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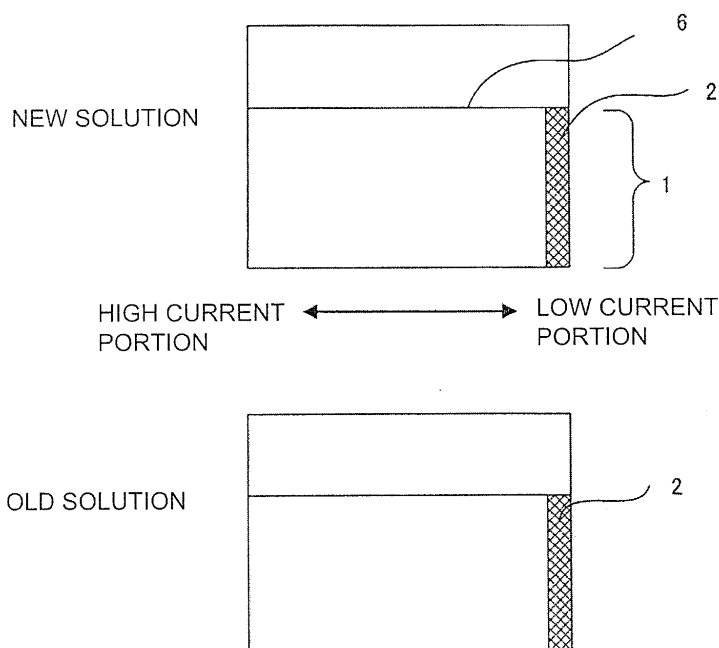
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(54) **ACIDIC ZINC PLATING BATH**

(57) Provided is an acidic zinc plating bath having improved long-term stability even at a temperature as high as from 30 to 50°C. The acidic zinc plating bath

contains a conductive salt, a metallic zinc, and a brightener and the brightener contains, as a component thereof, at least one cumylphenol anionic surfactant.

FIG.1



Description

Technical Field

5 **[0001]** The present invention relates to an acidic zinc plating bath, for example, for zinc electroplating suited for bright zinc plating of metal parts.

Background Art

10 **[0002]** With regards to various metal parts such as processed goods or molded or formed products, for example, pins, bolts, and nuts, zinc plating has been widely used in order to enhance their corrosion resistance and fine appearance.

[0003] Zinc plating includes hot dip galvanizing, zinc electroplating, and the like. When various metal parts are plated through zinc electroplating, a plating bath is used. In this case, a cyan bath or zincate bath is used as an alkali bath, while a sulfate bath or chloride bath is used as an acidic bath (refer to, for example, Patent Documents 1 to 5)

15 **[0004]** The acidic bath is popularly used as a plating bath of industrial products such as bolts and nuts because it has a good current efficiency and is therefore suited for processing large quantities. A chloride bath features high productivity and high plating adherence to castings so that it is used popularly. A chloride bath includes an ammonium bath, and a potassium bath, and an eclectic bath using both. Recently, the ammonium bath and the potassium bath however cannot be used freely because of strict regulations on nitrogen-containing effluent and regulations on effluent containing boron
20 derived from boric acid added as a buffer, respectively. The potassium bath uses no ammonium but compared with the ammonium bath or eclectic bath, abnormal depositions called "burnt deposits" appear at a high current portion so that it is inferior in productivity. Therefore, an eclectic bath has been popular.

[0005] In a bright zinc plating using an acidic plating bath, addition of an organic compound called "brightener" is inevitable in order to give brightness to plating. A naphthol anionic surfactant has conventionally been used as a brightener
25 component (refer to, for example, Patent Document 6).

[0006] Since the temperature of the acidic bath increases when a current is supplied thereto and due to an influence of the surfactant contained therein, the bath becomes turbid, which leads to loss of brightness, the bath has conventionally been used often at a temperature as low as from about 20 to 25°C. It therefore needs cooling, which is a factor of a cost increase. In contrast, in recent years, using it at a temperature as high as from 30 to 50°C has been increasing, partly
30 because plating at high temperatures improves a current efficiency.

Prior Art Documents

Patent Documents

35

[0007]

Patent Document 1: JP-A-08-283982

Patent Document 2: JP-A-11-158683

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Patent Document 3: JP-A-2002-004080

Patent Document 4: JP-A-2004-339596

Patent Document 5: JP-A-2006-322069

Patent Document 6: JP-A-56-102589

45 **[0008]** However, the conventional high-temperature acidic zinc plating baths have been inferior in stability of the bath. Variation in pH has occurred or turbidity or precipitate have appeared when using them at a temperature as high as from about 30 to 50°C. This means that in order to use them at a temperature as high as from 30 to 50°C, it is necessary to prevent turbidity which will otherwise occur due to the influence of a surfactant contained in a brightener. In addition, decomposition products or precipitates have been observed in the plating solution.

50 **[0009]** When plating is conducted continuously, a decrease in cloud point has been observed after predetermined energization. This means that it is difficult to keep the initial plating performance of a high-temperature bath and the plating bath has a problem in long-term stability. In order to raise the cloud point and thereby improve the solubility/dispersibility of the plating bath, an amount of the anionic surfactant can be increased but an excess amount becomes a cause for deteriorating the plating performance.

55 **[0010]** An object of the present invention is to provide an acidic zinc plating bath having improved long-term stability even at a temperature as high as about 30 to 50°C.

Summary of the Invention

[0011] The present inventors have found that the above-described object can be achieved by using a cumylphenol anionic surfactant for a brightener. In short, the present invention provides the following acidic zinc plating bath.

[0012] [1] An acidic zinc plating bath including a conductive salt, a metallic zinc, and a brightener and containing, as a component of the brightener, at least one kind of cumylphenol anionic surfactant.

[0013] [2] The acidic zinc plating bath as described above in [1], containing, as an acidic bath component thereof, zinc chloride and at least one compound selected from the group consisting of ammonium chloride, potassium chloride, and sodium chloride.

[0014] [3] The acidic zinc plating bath as described above in [1] or [2], wherein the cumylphenol anionic surfactant is an alkylene oxide adduct of a sulfate.

