

## Description

Title of Invention: ZINC ALLOY PLATING METHOD

Technical Field

The present invention relates to a zinc alloy plating  
5 method. Specifically, the present invention relates to a  
plating method by which a plating bath can be used for a long  
period with the performance of the plating bath being maintained  
with a simple anode separation apparatus in performing alkaline  
zinc alloy plating excellent in corrosion prevention  
10 characteristics on a steel member or the like.

Background Art

Zinc alloy plating has a better corrosion resistance than  
zinc plating, and hence has been widely used for automobile  
components and the like. Among types of zinc alloy plating,  
15 especially alkaline zinc-nickel alloy plating has been used for  
fuel system components required to have high corrosion  
resistance and engine components placed under high-temperature  
environments. An alkaline zinc-nickel alloy plating bath is  
a plating bath in which nickel is dissolved with an amine-based  
20 chelating agent selected to be suitable in terms of Ni  
co-deposition ratio, and zinc and nickel are co-deposited in  
a plated coating. However, when alkaline zinc-nickel alloy  
plating is performed, there arises a problem of oxidative  
decomposition of the amine-based chelating agent in the  
25 vicinity of the anode during current application. The  
oxidative decomposition of the amine-based chelating agent is  
caused by active oxygen generated at the anode. When ions of  
an iron group metal such as nickel ions or iron ions are  
coexistent, these ions act as an oxidation catalyst, and further  
30 promote the oxidative decomposition of the amine-based

chelating agent. Accordingly, when an alkaline zinc-nickel alloy plating liquid comes into contact with an anode, the amine-based chelating agent rapidly decomposes, resulting in deterioration in plating performance. Accumulation of products of the decomposition causes many problems such as decrease in current efficiency, increase in bath voltage, decrease in plating thickness, decrease in nickel content in plated coating, narrowing of a permissible current density range for the plating, decrease in gloss, and increase in COD. For this reason, the plating liquid cannot be used for a long period, and has to be exchanged.

As methods for improvement in this point, some methods have been known so far. For example, Published Japanese Translation of PCT International Application No. 2002-521572 discloses a method in which a catholyte and an acidic anolyte in an alkaline zinc-nickel bath are separated from each other by a cation exchange membrane made of a perfluorinated polymer. However, when an acidic liquid is used as the anolyte, it is necessary to use an expensive corrosion-resistant member, such as platinum-plated titanium, as the anode. In addition, when the separation membrane is broken, there is a possibility of an accident in which the acidic solution on the anode side and the alkaline solution on the cathode side are mixed with each other to cause a rapid chemical reaction. Meanwhile, a plating test conducted by the present inventors has revealed that when an alkaline liquid is used as the anolyte instead of the acidic liquid, the anolyte rapidly moves to the catholyte upon current application, causing the lowering of the liquid level of the anolyte and the elevation of the liquid level of the catholyte simultaneously.

As a method for solving the above-described problems, Japanese Patent Application Publication No. 2007-2274 describes a method in which a cation exchange membrane is used, and an alkali component is supplemented to an alkaline anolyte.

5 However, this method requires an additional apparatus, liquid management, and the like, which complicate the operations.

In addition, Published Japanese Translation of PCT International Application No. 2008-539329 discloses a zinc alloy plating bath in which a cathode and an anode are separated  
10 from each other by a filtration membrane. However, a test conducted by the present inventors has shown that the disclosed filtration membrane is incapable of preventing movement between the catholyte and the anolyte, and incapable of preventing decomposition of a chelating agent at the anode. In addition,  
15 since a zinc alloy plating liquid is used also as the anolyte, the decomposition of the anolyte is promoted very much. Accordingly, the anolyte has to be exchanged, and when the anolyte is not exchanged, the decomposition product moves into the plating liquid at the cathode. For this reason, it has been  
20 found that this method does not lead to substantial extension of the lifetime of the liquid.

#### Summary

An object of the present disclosure is to provide a plating method which can achieve lifetime extension of a zinc alloy  
25 plating bath by maintaining the performance of the zinc alloy plating bath with an economical apparatus in which the anode separation is achieved easily and in which the liquid level is easy to manage.

In one aspect of the present disclosure, there is provided  
30 a zinc alloy electroplating method comprising applying a

current through an alkaline zinc alloy electroplating bath comprising a cathode and an anode, wherein

a cathode region including the cathode and an anode region including the anode are separated from each other by a separator  
5 comprising an electrically conductive electrolyte gel.

