidazole , 1-vinylimidazole, 2-metyl-1-vinylimidazole, 1-(2′-hydroxyethyl)imidazole, and 1-(2′-hydroxyethyl)2-methylimidazole.

Epihalohydrin suitable for forming the brightening agent 3 are epichlorohydrin and epibromohydrin.

Aliphatic amine usable for forming the brightening agent 3 are methylamine, dimethylamine, trimethylamine, ethylamine, diethylamine, triethylamine, propylamine, dipropylamine, tripropylamine, and ethyleneamine such as ethylenediamine and dietylenetriamine.

The dosage of the brightening agent 3 can range from 0.1 to 50 g/l (preferably from 0.5 to 10 g/l).

Each of the brightening agents 1 and 2 may acts as a main brightening agent. The brightening agent 3 may act as an auxiliary brightening agent to enhance glossiness of the electroplating film. Therefore, the brightening agent 3 is not necessarily required to be added to the electroplating bath of the present invention.

In the electroplating bath of the present invention, one or more auxiliary brightening agents may be used, if required, together with the brightening agents 1 and 2 in order to further improve glossiness of the electroplating film. Compounds usable as such auxiliary brightening agents are members selected from the group consisting of water soluble polymers such as polyvinyl alcohol (PVA) and gelatin; sulfur compounds such as thiourea; aromatic aldehydes such as anisaldehyde, heliotropin and vanillin; and mixture thereof.

Now, the examples of the present invention will be described.

Preparation of the Brightening Agent 1

Four kinds of derivatives of thiourea were dissolved in 100 grams of water. The solutions were cooled to 50°C with water, and dimethyl sulfate was added to each of the solutions for 30 minutes with stirring. The mixtures were heated to 80°C with stirring and the condition was maintained for 2 hours. Stirring was discontinued and the mixtures were left to cool to obtain reaction products I to VI.

Table 1 shows the kinds and amount of the derivatives of thiourea and the amount of dimethyl sulfate used to obtain the above reaction products I to VI.

TABLE 1

Reaction Products No.	Derivatives of Thiourea: Kind	Derivatives of Thiourea: Amount (g)	Dimethyl Sulfate: Amount (g)
I	Thiocarbazide	22	150
II	Bisaminoethylthiourea	33	50
III	Bisdimethylaminopropylthiourea	50	50
IV	Bisaminoethylthiourea	33	100
V	Bisdimethylaminopropylthiourea	50	100
VI	Bismethylaminoethylthiourea	41	75

Preparation of the Brightening Agent 2

Three kinds of polyethyleneimines having different molecular weights were dissolved in 100 grams of wa-

ter. The solutions were cooled with water, and dimethyl sulfate was added to each of the solutions for 30 minutes with stirring. The mixtures were heated to 80°C with stirring and the condition was maintained for 2 hours. Stirring was discontinued and the mixtures were left to cool to obtain reaction products VII to IX.

Table 2 shows the molecular weight and amount of polyethyleneimine and the amount of dimethyl sulfate used to obtain the above reaction products VII to IX.

TABLE 2

Reaction Products No.	Polyethyleneimine		Dimethyl Sulfate
	Molecular Weight	Amount (g)	Amount (g)
VII	600	20	88
VIII	1400	40	58
IX	3000	40	58

Preparation of the Brightening Agent 3

Twenty grams of imidazole were dissolved in 100 grams of water. The solution was cooled with water, and 27 grams of epichlorohydrin were added to the solution for 30 minutes with stirring. The mixture was heated to 95°C with stirring and the condition was maintained for 2 hours. Stirring was discontinued and the mixture was left to cool to obtain a reaction product X.

Preparation of the Zn-Fe Alloy Electroplating Bath

Twenty one kinds of zincate type Zn-Fe alloy electroplating baths Nos. 1 to 21 according to the present invention were prepared for testing. The baths contain ZnO as a Zn compound, NaOH as an alkali hydroxide, $Fe_2(SO_4)_3 \cdot 7H_2O$ as an Fe salt, triethanolamine as a complexing agent, and the brightening agents 1 and 2. Twenty (No. 1 to 20) of these baths contain at least one of the auxiliary brightening agents such as the brightening agent 3, vanillin, PVA and thiourea. The remaining one (No. 21) of these baths contains no auxiliary brightening agent.