[0015] [4] The acidic zinc plating bath as described above in [3], wherein the alkylene oxide adduct of a sulfate has from 1 to 30 moles ethylene oxide as alkylene oxide.

[0016] [5] The acidic zinc plating bath as described above in [3], wherein the alkylene oxide adduct of a sulfate is polyoxyethylene para-cumylphenyl ether sulfate.

[0017] A cumylphenol anionic surfactant has good dispersibility and is effective for increasing a cloud point so that the cloud point of a plating solution stably changes upon using and the plating solution is free from turbidity and precipitation. In short, it improves the long-term stability upon using a bath. In addition, using a cumylphenol anionic surfactant as a brightener enables to keep the brightness of plating upon using (from room temperature to 70°C). The plating bath containing it can therefore be used stably at a high temperature at which the conventional bath is inferior in stability.

Brief Description of the Drawings

[0018]

Fig. 1 is a schematic view showing the results of a hull cell test of a plating bath of Example 1 which is an eclectic bath (NH₄Cl-K).

Fig. 2 is a schematic view showing the results of a hull cell test of a plating bath of Comparative Example 4 which is a β-naphthol eclectic bath (NH₄Cl-K).

FIG. 3 is a schematic view showing the results of a hull cell test of a β-naphthol eclectic bath (NH₄Cl-K).

FIG. 4 is a schematic view showing the results of a hull cell test of a β-naphthol eclectic bath (NH₄Cl-Na).

FIG. 5 is a schematic view showing the results of a hull cell test of a potassium chloride bath and a sodium chloride bath.

FIG. 6 is a schematic view showing the results of a hull cell test of a potassium chloride bath and a sodium chloride bath, each containing boric acid.

FIG. 7 is a schematic view showing the results of a hull cell test of an ammonium chloride bath.

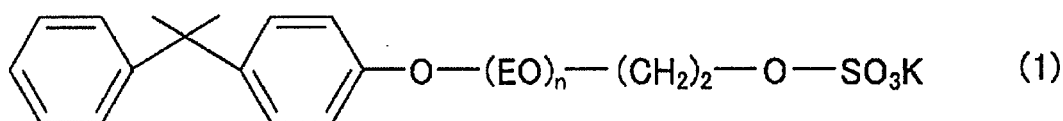
Mode for Carrying out the Invention

[0019] The embodiments of the present invention will next be described referring to some drawings. It should however be noted that the present invention is not limited to or by the following embodiments and it can be changed, modified, or improved without departing from the scope of the present invention.

[0020] The acidic zinc plating bath of the present invention includes a conductive salt, a metallic zinc, and a brightener and it contains, as a component of the brightener, at least one kind of cumylphenol anionic surfactant. The cumylphenol anionic surfactant is preferably an alkylene oxide adduct of a sulfate, with a 1-30 moles ethylene oxide adduct of a sulfate being especially preferred. As an example of the alkylene oxide adduct of a cumylphenol sulfate, polyoxyethylene para-cumylphenyl ether sulfate (the following formula (1)) will next be given.

[0021]

[Chemical formula 1]



[0022] In the above formula, EO represents ethylene oxide and n stands for the number of moles of EO, preferably

from 1 to 30, more preferably from 5 to 15, most preferably 7. It is contained in the acidic zinc plating solution in an amount of preferably from 1 to 3 g/L, more preferably 2 g/L. The sulfate is preferably potassium salt, but sodium salt and amine salt are also usable.

[0023] When cumylphenol selected as the anionic surfactant is incorporated in an acidic zinc plating bath, it enables stable change of the cloud point of the plating solution upon plating and is therefore effective for preventing generation of turbidity or precipitate of the plating solution. As an anionic surfactant, components other than cumylphenol one can be contained in the bath. For example, addition of a cumylphenol anionic surfactant to a bath containing, for example, a β -naphthol anionic surfactant is also effective for increasing the cloud point. This means that the effect of increasing the cloud point can be attained not only by replacement of the β -naphthol anionic surfactant, which is a conventionally used surfactant added to a zinc chloride plating bath, with the cumylphenol anionic surfactant but also by addition of the cumylphenol anionic surfactant to the β -naphthol-added plating bath and use them in combination. Addition of the cumylphenol anionic surfactant increases the cloud point, widens the area of a bright plated surface (hull cell), and stabilizes the plating bath.

[0024] As the brightener, a brightener base and a brightener are used. The brightener base contains an anionic surfactant (containing from 10 to 15 mass%), a nonionic surfactant, an aromatic carboxylate, and an organic amine salt. The brightener contains an anionic surfactant (containing from 10 to 15 mass%), a nonionic surfactant, an aromatic carboxylate, an organic amine salt, and an aromatic aldehyde. The brightener base and the brightener are supplied to a plating bath so that the bath contains the following components at the following concentrations, respectively: an anionic surfactant (from 1 to 5 g/L), a nonionic surfactant (from 1 to 5 g/L), an organic amine (from 0.5 to 5 g/L), an aromatic carboxylate (from 1 to 2 g/L), and an aromatic aldehyde (from 0.01 to 0.1 g/L).

[0025] The brightener base and the brightener containing, as the anionic surfactant, the above alkylene oxide adduct of a cumylphenol sulfate can help the aromatic aldehyde, which is a component of the brightener to give brightness, to improve the brightness. The alkylene oxide adduct of a cumylphenol sulfate undergoes less deterioration in performance when current is applied for plating so that it is anti-aging. In addition, it can increase the cloud point and thereby decrease turbidity and precipitation of the plating solution.

[0026] An increase in the cloud point leads to an increase in solubility/dispersibility of the surfactant so that it is suited for use at high temperatures. It is desired to set the cloud point high because electrical decomposition products appear in the Zn plating bath upon plating, which decreases the cloud point. Among the components of the brightener of acidic Zn plating for use at high temperatures (from 30 to 70°C), the anionic surfactant plays an important role. The cumylphenol anionic surfactant is superior in the performance of dissolving/dispersing the other components and this increases the cloud point.