The present disclosure has been made based on the following finding. Specifically, in an alkaline zinc alloy

electroplating bath comprising a cathode and an anode, a cathode region including the cathode and an anode region including the anode are separated from each other by a separator comprising an electrically conductive electrolyte gel. In this case, it is possible to suppress or prevent the movement of a plating liquid, especially, the movement of a quaternary ammonium salt-based brightening agent and an amine-based chelating agent, so that the oxidative decomposition of the amine-based chelating agent and the quaternary ammonium salt-based brightening agent in the bath is suppressed. In addition, it has been found that the electrolyte in the anode region does not move to the cathode region, either, and the liquid level in each region does not change, so that the liquid levels can be managed without any problem. Specifically, the present disclosure provides a zinc alloy electroplating method comprising applying a current through an alkaline zinc alloy electroplating bath comprising a cathode and an anode, wherein a cathode region including the cathode and an anode region including the anode are separated from each other by a separator comprising an electrically conductive electrolyte gel.

The present disclosure makes it possible to provide a plating method which can achieve lifetime extension of a zinc alloy plating bath by maintaining the performance of the zinc alloy plating bath with an economical apparatus in which the anode separation is achieved easily and in which the liquid level is easy to manage.

#### Brief Description of Drawings

Fig. 1 shows plating test results (appearance of plating) of Examples 1 and 2 and Comparative Example 1.

Fig. 2 shows plating test results (plating thickness

distribution) of Example 1.

Fig. 3 shows plating test results (plating thickness distribution) of Example 2.

Fig. 4 shows plating test results (plating thickness distribution) of Comparative Example 1.

Fig. 5 shows plating test results (Ni co-deposition ratio distribution) of Example 1.

Fig. 6 shows plating test results (Ni co-deposition ratio distribution) of Example 2.

Fig. 7 shows plating test results (Ni co-deposition ratio distribution) of Comparative Example 1.

#### Description of Embodiments

A method of the present invention is a zinc alloy electroplating method comprising applying a current through an alkaline zinc alloy electroplating bath comprising a cathode and an anode, wherein a cathode region including the cathode and an anode region including the anode are separated from each other by a separator comprising an electrically conductive electrolyte gel.

The metal used in combination with zinc in the zinc alloy plating is, for example, one or more metals selected from nickel, iron, cobalt, tin, and manganese. Specifically, the zinc alloy plating may be zinc-nickel alloy plating, zinc-iron alloy plating, zinc-cobalt alloy plating, zinc-manganese alloy plating, zinc-tin alloy plating, zinc-nickel-cobalt alloy plating, or the like, but is not limited to these types of alloy plating. The zinc alloy plating is preferably zinc-nickel alloy plating.

The separator preferably comprises the electrically conductive electrolyte gel and a support. The separator more

preferably comprises a composite membrane in which a membrane of the electrically conductive electrolyte gel and a support are stacked on each other. The separator further preferably comprises a three-layered composite membrane in which a support,  
5 a membrane of the electrically conductive electrolyte gel, and another support are stacked in this order.

The electrically conductive electrolyte gel is an electrolyte gel of a water-absorbing synthetic polymer with an electrical conductivity of preferably 140000  $\mu\text{S}/\text{cm}$  or higher,  
10 and more preferably 300000  $\mu\text{S}/\text{cm}$  or higher. In addition, the electrically conductive electrolyte gel is preferably an electrolyte gel of a water-absorbing synthetic polymer swollen by absorption of an aqueous sodium hydroxide solution as an electrolyte with a volume expansion ratio of, for example, 100%  
15 or higher and preferably 150 to 300%. The water-absorbing synthetic polymer is not particularly limited, unless a function of the electrolyte gel according to the present invention is impaired. Examples of the water-absorbing synthetic polymer include polyvinyl alcohol, polyethylene glycol, poly(carboxylic acids), polyacrylamide, and polyvinyl  
20 acetal, as well as modified products thereof such as sodium salts, products of modification by introducing carboxy groups, sulfone groups, or cationic functional groups, or the like. The water-absorbing synthetic polymer is preferably polyvinyl alcohol, polyethylene glycol, a poly(carboxylic acid), or a  
25 modified product thereof. In addition, these synthetic polymers may be used, after being cross-linked with a cross-linking agent such as a boronic acid ester compound. One of these synthetic polymers may be used alone, or two or more  
30 thereof may be used in combination.

The support is not particularly limited, unless a function of the electrolyte gel contained in the separator is impaired. The support may be, for example, an ion exchange membrane, a filtration membrane, or the like.

5       The ion exchange membrane may be an anion exchange membrane, a cation exchange membrane, or the like.

          The anion exchange membrane is preferably a hydrocarbon-based anion exchange membrane, and particularly preferably a hydrocarbon-based quaternary ammonium base-type  
10   anion exchange membrane. The form of the anion exchange membrane is not particularly limited, either, and the anion exchange membrane may be a membrane of an ion-exchange resin itself, a membrane obtained by filling pores of a microporous film such as an olefin-based microporous film with an anion  
15   exchange resin, a layered membrane of a microporous film and an anion exchange membrane.

          In addition, the filtration membrane is preferably an UF membrane, a NF membrane, a RO membrane, or the like of a ceramic, PTFE, polysulfone, polypropylene, or the like with a pore  
20   diameter of about 0.1 to 10  $\mu\text{m}$ .