Further, seven kinds of zincate type Zn-Fe alloy electroplating baths Nos. 1′ to 7′ were prepared as controls. The baths contain ZnO as a Zn compound, NaOH as an alkali hydroxide, $Fe_2(SO_4)_3 \cdot 7H_2O$ as an Fe salt, and triethanolamine as a complexing agent. These baths contain at least one of the brightening agent 2 and the auxiliary brightening agents such as the brightening agent 3, vanillin, PVA and thiourea, but not contain the brightening agent 1.

Compositions of the above electroplating baths are presented in Table 3.

TABLE 3

COMPOSITIONS OF ELECTROPLATING BATHS

Bath No.	Essential Components			
	1	2	3	4
	ZnO (g/l)	NaOH (g/l)	$Fe_2(SO_4)_3 \cdot 7H_2O$ (g/l)	Triethanolamine (g/l)
1	10	80	0.5	0.6
2	10	130	0.5	21.4
3	10	150	2.4	13.4
4	10	100	2.4	53.4
5	40	130	0.5	1.4
6	40	100	0.5	21.4
7	40	80	9.5	10.7
8	40	150	9.5	107
9	25	130	1.9	42.7
10	25	130	1.9	42.7
11	25	130	1.9	42.7
12	25	130	1.9	42.7
13	25	130	1.9	42.7
14	25	130	1.9	42.7
15	25	130	1.9	42.7
16	25	130	1.9	42.7
17	25	130	1.9	42.7
18	25	130	1.9	42.7
19	25	130	1.9	42.7
20	25	130	1.9	42.7
21	25	130	1.9	42.7
1'	25	130	1.9	42.7
2'	25	130	1.9	42.7
3'	25	130	1.9	42.7
4'	25	130	1.9	42.7
5'	25	130	1.9	42.7
6'	25	130	1.9	42.7
7'	25	130	1.9	42.7

TABLE 3 (cont.)

COMPOSITIONS OF ELECTROPLATING BATHS

	Main Brightening Agents				Auxiliary Brightening Agents	
	5		6		7	
	Brightening Agent 1		Brightening Agent 2		Brightening Agent 3	
Bath No.	No.	Amount (g/l)	No.	Amount (g/l)	No.	Amount (g/l)
1	I	3	VII	3	X	1
2	II	3	VIII	3	X	1
3	III	3	VIII	3	X	1
4	IV	3	VIII	3	X	1
5	V	3	IX	3	X	1
6	VI	3	VIII	3	X	1
7	III	3	VIII	3	X	1
8	V	3	IX	3	X	1
9	III	3	VIII	3	X	1
10	III	3	VIII	3	X	1
11	III	3	VIII	3	X	1
12	III	20	VIII	3	X	1
13	III	20	VIII	3	X	1
14	III	20	VIII	3	X	1
15	III	0.5	VIII	3	X	1
16	III	0.5	VIII	3	X	1
17	III	0.5	VIII	3	X	1
18	III	3	VIII	3	X	0.5
19	III	3	VIII	3	X	0.5
20	III	3	VIII	3	X	0.5
21	III	3	VIII	3	-	-
1'	-	-	VIII	3	X	3
2'	-	-	VIII	3	-	-
3'	-	-	-	-	X	3
4'	-	-	VIII	3	X	3
5'	-	-	VIII	3	-	-
6'	-	-	-	-	X	3
7'	-	-	VIII	3	X	3

TABLE 3 (cont.)

COMPOSITIONS OF ELCTROPLATING BATHS

Bath No.	Auxiliary Brightening Agents 8 Vanillin (g/l)	9 PVA (g/l)	10 Thiourea (g/l)
1	-	0.2	0.2
2	-	0.2	0.2
3	-	0.2	0.2
4	-	0.2	0.2
5	-	0.2	0.2
6	-	0.2	0.2
7	-	0.2	0.2
8	-	0.2	0.2
9	-	0.2	0.2
10	0.05	0.2	0.2
11	-	-	-
12	-	0.2	0.2
13	0.05	0.2	0.2
14	-	-	-
15	-	0.2	0.2
16	0.05	0.2	0.2
17	-	-	-
18	-	0.2	0.2
19	0.05	0.2	0.2
20	-	-	-
21	-	-	-
1'	-	0.2	0.2
2'	-	0.2	0.2
3'	-	0.2	0.2
4'	0.05	0.2	0.2
5'	0.05	0.2	0.2
6'	0.05	0.2	0.2
7'	0.15	0.2	0.2

Zn-Fe Alloy Electroplating Procedure

To demonstrate how the present invention provides improved Zn-Fe alloy films, Zn-Fe alloy films were deposited on substrates from each of the electroplating baths shown in Table 3. The electroplating conditions were as follows.