[0027] Adding the anionic surfactant has improved brightness and it has a higher cloud point with an increase in the amount of the anionic surfactant. The cloud point cannot be maintained when an amount of the anionic surfactant is small. On the other hand, excessive addition causes stain and foaming as well as deterioration in throwing power and plating appearance, which results in deterioration in plating performance. The amount of the anionic surfactant is preferably from 1 to 5 g/L with respect to the plating appearance.

[0028] Adding the nonionic surfactant has improved uniform electrodeposition and improved brightness at a low current portion. Examples of the nonionic surfactant include polyoxyethylene oxide.

[0029] The acidic zinc plating bath containing the aromatic carboxylate can have improved brightness at a low current portion. Examples of the aromatic carboxylate include benzoates, salicylates, cinnamates, and m. P-chlorobenzoates and soluble salts thereof.

[0030] Adding the organic amine salt causes less burnt deposits at a high current portion. Examples of the organic amine salt include polyethyleneimine, modified polyethyleneimine, and polyalkylene polyamine.

[0031] Adding the aromatic aldehyde can have improve brightness. Examples of the aromatic aldehyde include benzaldehyde and benzylidene acetone.

[0032] The acidic zinc plating bath of the present invention is an acidic zinc electroplating bath and it includes various acidic baths containing a conductive salt. That is, the various acidic baths have improved long-term stability by containing a cumylphenol anionic surfactant. As the acidic zinc plating bath, a chloride bath containing zinc chloride is preferred. Examples of the chloride bath include ammonium chloride bath, potassium chloride bath, and sodium chloride bath, and eclectic baths thereof. It can be used for any of them. This means that it can be used for a chloride bath containing at least any of ammonium chloride, potassium chloride, and sodium chloride. In particular, an eclectic bath containing zinc chloride, ammonium chloride, and potassium chloride is particularly preferred. Although a sodium salt is conventionally unsatisfactory in long-term stability because it decreases the cloud point more than a potassium salt, the sodium chloride bath containing the cumylphenol anionic surfactant has an improved cloud point and can be used stably. The acidic zinc plating has the following characteristics: it does not use cyan, has a good current efficiency and has therefore a high plating rate, and can be used for direct plating to cast or heat-treated products.

[0033] As a zinc ion supply source, one or more zinc salts selected from zinc chloride, zinc sulfate, zinc sulfite, zinc borofluoride, zinc sulfamate, and zinc methanesulfonate can be used. As the zinc ion supply source, zinc chloride is

preferred. Alternatively, the zinc ion is supplied by electrodisolution of a metallic zinc of a polar plate.

[0034] The acidic zinc plating bath of the present invention can contain, in addition to the above components, minor components ordinarily added to a plating solution such as anti-foaming agent. The pH range of the plating solution is preferably from 5 to 7, more preferably from 5.8 to 6.3. The plating solution is therefore acidic.

[0035] No particular limitation is imposed on the composition of the acidic zinc plating bath of the present invention but the following is an example of a preferable composition of the plating solution.

Zinc chloride: from 30 to 60 g/L (range of use: from 10 to 120 g/L)
 Ammonium chloride: from 50 to 200 g/L (range of use: from 0 to 300 g/L)
 Potassium chloride: from 0 to 150 g/L (range of use: from 0 to 300 g/L)
 Nonionic surfactant: from 1 to 5 g/L Polyethyleneimine: from 0.5 to 5 g/L
 Benzylidene acetone: from 0.01 to 0.1 g/L
 Sodium benzoate: from 1 to 5 g/L
 pH: from 5.8 to 6.3

[0036] In the present invention, when the content of zinc chloride is outside the above range, it is impossible to carry out desired bright zinc plating efficiently. It is preferably from 30 to 60 g/L. Contents of ammonium chloride exceeding 300 g/L lead to a high nitrogen concentration. It is preferably from 50 to 150 g/L. Potassium chloride is contained in order to maintain the conductivity of the plating bath and decrease a nitrogen concentration. Potassium chloride is contained in an amount of preferably from 50 to 150 g/L. In order to maintain the conductivity of the plating bath, it is replenished with ammonium chloride or potassium chloride to give a chloride ion amount of from 120 to 180 g/L.

[0037] In the present invention, an ordinarily used surfactant such as nonionic surfactant may be added as needed. Components of the plating bath are added in predetermined amounts and constitute an aqueous solution thereof. The pH of the solution is adjusted, for example, with hydrochloric acid to usually from 5.8 to 6.3. The acidic zinc plating bath of the present invention may contain from 1 to 50 g/L of boric acid.

[0038] Bright zinc plating of metal parts with the plating bath thus adjusted may be performed in a conventional manner and no particular limitation is imposed in the present invention. In the present invention, however, due to a reduction in nitrogen concentration, improvement in the working environment and simplification of effluent treatment can be realized.

[0039] A current density can be set at from 0.3 to 5.0 A/dm² on average, which is almost equal to that in the conventional zinc chloride plating bath. Thus, the plating bath of the present invention is comparable to the conventional one also in the plating efficiency. As described above, use of a cumylphenol anionic surfactant as a brightener leads to improvement in the long-term stability of a plating solution when it is used at a temperature of from room temperature to 70°C.

Examples

[0040] The present invention will hereinafter be described more specifically based on Examples. It should however be noted that the present invention is not limited to or by them.

1-1. Eclectic bath (NH₄Cl-K)

[0041] As a solution with a basic composition to be used for a plating solution, a basic solution A shown in Table 1 was prepared. The basic solution A was a mixture of 40 g/L of zinc chloride, 150 g/L of potassium chloride, and 50 g/L of ammonium chloride and had a pH of 6.0.