          The separator more preferably comprises a composite membrane in which a membrane of the synthetic polymer electrolyte gel and at least one of an ion exchange membrane and a filtration membrane are stacked on each other. The  
25   separator further preferably comprises a three-layered composite membrane in which an anion exchange membrane, a membrane of the synthetic polymer electrolyte gel, and another anion exchange membrane are stacked in this order.

          The anode is preferably iron, stainless steel, nickel,  
30   carbon, or the like, or also may be a corrosion resistant metal

such as platinum-plated titanium or palladium-tin alloy.

The cathode is a workpiece to be plated with a zinc alloy. The workpiece may be one made of a metal or an alloy such as iron, nickel, and copper, an alloy thereof, or zincated aluminum  
5 in a shape a plate, a cuboid, a solid cylinder, a hollow cylinder, a sphere, or the like.

In the present invention, a catholyte contained in the cathode region is an alkaline zinc alloy plating liquid.

The alkaline zinc alloy plating liquid contains zinc ions.  
10 The concentration of the zinc ions is preferably 2 to 20 g/L, and further preferably 4 to 12 g/L. A zinc ion source may be  $\text{Na}_2[\text{Zn}(\text{OH})_4]$ ,  $\text{K}_2[\text{Zn}(\text{OH})_4]$ ,  $\text{ZnO}$ , or the like. One of these zinc ion sources may be used alone, or two or more thereof may be used in combination.

15 In addition, the alkaline zinc alloy plating liquid contains metal ions of one or more species selected from nickel ions, iron ions, cobalt ions, tin ions, and manganese ions. The total concentration of the metal ions is preferably 0.4 to 4 g/L, and further preferably 1 to 3 g/L. Sources of the metal  
20 ions include nickel sulfate, iron(II) sulfate, cobalt sulfate, tin(II) sulfate, manganese sulfate, and the like. One of these metal ion sources may be used alone, or two or more thereof may be used in combination. The alkaline zinc alloy plating liquid is preferably an alkaline zinc-nickel alloy plating liquid  
25 containing nickel ions as the metal ions.

In addition, the alkaline zinc alloy plating liquid preferably contains a caustic alkali. The caustic alkali may be sodium hydroxide, potassium hydroxide, or the like. The concentration of the caustic alkali is preferably 60 to 200 g/L,  
30 and further preferably 100 to 160 g/L.

In addition, the alkaline zinc alloy plating liquid preferably contains an amine-based chelating agent. Examples of the amine-based chelating agent include alkyleneamine compounds such as ethylenediamine, triethylenetetramine, and  
5 tetraethylenepentamine; ethylene oxide or propylene oxide adducts of the above-described alkyleneamines; amino alcohols such as N-(2-aminoethyl)ethanolamine and 2-hydroxyethylaminopropylamine; poly(hydroxyalkyl)alkylenediamines such as  
10 N-2(-hydroxyethyl)-N,N',N'-triethylethylenediamine, N,N'-di(2-hydroxyethyl)-N,N'-diethylethylenediamine, N,N,N',N'-tetrakis(2-hydroxyethyl)propylenediamine, and N,N,N',N'-tetrakis(2-hydroxypropyl)ethylenediamine; poly(alkyleneimines) obtained from ethyleneimine,  
15 1,2-propyleneimine, and the like; poly(alkyleneamines) and poly(amino alcohols) obtained from ethylenediamine, triethylenetetramine, ethanolamine, diethanolamine, and the like; etc. One of these amine-based chelating agents may be used alone, or two or more thereof may be used in combination.  
20 The concentration of the amine-based chelating agent is preferably 5 to 200 g/L, and further preferably 30 to 100 g/L.

The alkaline zinc alloy plating liquid used in the present invention may further comprise one or more selected from the group consisting of auxiliary additives such as brightening  
25 agents and leveling agents, and anti-foaming agents. The alkaline zinc alloy plating liquid used in the present invention preferably comprises a brightening agent.

The brightening agent is not particularly limited, as long as the brightening agent is known for a zinc-based plating  
30 bath. Examples of the brightening agent include (1) nonionic

surfactants such as polyoxyethylene-polyoxypropylene block polymer and EO adduct of acetylene glycol, and anionic surfactants such as polyoxyethylene lauryl ether sulfuric acid salts and alkyl diphenyl ether disulfonic acid salts; (2)

5 polyamine compounds including polyallylamines such as a copolymer of diallyldimethylammonium chloride and sulfur dioxide; polyepoxy-polyamines such as a condensation polymer of ethylenediamine with epichlorohydrin, a condensation polymer of dimethylaminopropylamine with epichlorohydrin, a

10 condensation polymer of imidazole with epichlorohydrin, condensation polymers of imidazole derivatives such as 1-methylimidazole and 2-methylimidazole with epichlorohydrin, and condensation polymers of heterocyclic amine including triazine derivatives such as acetoguanamine and benzoguanamine