Electroplating Conditions

Bath temperature (°C)	: 25
Plating Time (min)	: 10
Cathode (substrate)	: polished iron plate
Cathode current density (A/dm^2)	: 0.1, 0.5, 2, 5, 10, 20, 30
Anode	: iron plate
Stirring means	: cathode rocking

The data for the Zn-Fe alloy films deposited from the baths Nos. 1 to 21 of the present invention under these conditions, compared to the Zn-Fe alloy films deposited from the baths Nos. 1′ to 7′ as controls, are shown in Tables 4 and 5. Table 4 shows data as to the appearances of the films in relation to the current density. Table 5 shows data as to the deposition ratios of Fe to Zn in relation to the current density. The appearances of the films were visually examined, and the deposition ratios of Fe to Zn were determined by applying the films peeled from the substrates to atomic absorption spectrometry.

TABLE 4

APPEARANCES OF ELECTROPLATING FILMS

Bath No.	Current Density (A/dm^2) 0.1	0.5	2	5	10	20	30
1	A	A	A	A	A	A	A
2	A	A	A	A	A	A	A
3	A	A	A	A	A	A	A
4	A	A	A	A	A	A	A
5	A	A	A	A	A	A	A
6	A	A	A	A	A	A	A
7	A	A	A	A	A	A	A
8	A	A	A	A	A	A	A
9	A	A	A	A	A	A	A
10	S	S	S	S	S	S	S
11	A	A	A	A	A	A	A
12	A	A	A	A	A	A	A
13	S	S	S	S	S	S	S
14	A	A	A	A	A	A	A
15	A	A	A	A	A	A	A
16	S	S	S	S	S	S	S
17	A	A	A	A	A	A	A
18	A	A	A	A	A	A	A
19	S	S	S	S	S	S	S
20	A	A	A	A	A	A	A
21	A	A	A	A	A	A	A
1'	B	B	B	B	B	B	C
2'	B	B	B	B	C	C	D
3'	D	D	C	C	B	B	B
4'	A	A	A	A	A	A	C
5'	A	A	A	A	B	B	C
6'	C	C	B	A	A	A	B
7'	S	S	S	S	S	S	A

S: high glossy
A: glossy
B: semi-glossy
C: partially dull
D: partially burnt and partially extremely dull

TABLE 5

DEPOSITION RATIOS OF Fe IN ELECTROPLATING FILMS

Bath No.	Current Density (A/dm^2) 0.1	0.5	2	5	10	20	30
1	5.0	4.0	2.1	1.4	1.2	1.0	0.9
2	0.35	0.33	0.31	0.30	0.27	0.25	0.22
3	2.2	2.1	2.0	1.7	1.5	1.3	1.0
4	1.5	1.4	1.4	1.1	1.0	0.92	0.90
5	1.1	0.92	0.51	0.35	0.29	0.24	0.21
6	0.31	0.24	0.19	0.16	0.14	0.13	0.11
7	10.2	9.1	7.1	6.0	4.7	3.5	3.0
8	1.9	1.8	1.6	1.4	1.1	1.0	0.98
9	0.55	0.53	0.52	0.51	0.50	0.49	0.47
10	0.55	0.53	0.52	0.51	0.50	0.50	0.49
11	0.57	0.56	0.53	0.51	0.50	0.49	0.47
12	0.50	0.49	0.48	0.48	0.47	0.46	0.46
13	0.50	0.49	0.48	0.48	0.47	0.47	0.47
14	0.53	0.51	0.50	0.49	0.48	0.47	0.46
15	0.56	0.55	0.51	0.50	0.49	0.49	0.47
16	0.56	0.55	0.51	0.50	0.49	0.49	0.48
17	0.57	0.56	0.52	0.51	0.50	0.49	0.48
18	0.56	0.54	0.53	0.52	0.51	0.50	0.48
19	0.55	0.53	0.52	0.51	0.50	0.50	0.49
20	0.57	0.56	0.53	0.51	0.50	0.49	0.47
21	0.56	0.55	0.53	0.52	0.51	0.50	0.48
1'	0.56	0.54	0.51	0.50	0.49	0.47	0.45
2'	0.45	0.43	0.42	0.41	0.38	0.35	0.30
3'	0.65	0.63	0.59	0.53	0.52	0.50	0.48
4'	0.57	0.55	0.52	0.50	0.49	0.48	0.46
5'	0.45	0.43	0.42	0.41	0.40	0.38	0.35
6'	0.65	0.63	0.59	0.54	0.53	0.52	0.50
7'	0.57	0.55	0.52	0.50	0.49	0.48	0.46