[0042]

[Table 1]

Basic solution	A	B	C	E	D	F	G
Bath	Eclectic bath (NH ₄ Cl-K)	Eclectic bath (NH ₄ Cl-Na)	Potassium chloride bath	Potassium chloride bath (containing boric acid)	Sodium chloride bath	Sodium chloride bath (containing boric acid)	Ammonium chloride bath
Zinc chloride	40 g/L	40 g/L	60 g/L	60 g/L	60 g/L	60 g/L	40 g/L
Potassium chloride	150 g/L	-	265 g/L	250 g/L	-	-	-
Sodium chloride	-	150 g/L	-	-	265 g/L	250 g/L	-

(continued)

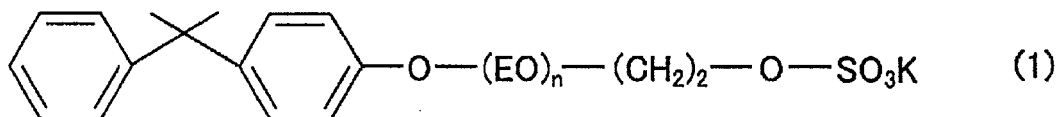
Basic solution		A	B	C	E	D	F	G
Hull cell test	Bath	Eclectic bath (NH ₄ Cl-K)	Eclectic bath (NH ₄ Cl-Na)	Potassium chloride bath	Potassium chloride bath (containing boric acid)	Sodium chloride bath	Sodium chloride bath (containing boric acid)	Ammonium chloride bath
	Ammonium chloride	50 g/L	50g/L	-	-	-	-	200 g/L
	Boric acid	-	-	-	25 g/L	-	25 g/L	-
Hull cell test	pH	6.0	6.0	6.0	6.0	6.0	6.0	6.0
	Bath temperature	40°C	40°C	40°C	40°C	40°C	40°C	40°C
	Current density (average)	2 A/dm ²	2 A/dm ²	2 A/dm ²	2 A/dm ²	2 A/dm ²	2 A/dm ²	2 A/dm ²

(Example 1)

[0043] Next, to the basic solution A of Table 1 was added an anionic surfactant listed in Table 2. For example, in Example 1, the basic composition A composed of 40 g/L of zinc chloride, 150 g/L of potassium chloride, and 50 g/L of ammonium chloride was mixed with 1 g/L of a 7 mole EO polyoxyethylene para-cumylphenyl ether sulfate, specifically potassium salt. Further, it was mixed with a nonionic surfactant, 2 g/L of an aromatic carboxylate, 1 g/L of an organic amine salt, and 0.05 g/L of an aromatic aldehyde. Similarly, respective mixtures with 2 g/L and 3 g/L of a 7 mole EO polyoxyethylene para-cumylphenyl ether sulfate, specifically potassium salt were prepared. The following is the potassium polyoxyethylene para-cumylphenyl ether sulfate (represented by the following formula (1)).

[0044]

[Chemical formula 2]



(Examples 2 to 4)

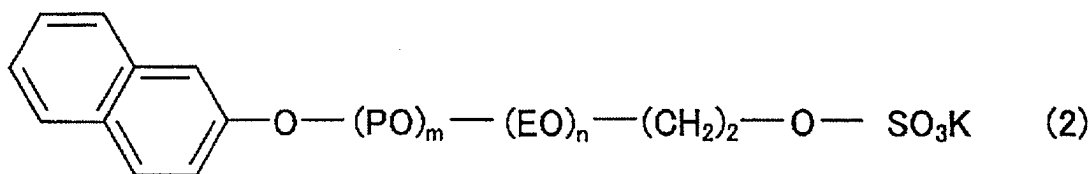
[0045] In a similar manner to Example 1, plating baths having the composition as shown in Table 2 were prepared.

(Comparative Example 1)

[0046] As shown in Table 2, a plating bath was prepared by mixing a naphthol anionic surfactant with the basic solution A. In Comparative Example 1, the anionic surfactant is the following potassium polyoxyethylene β-naphthyl ether sulfate (m=3, n=12) (represented by the following formula (2)). In the formula, EO represents ethylene oxide and PO represents propylene oxide.

[0047]

[Chemical formula 3]

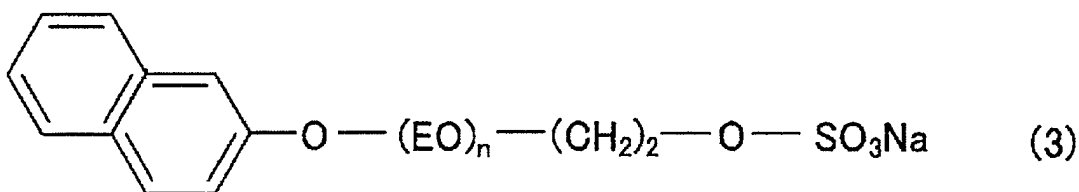


(Comparative Example 2)

[0048] As shown in Table 2, a plating bath was prepared by mixing a naphthol anionic surfactant with the basic solution A. In Comparative Example 2, the anionic surfactant is the following sodium polyoxyethylene β -naphthyl ether sulfate ($n=12$) (represented by the following formula (3)).

[0049]

[Chemical formula 4]

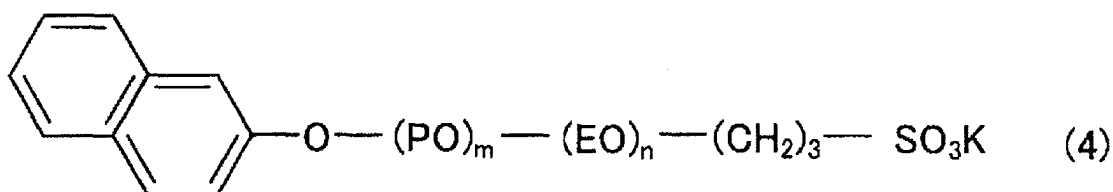


(Comparative Example 3)

[0050] As shown in Table 2, a plating bath was prepared by mixing a naphthol anionic surfactant with the basic solution A. In Comparative Example 2, the anionic surfactant is the following potassium polyoxyethylene oxypropylene naphthyl sulfonate ($m=3$, $n=13$) (represented by the following formula (4)).