15 and the like with epichlorohydrin; polyamide-polyamines including polyamine-polyurea resins such as a condensation polymer of 3-dimethylaminopropylurea with epichlorohydrin and a condensation polymer of bis(N,N-dimethylaminopropyl)urea with epichlorohydrin and water-soluble nylon resins such as

20 condensation polymers of N,N-dimethylaminopropylamine, an alkylenedicarboxylic acid, and epichlorohydrin, and the like; polyalkylene-polyamines such as condensation polymers of diethylenetriamine, dimethylaminopropylamine, or the like with 2,2'-dichlorodiethyl ether, a condensation polymer of

25 dimethylaminopropylamine with 1,3-dichloropropane, a condensation polymer of N,N,N',N'-tetramethyl-1,3-diaminopropane with 1,4-dichlorobutane, a condensation polymer of N,N,N',N'-tetramethyl-1,3-diaminopropane with

30 1,3-dichloropropan-2-ol; and the like; (3) condensation

polymers of dimethylamine or the like with dichloroethyl ether;  
(4) aromatic aldehydes such as veratraldehyde, vanillin, and  
anisaldehyde, benzoic acid, and salts thereof; (5) quaternary  
ammonium salts such as cetyltrimethylammonium chloride and  
5 3-carbamoylbenzylpyridinium chloride; and the like. Of these  
brightening agents, quaternary ammonium salts and aromatic  
aldehydes are preferable. One of these brightening agents may  
be used alone, or two or more thereof may be used in combination.  
The concentration of the brightening agent is preferably 1 to  
10 500 mg/L, and further preferably 5 to 100 mg/L in the case of  
an aromatic aldehyde, benzoic acid, or a salt thereof. In other  
cases, the concentration is preferably 0.01 to 10 g/L, and  
further preferably 0.02 to 5 g/L.

In addition, the alkaline zinc alloy plating liquid used  
15 in the present invention preferably comprises a brightening  
agent being a nitrogen-containing heterocyclic quaternary  
ammonium salt. The nitrogen-containing heterocyclic  
quaternary ammonium salt brightening agent is more preferably  
a carboxy group- and/or hydroxy group-substituted  
20 nitrogen-containing heterocyclic quaternary ammonium salt.  
Examples of the nitrogen-containing heterocycle of the  
nitrogen-containing heterocyclic quaternary ammonium salt  
include a pyridine ring, a piperidine ring, an imidazole ring,  
an imidazoline ring, a pyrrolidine ring, a pyrazole ring, a  
25 quinoline ring, a morpholine ring, and the like. The  
nitrogen-containing heterocycle is preferably a pyridine ring.  
A quaternary ammonium salt of nicotinic acid or a derivative  
thereof is particularly preferable. In the quaternary  
ammonium salt compound, the carboxy group and/or the hydroxy  
30 group may be introduced onto the nitrogen-containing

heterocycle as a substituent through another substituent as in the case of, for example, a carboxymethyl group. Moreover, the nitrogen-containing heterocycle may have substituents such as alkyl groups, in addition to the carboxy group and/or the hydroxy group. In addition, unless an effect achieved by the brightening agent contained is impaired, the N substituents forming the heterocyclic quaternary ammonium cation are not particularly limited, and examples thereof include substituted or non-substituted alkyl, aryl, or alkoxy groups, and the like.

In addition, examples of the counter anion forming the salt include halogen anions, oxyanions, borate anions, sulfonate anion, phosphate anions, imide anion, and the like, and the counter anion is preferably a halogen anion. Such a quaternary ammonium salt is preferable, because it contains both a quaternary ammonium cation and an oxyanion in its molecule, and hence it behaves also as an anion. Specific examples of the nitrogen-containing heterocyclic quaternary ammonium salt compound include

|    |                                                |           |
|----|------------------------------------------------|-----------|
|    | N-benzyl-3-carboxypyridinium                   | chloride, |
|    | N-phenethyl-4-carboxypyridinium                | chloride, |
| 20 | N-butyl-3-carboxypyridinium                    | bromide,  |
|    | N-chloromethyl-3-carboxypyridinium             | bromide,  |
|    | N-hexyl-6-hydroxy-3-carboxypyridinium          | chloride, |
|    | N-hexyl-6-3-hydroxypropyl-3-carboxypyridinium  | chloride, |
|    | N-2-hydroxyethyl-6-methoxy-3-carboxypyridinium | chloride, |
| 25 | N-methoxy-6-methyl-3-carboxypyridinium         | chloride, |
|    | N-propyl-2-methyl-6-phenyl-3-carboxypyridinium | chloride, |
|    | N-propyl-2-methyl-6-phenyl-3-carboxypyridinium | chloride, |
|    | N-benzyl-3-carboxymethylpyridinium             | chloride, |
|    | 1-butyl-3-methyl-4-carboxyimidazolium          | bromide,  |
| 30 | 1-butyl-3-methyl-4-carboxymethylimidazolium    | bromide,  |

1-butyl-2-hydroxymethyl-3-methylimidazolium chloride,  
1-butyl-1-methyl-3-methylcarboxypyrrolidinium chloride,  
1-butyl-1-methyl-4-methylcarboxypiperidinium chloride, and  
the like. One of these nitrogen-containing heterocyclic  
5 quaternary ammonium salts may be used alone, or two or more  
thereof may be used in combination. The concentration of the  
nitrogen-containing heterocyclic quaternary ammonium salt is  
preferably 0.01 to 10 g/L, and further preferably 0.02 to 5 g/L.