Chromating Procedure

To demonstrate how Zn-Fe alloy films deposited from the baths of the present invention provide good silver free black chromating films when treated by the nonsilver black chromating, the Zn-Fe alloy films formed on substrates were treated by the nonsilver black chromating. Nonsilver black chromating bath was prepared from "METHATH ULTRAMATE NONSILVER 637" sold by Yuken Kogyo Kabushiki Kaisha, the assignee of the present invention. The chromating bath was prepared by diluting METHATH ULTRAMATE NONSILVER 637 by water so as to contain 10% by volume of it. The chromating bath was maintained at 20 to 25°C. Also, treating time was 40 to 60 seconds.

To form the Zn-Fe alloy films on the substrates, the electroplating baths shown in Table 3 were used. Also, the electroplating procedure were carried out under the conditions as described above except that the upper limit of the current was set to 20 A/dm^2.

Further, as described above, it has been known that good nonsilver black chromating film is not formed on Zn-Fe alloy film which has deposition ratio of Fe to Zn outside the range of 0.3 to 0.6%. Therefore, the Zn-

Fe alloy films deposited from the electroplating baths Nos. 1 to 8 were not tested.

The data for the nonsilver black chromating films formed on the Zn-Fe alloy films deposited from the baths Nos. 9 to 21 of the present invention, compared to the nonsilver black chromating films formed on the Zn-Fe alloy films deposited from the baths Nos. 1′ to 7′ as controls, are shown in Tables 6. Table 6 shows data as to the appearances of the chromating films in relation to the current density which was applied to deposit the Zn-Fe alloy films.

TABLE 6

APPEARANCES OF CHROMATING FILMS

Bath No.	Current Density Applied to Deposit Zn-Fe Alloy Films (A/dm^2)						
	0.1	0.5	2	5	10	15	20
1	-	-	-	-	-	-	-
2	-	-	-	-	-	-	-
3	-	-	-	-	-	-	-
4	-	-	-	-	-	-	-
5	-	-	-	-	-	-	-
6	-	-	-	-	-	-	-
7	-	-	-	-	-	-	-
8	-	-	-	-	-	-	-
9	A	A	A	A	A	A	A
10	A	A	A	A	A	A	A
11	A	A	A	A	A	A	A
12	A	A	A	A	A	A	A
13	A	A	A	A	A	A	A
14	A	A	A	A	A	A	A
15	A	A	A	A	A	A	A
16	A	A	A	A	A	A	A
17	A	A	A	A	A	A	A
18	A	A	A	A	A	A	A
19	A	A	A	A	A	A	A
20	A	A	A	A	A	A	A
21	A	A	A	A	A	A	A
1′	B	B	B	B	B	C	C
2′	B	B	B	B	C	C	C
3′	D	D	C	C	C	C	C
4′	A	A	A	A	A	C	C
5′	A	A	A	A	C	C	D
6′	C	C	C	C	C	C	C
7′	A	A	A	A	B	C	D

A: uniform glossy black
B: uniform black
C: partially white dull
D: faulty chromating film
(due to insufficient chromating reaction)

Results

From the data shown in Table 4, it can be seen that all of the Zn-Fe alloy electroplating baths Nos. 1 to 21 provide good glossy Zn-Fe alloy films under the current density range of 0.1 to 30A/dm^2.

From the data shown in Table 5, it can be seen that the Zn-Fe alloy electroplating baths Nos. 9 to 21 provide Zn-Fe alloy films having stable deposition ratios of Fe to Zn under the current density range of 0.1 to 30A/dm^2.

From the data shown in Tables 4 and 6, it can be seen that all of the glossy Zn-Fe alloy films deposited from the baths Nos. 9 to 21 provide excellent nonsilver black chromating films, whereas the glossy Zn-Fe alloy films (specially, deposited under high current density) deposited from the conventional baths Nos. 1′ to 7′ do not necessarily provide excellent nonsilver black chromating films. Since it has been known that chromating film having good appearance generally exhibit superior corrosion resistance, the Zn-Fe alloy film deposited from the bath of the present invention, when treated by chromating, will exhibit superior corrosion resistance.