[0051]

[Chemical formula 5]



(Comparative Examples 4 to 5)

[0052] As shown in Table 2, a plating bath using a β -naphthol anionic surfactant was prepared. In Comparative Examples 4 and 5, the basic solutions were obtained by adding a base agent A (MZ-996A in Comparative Example 4 and ZB-627A in Comparative Example 5) and a brightener GC as needed (refer to the amount listed in Table 2), respectively. The base agent A and the brightener GC contain an anionic surfactant, a nonionic surfactant, an aromatic carboxylate, an organic amine, and an aromatic aldehyde.

(Cloud point)

[0053] The cloud point was measured in the following manner. First, 100 ml of a sample solution (plating solution) was weighed in a 100-ml heat-resistant glass beaker. Then, the sample solution was heated with an electric heater or the like and then stirred so as to give a uniform solution temperature. The temperature at which, when a thermometer was stood at the center of the 100-ml beaker, the thermometer disappeared due to turbidity was recorded.

[0054]

[Table 2]

	Plating bath						Cloud point
		Amount of brightener	Anionic surfactant				
			Salt used		Amount		
Example 1	Basic solution A		K salt 7 moles of EO	Polyoxyethylene para-cumylphenyl ether sulfate	1 g/L		65°C
					2 g/L	Recommended	80°C
					3 g/L		95°C
Example 2	Basic solution A		K salt 5 moles of EO	Polyoxyethylene para-cumylphenyl ether sulfate	1 g/L		65°C
					2 g/L	Recommended	80°C
					3 g/L		95°C
Example 3	Basic solution A		K salt 13 moles of EO	Polyoxyethylene para-cumylphenyl ether sulfate	1 g/L		65°C
					2 g/L	Recommended	80°C
					3 g/L		95°C
Example 4	Basic solution A		K salt 15 moles of EO	Polyoxyethylene para-cumylphenyl ether sulfate	1 g/L		70°C
					2 g/L	Recommended	85°C
					3 g/L		98°C
Comp. Ex. 1	Basic solution A		K salt 13 moles of EO	Polyoxyethylene naphthyl ether sulfate	1 g/L		50°C
					2 g/L	Normal	55°C
					3 g/L		60°C
Comp. Ex. 2	Basic solution A		Na salt 13 moles of EO & 3 moles of PO	Polyoxyethylene oxypropylene naphthyl sulfate	1 g/L		55°C
					2 g/L	Normal	65°C
					3 g/L		70°C
Comp. Ex. 3	Basic solution A		K salt 13 moles of EO & 3 moles of PO	Polyoxyethylene oxypropylene naphthyl sulfonate	1 g/L		65°C
					2 g/L	Normal	70°C
					3 g/L		75°C
Comp. Ex. 4	Basic solution A Plating bath for high bath temperature METASU MZ-996A/GC	MZ-996A: 20 mL/L GC:0.5 mL/L		β-Naphthol			72°C
Comp. Ex. 5	Basic solution A General bath METASU ZB-627A/GC	ZB-627A: 30 mL/L GC:1 mL/L		β-Naphthol			50°C

(continued)

	Plating bath					Cloud point
		Amount of brightener	Anionic surfactant			
			Salt used		Amount	
Example 5	Basic solution A Plating bath for high bath temperature METASU MZ-996A/GC	MZ-996A: 20 ML/L GC:0.5 mL/L	K salt 7 moles of EO	Polyoxyethylene para-cumylphenyl ether sulfate	2 g/L	75°C
Example 6	Basic solution A General bath METASU ZB-627A/G	ZB-627A: 30 mL/L G: 1 mL/L	K salt 7 moles of EO	Polyoxyethylene para-cumylphenyl ether sulfate	2 g/L	70°C
* METASU MZ-996A/GC: product of Yuken Industry * METASU ZB-627AIGC: product of Yuken Industry						

[0055] As shown in Table 2, Examples using a cumylphenol surfactant have a higher cloud point than that of Comparative Examples. A new solution of Comparative Example 4 had a cloud point of 72°C, but it was not suited for long-term use because it decrease due to aging of the solution as a result of current application. The term "recommended" or "normal" amount in the table means the most suited amount. Since an increase in the amount of the anionic surfactant leads to deterioration in throwing power, the "normal" amount is used as the most appropriate amount in Comparative Examples and the "recommended" amount is used as the most appropriate amount in Examples.

[0056] Each of a new solution and an old solution of Example 1 and Comparative Example 4 was studied for cloud point, turbidity, and stability. The term "old solution" means a plating solution supplied with a current continuously for plating (120 AH/L). This corresponds to an amount of current supplied to a common plating line per month.

[0057]

[Table 3]

		Example 1	Comp. Ex. 4
Cloud point	New solution	80°C	72°C
	Old solution	85°C	70°C
Turbidity		Good	Fair
Stability		Good	Fair

[0058] As shown in Table 3, Example 1 has a higher cloud point and has improved turbidity and stability irrespective of the new solution or old solution, compared with that of Comparative Example 4. Incidentally, having no turbidity/precipitate and showing no change was rated "good, while having slight turbidity/precipitate was rated "fair".

(Hull cell test)

[0059] In addition, a hull cell test was performed to observe the condition of a plating bath. The hull cell test was performed for a new solution and an old solution of each of Example 1 and Comparative Example 4 by supplying a current of 1A to the plating bath for 10 minutes while adjusting the temperature of the bath to 40°C.

[0060] The results of the hull cell test of Example 1 are shown schematically in FIG. 1, while those of Comparative Example 4 are shown schematically in FIG. 2. As illustrated in FIG. 1, slight cloudiness is observed at a low current portion in both the new solution and the old solution in Example 1. In Comparative Example 4, on the other hand, widespread cloudiness is observed at a low current portion as illustrated in FIG. 2. In addition, in Comparative Example

4, burnt deposits are observed at a high current portion.

(Trivalent Cr chemical conversion treatment)

5 **[0061]** Test pieces which had been zinc plated with Example 1 and Comparative Example 4 were subjected to trivalent Cr chemical conversion treatment, respectively.

(1) YFA treatment:

10 **[0062]** Trivalent Cr chemical conversion treatment was performed using a trivalent Cr chemical conversion agent produced by Yuken Industry. The treatment was performed for 40 seconds in a plating bath of 40°C and pH 2.0 by using 100 ml/L of YFA-M and 10 ml/L of YFA-HR.