Examples of the auxiliary additives include organic acids,  
10 silicates, mercapto compounds, and the like. One of these the  
auxiliary additives may be used alone, or two or more thereof  
may be used in combination. The concentration of the auxiliary  
additive is preferably 0.01 to 50 g/L.

Examples of the anti-foaming agents include surfactants  
15 and the like. One of these anti-foaming agents may be used alone,  
or two or more thereof may be used in combination. The  
concentration of the anti-foaming agent is preferably 0.01 to  
5 g/L.

In the present invention, an anolyte contained in the  
20 anode region is an aqueous alkaline solution.

The aqueous alkaline solution may be, for example, an  
aqueous solution containing one or more selected from the group  
consisting of caustic alkalis, sodium, potassium, and ammonium  
salts of inorganic acids, and quaternary tetraalkylammonium  
25 hydroxides. The caustic alkalis include sodium hydroxide,  
potassium hydroxide, and the like. The inorganic acids include  
sulfuric acid and the like. The quaternary tetraalkylammonium  
hydroxides (preferably, the alkyls are alkyls having 1 to 4  
carbon atoms) include quaternary tetramethylammonium  
30 hydroxide and the like. When the aqueous alkaline solution is

an aqueous solution containing a caustic alkali, the concentration of the caustic alkali is preferably 0.5 to 8 mol/L, and further preferably 2.5 to 6.5 mol/L. When the aqueous alkaline solution is an aqueous solution containing a sodium, potassium, or ammonium salt of an inorganic acid, the concentration of the inorganic acid salt is preferably 0.1 to 1 mol/L, and further preferably 0.2 to 0.5 mol/L. When the aqueous alkaline solution is an aqueous solution containing a quaternary tetraalkylammonium hydroxide, the concentration of the quaternary tetraalkylammonium hydroxide is preferably 0.5 to 6 mol/L, and further preferably 1.5 to 3.5 mol/L. The aqueous alkaline solution is preferably an aqueous solution containing a caustic alkali, and more preferably an aqueous solution containing sodium hydroxide.

The temperature for performing the zinc alloy plating is preferably 15°C to 40°C, and further preferably 25 to 35°C. The cathode current density for performing the zinc alloy plating is preferably 0.1 to 20 A/dm<sup>2</sup>, and further preferably 0.2 to 10 A/dm<sup>2</sup>.

In addition, the zinc alloy electroplating method of the present invention preferably comprises controlling the alkali concentration by adding an alkali component to the aqueous alkaline solution.

Next, the present invention is described based on Examples and Comparative Examples; however, the present invention is not limited thereto.

#### Examples

##### (Example 1)

Zinc-nickel alloy plating was obtained as follows. Specifically, a cathode and an anode were separated from each

other by a polyolefin film which had a pore diameter of 3  $\mu\text{m}$  and which was filled with an electrically conductive electrolyte gel obtained by swelling polyvinyl alcohol by absorption of a 130 g/L aqueous sodium hydroxide solution (volume expansion ratio: 200%) and having an electric conductivity of approximately 380000  $\mu\text{S/cm}$ . An alkaline zinc-nickel alloy plating liquid shown below was used as a catholyte for a cathode chamber (500 mL), and a 130 g/L (3.3 mol/L) aqueous caustic soda solution was used as an anolyte for an anode chamber (50 mL). A current was applied at 400 Ah/L. The cathode current density was 4 A/dm<sup>2</sup>, the anode current density was 16 A/dm<sup>2</sup>, and the plating bath temperature was 25°C. The plating liquid was kept at 25°C by cooling. An iron plate was used as the cathode, and a nickel plate was used as the anode.

Note that the iron plate serving as the cathode was exchanged every 16 Ah/L during the current application. The zinc ion concentration in the catholyte was kept constant by immersing and dissolving zinc metal. The nickel ion concentration was kept constant by supplying an aqueous solution containing 25% by weight of nickel sulfate hexahydrate and 10% by weight of IZ-250YB. The caustic soda concentrations in the catholyte and the anolyte were periodically analyzed, and caustic soda was supplied to keep the concentrations constant. As brightening agents, polyamine-based IZ-250YR1 (manufactured by DIPSOL CHEMICALS Co., Ltd.) and nitrogen-containing heterocyclic quaternary ammonium salt-based IZ-250YR2 (manufactured by DIPSOL CHEMICALS Co., Ltd.) were supplied at supply rates of 15 mL/kAh and 15 mL/kAh, respectively, for the plating. The amine-based chelating agent IZ-250YB was supplied at an IZ-250YB supply rate of 80 mL/kAh for the plating. Every 200

Ah/L current application, the concentration of the amine-based chelating agent and the concentration of the nitrogen-containing heterocyclic quaternary ammonium salt-based brightening agent in the catholyte were analyzed.