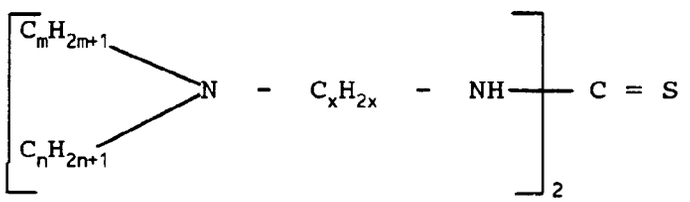
Moreover, referring to the baths Nos. 11, 14, 17, 20 and 21 shown in Tables 3 and 4, it would appear that the bath of the present invention provide a good Zn-Fe alloy film even if it does not contain an auxiliary brightening agent such vanillin (aromatic carbonyl compound), PVA and thiourea.

While the invention has been described and illustrated herein by references to various specific materials, procedures and examples, it is understood that the invention is not restricted to the particular materials, combinations of materials, and procedures selected for that purpose. Numerous variations of such details can be employed, as will be appreciated by those skilled in the art.

Claims

1. A zincate type Zn-Fe alloy electroplating bath containing a Zn compound, an alkali hydroxide, a Fe(II, III) salt, a complexing agent for dissolving said Fe(II, III) salt, and a brightening agent, characterised in that the brightening agent comprises:

   (i) a compound obtainable by quaternizing a derivative of thiourea of the following general formula:



   wherein each of x, m and n is, independently, an integer from 0 to 5, with an alkylating agent bearing one or more C_1-C_4 alkyl groups, and

   (ii) an alkylated polyalkylene polyamine obtainable by alkylating one or more of the basic nitrogen atoms of a polyalkylene polyamine with an alkylating agent bearing one or more C_1-C_3 alkyl groups.

2. An electroplating bath according to claim 1 which further comprises a compound which is obtainable by reacting imidazole or a derivative thereof with epihalohydrin, or by reacting imidazole or a derivative thereof with epihalohydrin in the presence of an aliphatic amine.

3. An electroplating bath according to claim 1 or 2 which further comprises a water soluble polymer, a sulphur compound or an aromatic aldehyde.

4. An electroplating bath according to claim 3 wherein the water soluble polymer is selected from polyvinyl alcohol and gelatin, the sulphur compound is thiourea, and the aromatic aldehyde is selected from vanillin, anisaldehyde and heliotropin.

5. An electroplating bath according to any one of the preceding claims wherein the derivative of thiourea is selected from bis(dimethylaminobutyl)thiourea, bis(methylaminopropyl)thiourea, thiocarbazide, bis(aminoethyl)thiourea, N-aminoethyl-N′-methylaminoethylthiourea, bis(dimethylaminopropyl)thiourea, bis(dimethylaminoethyl)thiourea, bis(aminopropyl)thiourea, bis(methylaminoethyl)thiourea and N-methylaminoethyl-N′-dimethylaminoethylthiourea.

6. An electroplating bath according to any one of the preceding claims wherein the alkylating agent bearing C_1-C_4 alkyl groups is selected from CH_3C1, CH_3Br, CH_3I, C_2H_5C1, C_2H_5Br, C_2H_5I, $(CH_3)_2SO_4$, $(C_2H_5)_2SO_4$, C_3H_7C1, C_3H_7Br and C_3H_7I.

7. An electroplating bath according to any one of the preceding claims wherein the polyalkylene polyamine is selected from polyethyleneimine, polypropyleneimine and polybutyleneimine, each of which has a molecular weight of from 300 to 5,000.

8. An electroplating bath according to any one of the preceding claims wherein the alkylating agent bearing C_1-C_3 alkyl groups is selected from CH_3C1, CH_3Br, CH_3I, C_2H_5Br, C_2H_5I, $(CH_3)_2SO_4$, $(C_2H_5)_2SO_4$, C_3H_7I, C_3H_7C1 and C_3H_7Br.

9. An electroplating bath according to any one of the preceding claims wherein the compound obtainable by quaternizing a derivative of thiourea with an alkylating agent is contained in an amount of 0.5-30 g/l.

10. An electroplating bath according to any one of the preceding claims wherein the alkylated polyalkylene polyamine obtainable by alkylating a polyalkylene polyamine with an alkylating agent is contained in an amount of 0.5-10 g/l.