(2) YFB treatment:

15 **[0063]** Trivalent Cr chemical conversion treatment was performed using a black trivalent Cr conversion agent produced by Yuken Industry. The treatment was performed for 60 seconds in a plating bath of 40°C and pH 2.5 by using 60 ml/L of YFB-A3, 100 ml/L of YFB-B3, and 60 ml/L of YFB-C3. As finishing treatment, the treatment was conducted for 3 seconds in a plating bath of 40°C by using 200 ml/L of CR-U and 10 ml/L of CR-I.

20 **[0064]** A hull cell test (at a plating bath temperature of 40°C for 10 minutes at 1A) of the test pieces of Example 1 and Comparative Example 4 which had been subjected to each of YFA treatment and YFB treatment was performed and their appearance was studied. Even after the YFA treatment or YFB treatment, the test piece of Example 1 showed an appearance as good as that of Comparative Example 4, a conventional product.

25 1-2. Eclectic bath ($\text{NH}_4\text{Cl-K}$, containing a surfactant other than cumylphenol one)

(Examples 5 to 6)

30 **[0065]** To the base solution A was added a plating bath applicable to high temperature (METASU MZ-996A/GC: product of Yuken Industry). The resulting mixture was mixed with 2 g/L of a 7 mole EO polyoxyethylene para-cumylphenyl ether sulfate, specifically potassium salt as an anionic surfactant (Example 5). Separately, to the base solution A was added a general bath (METASU ZB-627A/G: product of Yuken Industry). The resulting mixture was mixed with 2 g/L of a 7 mole EO polyoxyethylene para-cumylphenyl ether sulfate, specifically potassium salt as an anionic surfactant (Example 6).

35 **[0066]** As shown in Table 2, Example 5 and Example 6 using a cumylphenol surfactant have a higher cloud point than that of Comparative Example 4 and Comparative Example 5, respectively. This means that addition of a cumylphenol surfactant to a β -naphthol type eclectic bath (ammonium/potassium bath) increases a cloud point. FIG. 3 shows the results of the hull cell test. The results of the hull cell test have revealed that Examples 5 and 6 containing a cumylphenol anionic surfactant provide a wider bright surface and therefore show better results than those of Comparative Examples 4 and 5, respectively.

2-1. Eclectic bath ($\text{NH}_4\text{Cl-Na}$)

(Example 7)

45 **[0067]** Next, a plating bath was prepared by mixing the basic solution B of Table 1 with 1 to 3 g/L of a 7 mole EO adduct of potassium polyoxyethylene para-cumylphenyl ether sulfate as an anionic surfactant as shown in Table 4.

(Comparative Examples 6 to 8)

50 **[0068]** For comparison, plating baths were prepared by mixing the basic solution B of Table 1 with, as an anionic surfactant, from 1 to 3 g/L of the polyoxyethylene naphthyl ether sulfate (Comparative Example 6), the polyoxyethylene oxypropylene naphthyl sulfate (Comparative Example 7), and the polyoxyethylene oxypropylene naphthyl sulfonate (Comparative Example 8), respectively, as shown in Table 4.

55 (Comparative Examples 9 and 10)

[0069] Further, as shown in Table 4, plating baths containing a β -naphthol anionic surfactant were prepared. More

specifically, the plating baths of Comparative Examples 9 and 10 were prepared by adding, to the basic solution B, a base agent A (MZ-996A in Comparative Example 9 and ZB-627A in Comparative Example 10) and a brightener (GC in Comparative Example 9 and G in Comparative Example 10) as needed (refer to Table 4 for the amount).

[0070] A decrease in the cloud point was observed in the plating bath containing sodium chloride, compared with the plating bath containing potassium chloride, due to a difference in solubility between K and Na. As shown in Table 4, addition of a cumylphenol surfactant however increases the cloud point even in the eclectic bath containing both ammonium and sodium.

2-2. Eclectic bath (NH₄Cl-Na, containing a surfactant other than a cumylphenol surfactant)

(Examples 8 and 9)

[0071] As shown in Table 4, to the basic solution B was added a plating bath for high bath temperature (METASU MZ-996A/GC, product of Yuken Industry). The resulting mixture was mixed with, as an anionic surfactant, 2 g/L of a 7 mole EO polyoxyethylene para-cumylphenyl ether sulfate, specifically potassium salt (Example 8). Separately, to the basic solution B was added a general bath (METASU ZB-627A/G: product of Yuken Industry). The resulting mixture was mixed with, as an anionic surfactant, 2 g/L of a 7 mole EO polyoxyethylene para-cumylphenyl ether sulfate, specifically potassium salt (Example 9).

[0072]

[Table 4]

	Plating bath						Cloud point
		Amount of brightener	Anionic surfactant				
			Salt used		Amount		
Examples 7	Basic solution. B		K salt 7 moles of EO	Polyoxyethylene para-cumylphenyl ether sulfate	1 g/L		60°C
					2 g/L	Normal	73°C
					3 g/L		77°C
Comp.Ex. 6	Basic solution B		K shalt 13 moles of EO	Polyoxyethylene naphthyl ether sulfate	1 g/L		43°C
					2 g/L	Normal	45°C
					3 g/L		48°C
Comp. Ex. 7	Basic solution B		Na salt 13 moles of EO & 3 moles of PO	Polyoxyethylene oxypropylene naphthyl sulfate	1 g/L		50°C
					2 g/L	Normal	52°C
					3 g/L		55°C
Comp. Ex. 8	Basic solution B		K salt 13 moles of EO & 3 moles of PO	Polyoxyethylene oxypropylene naphthyl sulfonate	1 g/L		62°C
					2 g/L	Normal	65°C
					3 g/L		66°C
Comp. Ex. 9	Basic solution B Plating bath for high bath temperature METASU MZ-996A/GC	MZ-996A: 20 mUL GC: 0.5 mL/L					63°C
Comp. Ex. 10	Basic solution B General bath METASU ZB-627A/G	ZB-627A: 30 mUL GC:1 mL/L					43°C