5 In addition, a plating test was conducted in accordance with the Hull cell test by using a long cell using a 20 cm iron plate as a cathode, and the appearance of the plating, the film thickness distribution, and the Ni co-deposition ratio distribution were measured. Note that the conditions for the  
10 plating test were 4 A, 20 minutes, and 25°C.

Composition of Plating Liquid:

Zn ion concentration: 8 g/L (Zn ion source was  $\text{Na}_2[\text{Zn}(\text{OH})_4]$ )

Ni ion concentration: 1.6 g/L (Ni ion source was  
15  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ )

Caustic soda concentration: 130 g/L

Amine-based chelating agent (alkylene oxide adduct of alkyleneamine) IZ-250YB (manufactured by DIPSOL CHEMICALS Co., Ltd.): 60 g/L

20 Brightening agent IZ-250YR1 (manufactured by DIPSOL CHEMICALS Co., Ltd.): 0.6 mL/L (polyamine: 0.1 g/L)

Brightening agent IZ-250YR2 (manufactured by DIPSOL CHEMICALS Co., Ltd.): 0.5 mL/L (quaternary ammonium salt of nicotinic acid: 0.2 g/L)

25 (Example 2)

Zinc-nickel alloy plating was obtained as follows. Specifically, an cathode and an anode were separated from each other by an anion exchange membrane SELEMION (manufactured by Asahi Glass Co., Ltd., hydrocarbon-based quaternary ammonium  
30 base-type anion exchange membrane) filled with an electrically

conductive electrolyte gel which was obtained by swelling polyvinyl alcohol by absorption of a 130 g/L aqueous sodium hydroxide solution (volume expansion ratio: 200%) and which had an electric conductivity of approximately 380000  $\mu\text{S}/\text{cm}$ . An  
5 alkaline zinc-nickel alloy plating liquid shown below was used as a catholyte for a cathode chamber (500 mL), and a 130 g/L aqueous caustic soda solution was used as an anolyte for an anode chamber (50 mL). A current was applied at 400 Ah/L. The cathode current density was 4  $\text{A}/\text{dm}^2$ , the anode current density  
10 was 16  $\text{A}/\text{dm}^2$ , and the plating bath temperature was 25°C. The plating liquid was maintained at 25°C by cooling. An iron plate was used as the cathode, and a nickel plate was used as the anode. Note that the iron plate serving as the cathode was exchanged every 16 Ah/L during the current application. The zinc ion  
15 concentration in the catholyte was kept constant by immersing and dissolving zinc metal. The nickel ion concentration was kept constant by supplying an aqueous solution containing a 25% by weight of nickel sulfate hexahydrate and 10% by weight of IZ-250YB. The caustic soda concentrations in the catholyte and  
20 the anolyte were periodically analyzed, and caustic soda was supplied to keep the concentrations constant. As brightening agents, polyamine-based IZ-250YR1 (manufactured by DIPSOL CHEMICALS Co., Ltd.) and nitrogen-containing heterocyclic quaternary ammonium salt-based IZ-250YR2 (manufactured by  
25 DIPSOL CHEMICALS Co., Ltd.) were supplied at supply rates of 15 mL/kAh and 15 mL/kAh, respectively, for the plating. An amine-based chelating agent IZ-250YB was supplied at an IZ-250YB supply rate of 80 mL/kAh for the plating. Every 200 Ah/L current application, the concentration of the amine-based  
30 chelating agent and the concentration of the

nitrogen-containing heterocyclic quaternary ammonium salt-based brightening agent in the catholyte were analyzed. In addition, a plating test was conducted in accordance with the Hull cell test by using a long cell using a 20 cm iron plate as a cathode, and the appearance of plating, the film thickness distribution, and the Ni co-deposition ratio distribution were measured. Note that the conditions for the plating test were 4 A, 20 minutes, and 25°C.

Composition of Plating Liquid:

10 Zn ion concentration: 8 g/L (Zn ion source was  $\text{Na}_2[\text{Zn}(\text{OH})_4]$ )

Ni ion concentration: 1.6 g/L (Ni ion source was  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ )

Caustic soda concentration: 130 g/L

15 Amine-based chelating agent IZ-250YB (manufactured by DIPSOL CHEMICALS Co., Ltd.): 60 g/L

Brightening agent IZ-250YR1 (manufactured by DIPSOL CHEMICALS Co., Ltd.): 0.6 mL/L

Brightening agent IZ-250YR2 (manufactured by DIPSOL  
20 CHEMICALS Co., Ltd.): 0.5 mL/L

(Comparative Example 1)

Without separating a cathode from an anode, zinc-nickel alloy plating was obtained by using an alkaline zinc-nickel alloy plating liquid (500 mL) shown below and applying a current at 400 Ah/L. The cathode current density was  $4 \text{ A/dm}^2$ , the anode current density was  $16 \text{ A/dm}^2$ , and the plating bath temperature was 25°C. The plating liquid was kept at 25°C by cooling. An iron plate was used as the cathode, and a nickel plate was used as the anode. Note that the iron plate serving as the cathode  
30 was exchanged every 16 Ah/L during the current application. The

zinc ion concentration was kept constant by immersing and dissolving zinc metal. The nickel ion concentration was kept constant by supplying an aqueous solution containing a 25% by weight of nickel sulfate hexahydrate and 10% by weight of IZ-250YB. The caustic soda concentration was periodically analyzed, and caustic soda was supplied to keep the concentration constant. As brightening agents, polyamine-based IZ-250YR1 (manufactured by DIPSOL CHEMICALS Co., Ltd.) and nitrogen-containing heterocyclic quaternary ammonium salt-based IZ-250YR2 (manufactured by DIPSOL CHEMICALS Co., Ltd.) were supplied at supply rates of 15 mL/kAh and 15 mL/kAh, respectively, for the plating. An amine-based chelating agent IZ-250YB was supplied at an IZ-250YB supply rate of 80 mL/kAh for the plating. Every 200 Ah/L current application, the concentration of the amine-based chelating agent and the concentration of the nitrogen-containing heterocyclic quaternary ammonium salt-based brightening agent were analyzed. In addition, a plating test was conducted in accordance with the Hull cell test by using a long cell using a 20 cm iron plate as a cathode, and the appearance of plating, the film thickness distribution, and the Ni co-deposition ratio distribution were measured. Note that the conditions for the plating test were 4 A, 20 minutes, and 25°C.

Composition of Plating Liquid:

25        Zn ion concentration: 8 g/L (Zn ion source was  $\text{Na}_2[\text{Zn}(\text{OH})_4]$ )

      Ni ion concentration: 1.6 g/L (Ni ion source was  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ )

      Caustic soda concentration: 130 g/L

30        Amine-based chelating agent IZ-250YB (manufactured by

DIPSOL CHEMICALS Co., Ltd.): 60 g/L

Brightening agent IZ-250YR1 (manufactured by DIPSOL CHEMICALS Co., Ltd.): 0.6 mL/L

Brightening agent IZ-250YR2 (manufactured by DIPSOL  
5 CHEMICALS Co., Ltd.): 0.5 mL/L

Table 1 Course of Concentrations of Amine-Based Chelating Agent and Nitrogen-Containing Heterocyclic Quaternary Ammonium Salt-Based Brightening Agent

| Amount of<br>current<br>applied<br>(Ah/L)                                 | Example 1             |                         | Example 2             |                         | Comp. Ex. 1           |                         |
|---------------------------------------------------------------------------|-----------------------|-------------------------|-----------------------|-------------------------|-----------------------|-------------------------|
|                                                                           | IZ-250<br>YB<br>(g/L) | IZ-250<br>YR2<br>(mL/L) | IZ-250<br>YB<br>(g/L) | IZ-250<br>YR2<br>(mL/L) | IZ-250<br>YB<br>(g/L) | IZ-250<br>YR2<br>(mL/L) |
| 0                                                                         | 60                    | 0.6                     | 60                    | 0.6                     | 60                    | 0.6                     |
| 200                                                                       | 59                    | 0.6                     | 61                    | 0.6                     | 51                    | 0.4                     |
| 400                                                                       | 56                    | 0.6                     | 57                    | 0.6                     | 32                    | 0.1                     |
| 400<br>(concentra<br>tion of<br>IZ-250YB<br>was<br>adjusted to<br>60 g/L) | -                     | -                       | -                     | -                       | 60                    | 0.1                     |

The following effects were observed in Examples 1 and 2  
10 in comparison with Comparative Example 1.

(1) Decomposition of the amine-based chelating agent was suppressed.

(2) Deterioration of appearance of the plating was suppressed.

(3) Decomposition of the nitrogen-containing heterocyclic  
15 quaternary ammonium salt-based brightening agent was suppressed.

(4) Decrease in Ni co-deposition ratio in a low-current portion was suppressed.

The present invention has enabled the lifetime extension of an alkaline zinc alloy plating liquid, especially an alkaline  
5 zinc-nickel alloy plating liquid, containing a nitrogen-containing heterocyclic quaternary ammonium salt-based brightening agent. In addition, the lifetime extension of an alkaline zinc alloy plating liquid, especially an alkaline zinc-nickel alloy plating liquid has enabled  
10 stabilization of plating qualities, reduction in plating time, and reduction of the load on wastewater treatment.