(continued)

	Plating bath					Cloud point
		Amount of brightener	Anionic surfactant			
			Salt used		Amount	
Example 8	Basic solution B Plating bath for high bath temperature METASU MZ-996A/GC	MZ-996A: 20 mUL GC: 0.5 mL/L	K salt 7 moles of EO	Polyoxyethylene para-cumylphenyl ether sulfate	2 g/L	70°C
Example 9	Basic solution B General bath METASU ZB-627A/G	ZB-627A: 30 mUL GC:1 mL/L	K salt 7 moles of EO	Polyoxyethylene para-cumylphenyl ether sulfate	2 g/L	65°C
* METASU MZ-996A/GC: product of Yuken Industry * METASU ZB-627A/GC: product of Yuken Industry						

[0073] As shown in Table 4, Examples 8 and 9 using a cumylphenol surfactant have a higher cloud point than Comparative Examples. This means that addition of a cumylphenol surfactant to a β -naphthol eclectic bath (containing both ammonium and sodium) increases the cloud point. The results of the hull cell test are shown in FIG. 4. Comparative Examples 9 and 10 using the conventional brightener have a low cloud point. In particular, a burnt deposit is wider at a high current portion in Comparative Example 10, while Examples 8 and 9 show equal or better results compared with Comparative Examples.

3. Potassium chloride bath

(Example 10 and Comparative Example 11)

[0074] As shown in Table 5, to the basic solution C was added a plating bath for high bath temperature (METASU FZ-300M/GR: product of Yuken Industry) (Comparative Example 11). The resulting mixture was mixed with 2 g/L of a 7 mole EO polyoxyethylene para-cumylphenyl ether sulfate, specifically potassium salt as an anionic surfactant (Example 10).

[0075]

[Table 5]

	Plating bath					Cloud point
		Amount of brightener	Anionic surfactant			
			Salt used		Amount	
Comp. Ex. 11	Potassium plating bath (boric acid-free) Base solution C METASU FZ-300M/GR	FZ-300M: 50 mL/L GR: 1.0 ml/L				64°C
Example 10	Potassium plating bath (boric acid-free) Base solution C METASUFZ-300M/GR	FZ-300M: 50 mL/L GR: 1.0 ml/L	K salt 7 moles of EO	Polyoxyethylene paracumylphenyl ether sulfate	2 g/L	80°C

(continued)

	Plating bath					Cloud point
		Amount of brightener	Anionic surfactant			
			Salt used		Amount	
Comp. Ex. 12	Sodium plating bath Basic solution D METASU FZ-300M/GR	FZ-300M: 50 mL/L GR: 1.0 ml/L				58°C
Example 11	Sodium plating bath Basic solution D METASU FZ-300M/GR	FZ-300M: 50 mL/L GR: 1.0 ml/L	K salt 7 moles of EO	Polyoxyethylene paracumylphenyl ether sulfate	2 g/L	75°C
Comp. Ex. 13	Potassium plating bath (containingboric acid) Basic solution E METASU ZB-612A/GR	ZB-612A: 30 mL/L GR: 1.0 ml/L				40°C
Example 12	Potassium plating bath (containingboric acid) Basic solution E METASU ZB-612A/GR	ZB-612A: 30 mL/L GR: 1.0 ml/L	K salt 7 moles of EO	Polyoxyethylene paracumylphenyl ether sulfate	2 g/L	70°C
Comp. Ex. 14	Plating bath Basic solution F METASU ZB-612A/GR	ZB-612A: 30 mL/L GR: 1.0 ml/L				30°C
Example 13	Plating bath Basic solution F METASU ZB-612A/GR	ZB-612A: 30 mL/L GR: 1.0 ml/L	K salt 7 moles of EO	Polyoxyethylene paracumylphenyl ether sulfate	2 g/L	60°C
* METASU FZ-300M/GR: product of Yuken Industry						
* METASU ZB-612A/GR: product of Yuken Industry						

[0076] Addition of a cumylphenol surfactant increased the cloud point of even a potassium chloride bath. The results of the hull cell test are shown in FIG. 5. The results of the hull cell test have revealed that Example 10 provides a wider bright surface and thus shows better results than those of Comparative Example.

4. Sodium chloride bath

(Example 11 and Comparative Example 12)

[0077] As shown in Table 5, to the basic solution D was added a plating bath for high bath temperature (METASU FZ-300M/GR: product of Yuken Industry) (Comparative Example 12). The resulting mixture was mixed with, as an anionic surfactant, 2 g/L of a 7 mole EO polyoxyethylene para-cumylphenyl ether sulfate, specifically potassium salt (Example 11).

[0078] Addition of a cumylphenol surfactant increased the cloud point of even a sodium chloride bath. As shown in FIG. 5, the results of the hull cell test have revealed that Example 11 provides a wider bright surface and thus shows better results than those of Comparative Example.

5. Potassium chloride bath (containing boric acid)

(Example 12 and Comparative Example 13)

[0079] As shown in Table 5, to the basic solution E was added a plating bath for high bath temperature (METASU ZB-612A/GR: product of Yuken Industry) (Comparative Example 13). The resulting mixture was mixed with, as an anionic surfactant, 2 g/L of a 7 mole EO polyoxyethylene para-cumylphenyl ether sulfate, specifically potassium salt (Example 12). The plating baths of Example 12 and Comparative Example 13 each contains boric acid.

[0080] Addition of a cumylphenol surfactant increased the cloud point of even a boric-acid containing potassium chloride bath. The results of the hull cell test are shown in FIG. 6. As a result of the hull cell test, the plating bath of Example 12 has comparable results to that of Comparative Example.

6. Sodium chloride bath (containing boric acid)

(Example 13 and Comparative Example 14)

[0081] As shown in Table 5, to the basic solution F was added a plating bath for high bath temperature (METASU ZB-612A/GR: product of Yuken Industry) (Comparative Example 14). The resulting mixture was mixed with, as an anionic surfactant, 2 g/L of a 7 mole EO polyoxyethylene para-cumylphenyl ether sulfate, specifically potassium salt (Example 13). Example 13 and Comparative Example 14 each contains boric acid.