## Claims

## Claim 1

A zinc alloy electroplating method comprising applying a current through an alkaline zinc alloy electroplating bath comprising a cathode and an anode, wherein

a cathode region including the cathode and an anode region including the anode are separated from each other by a separator comprising an electrically conductive electrolyte gel.

## Claim 2

The zinc alloy electroplating method according to claim 1, wherein

the separator comprises the electrically conductive electrolyte gel and a support.

## Claim 3

The zinc alloy electroplating method according to claim 2, wherein

the support is an ion exchange membrane and/or a filtration membrane.

## Claim 4

The zinc alloy electroplating method according to any one of claims 1 to 3, wherein

the electrically conductive electrolyte gel is an electrolyte gel of a water-absorbing synthetic polymer with an electrical conductivity of 140000  $\mu\text{S}/\text{cm}$  or higher.

## Claim 5

The zinc alloy electroplating method according to any one of claims 1 to 4, wherein

the electrically conductive electrolyte gel is an electrolyte gel of a water-absorbing synthetic polymer swollen by absorption of an aqueous sodium hydroxide solution as an

electrolyte.

Claim 6

The zinc alloy electroplating method according to claim 4 or 5, wherein

5 the water-absorbing synthetic polymer comprises one or more selected from the group consisting of polyvinyl alcohol, polyethylene glycol, poly(carboxylic acids), and modified products thereof.

Claim 7

10 The zinc alloy electroplating method according to any one of claims 4 to 6, wherein

the separator comprises a composite membrane in which a membrane of the synthetic polymer electrolyte gel and at least one of an ion exchange membrane and a filtration membrane are  
15 stacked on each other.

Claim 8

The zinc alloy electroplating method according to any one of claims 4 to 6, wherein

the separator comprises a three-layered composite  
20 membrane in which an anion exchange membrane, a membrane of the synthetic polymer electrolyte gel, and another anion exchange membrane are stacked in this order.

Claim 9

The zinc alloy electroplating method according to any one  
25 of claims 1 to 8, wherein

an anolyte contained in the anode region is an aqueous alkaline solution, and

the aqueous alkaline solution is an aqueous solution comprising one or more selected from the group consisting of  
30 sodium hydroxide, sodium, potassium, and ammonium salts of

inorganic acids, and quaternary tetraalkylammonium hydroxides.

Claim 10

The zinc alloy electroplating method according to claim  
5 9, wherein

the aqueous alkaline solution is an aqueous sodium hydroxide solution, and

the concentration of the aqueous sodium hydroxide solution is in a range from 0.5 to 8 mol/L.

10 Claim 11

The zinc alloy electroplating method according to claim 9 or 10, comprising controlling an alkali concentration of the aqueous alkaline solution by adding an alkali component to the aqueous alkaline solution.

15 Claim 12

The zinc alloy electroplating method according to any one of claims 1 to 11, wherein

a catholyte contained in the cathode region is an alkaline zinc alloy plating liquid.

20 Claim 13

The zinc alloy electroplating method according to claim 12, wherein

the alkaline zinc alloy plating liquid is an alkaline zinc-nickel alloy plating liquid.

25 Claim 14

The zinc alloy electroplating method according to claim 13, wherein

the alkaline zinc-nickel alloy plating liquid comprises zinc ions, nickel ions, a caustic alkali, an amine-based  
30 chelating agent, and a nitrogen-containing heterocyclic

quaternary ammonium salt-based brightening agent.

Claim 15

The zinc alloy electroplating method according to claim 14, wherein

5       the     nitrogen-containing     heterocyclic     quaternary  
ammonium salt-based brightening agent comprises a quaternary  
ammonium salt of nicotinic acid or a derivative thereof.

Claim 16

10       The zinc alloy electroplating method according to any one  
of claims 13 to 15, wherein

      the alkaline zinc-nickel alloy plating liquid further  
comprises one or more selected from the group consisting of a  
brightening agent comprising one or more selected from the group  
consisting of quaternary ammonium salts and aromatic aldehydes;  
15    an auxiliary additive comprising one or more selected from the  
group consisting of organic acids, silicates, and mercapto  
compounds; and an anti-foaming agents comprising a surfactant.

Claim 17

20       The zinc alloy electroplating method according to any one  
of claims 1 to 16, wherein

      the anode is selected from the group consisting of iron,  
stainless steel, nickel, and carbon.

## Abstract

## ZINC ALLOY PLATING METHOD

The present invention provides a zinc alloy electroplating method comprising applying a current through an alkaline zinc alloy electroplating bath comprising a cathode and an anode, wherein a cathode region including the cathode and an anode region including the anode are separated from each other by a separator comprising an electrically conductive electrolyte gel.

10 [No suitable figure]