[0082] Addition of a cumylphenol surfactant increased the cloud point of even a boric-acid containing sodium chloride bath. As shown in FIG. 6, when the hull cell test was performed, the plating bath of Example 13 has comparable results to that of Comparative Example.

7-1. Ammonium chloride bath

(Example 14 and Comparative Examples 15 to 18)

[0083] As shown in Table 6, the basic solution G was mixed with, as an anionic surfactant, from 1 to 3 g/L of a 7 mole EO polyoxyethylene para-cumylphenyl ether sulfate, specifically potassium salt (Example 14). The basic solution G was mixed with, as an anionic surfactant, from 1 to 3 g/L of the polyoxyethylene naphthyl ether sulfate (Comparative Example 15). Further, the basic solution G was mixed with METASU MZ-996A/GC (Comparative Example 16), METASU ZB-627A/G (Comparative Example 17), and a brightener component (Comparative Example 18), respectively.

[0084]

[Table 6]

	Plating bath						Cloud point
		Amount of brightener	Anionic surfactant				
			Salt used		Amount		
Example 14	Basic solution G		K salt 7 moles of EO	Polyoxyethylene para-cumylphenyl ether sulfate	1 g/L		65°C
					2 g/L	Normal	75°C
					3 g/L		80°C
Comp. Ex. 15	Basic solution G		K salt 13 moles of EO	Polyoxyethylene naphthyl ether sulfate	1 g/L		43°C
					2 g/L	Normal	47°C
					3 g/L		50°C
Comp. Ex. 16	Basic solution G Plating bath for high bath temperature METASU MZ-996A/GC	MZ-996A: 20 mUL GC:0.5 mL/L					65°C

(continued)

	Plating bath					Cloud point
		Amount of brightener	Anionic surfactant			
			Salt used		Amount	
Comp. Ex. 17	Basic solution G General bath METASU ZB-627A/G	B-627A: 30 mL G: 1 mL/L				45°C
Comp. Ex. 18	Basic solution G Brightener component added	Predetermined amount				40°C
Example 15	Basic solution G Plating bath for high bath temperature METASU 996A/GC	MZ-996A: 20 mUL GC:0.5 mL/L	K salt 7 moles of EO	Polyoxyethylene para-cumylphenyl ether sulfate	2 g/L	72°C
Example 16	Basic solution G General bath METASU ZB-627A/G	B-627A: 30 mL G:1 mL/L	K salt 7 moles of EO	Polyoxyethylene para-cumylphenyl ether sulfate	2 g/L	70°C
* METASU MZ-996A/GC: product of Yuken Industry						
* METASU ZB-627A/GC: product of Yuken Industry						

[0085] Addition of a cumylphenol surfactant increased the cloud point of even an ammonium chloride bath.

7-2. Ammonium chloride bath (containing a surfactant other than cumylphenol one)

(Examples 15 and 16)

[0086] As shown in Table 6, to the basic solution G was added a plating bath for high bath temperature (METASU MZ-996A/GC; product of Yuken Industry). The resulting mixture was mixed with, as an anionic surfactant, 2 g/L of a 7 mole EO polyoxyethylene para-cumylphenyl ether sulfate, specifically potassium salt (Example 15). Separately, to the basic solution G was added a general bath (METASU ZB-627A/G; product of Yuken Industry). The resulting mixture was mixed with, as an anionic surfactant, 2 g/L of a 7 mole EO polyoxyethylene para-cumylphenyl ether sulfate, specifically potassium salt (Example 16).

[0087] As shown in Table 6, Examples 15 and 16 using a cumylphenol surfactant have a higher cloud point than that of Comparative Examples. The results of the hull cell test are shown in FIG. 7. The hull cell test has revealed that Examples 15 and 16 provide a wider bright surface and thus show better results than those of Comparative Examples.

[0088] Using a cumylphenol surfactant has higher solubility/dispersibility of the components compared with a conventional product so that it is improved in the turbidity and precipitation of the plating solution. Also addition of a cumylphenol surfactant to a conventional product containing a β -naphthol surfactant has also succeeded in improvement in turbidity and precipitate of the plating solution. A high temperature bath is commonly used at from 30 to 50°C, but addition of a cumylphenol surfactant increases the cloud point, which enables good plating treatment even in a high temperature bath. In addition, this increases the solubility of a brightener component so that a bright appearance can be obtained. Even in a chemical conversion treatment, the bright appearance can be maintained.

[0089] As described above, it is possible to resolve the conventional problem and provide a plating bath which can

be used stably because there is less change in the brightener due to high temperature treatment, that is, current supply for plating. This means that an acidic zinc plating bath containing a cumylphenol surfactant can keep a high cloud point and keep its performance even against aging due to current supply.

5 Industrial Applicability

[0090] The acidic zinc plating bath of the present invention can be used as an acidic bath for zinc plating of bolts, nuts, and the like.

10 Description of Reference Numerals

[0091] 1: Plated surface, 2: Cloudiness, 3: Burnt deposit, 4: Severe burnt deposit, 5: Bright surface, 6: Solution level

15 **Claims**

1. An acidic zinc plating bath, comprising:

20 a conductive salt,
a metallic zinc, and
a brightener,
wherein the brightener contains at least one kind of cumylphenol anionic surfactant as a component thereof.

25 2. The acidic zinc plating bath according to Claim 1, comprising, as an acid bath composition, zinc chloride and at least one compound selected from the group consisting of ammonium chloride, potassium chloride, and sodium chloride.

30 3. The acidic zinc plating bath according to Claim 1 or 2, wherein the cumylphenol anionic surfactant is an alkylene oxide adduct of a sulfate.

4. The acidic zinc plating bath according to Claim 3, wherein the alkylene oxide adduct of a sulfate has from 1 to 30 moles ethylene oxide as alkylene oxide.

35 5. The acidic zinc plating bath according to Claim 3, wherein the alkylene oxide adduct of a sulfate is polyoxyethylene para-cumylphenyl ether sulfate.

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FIG.1

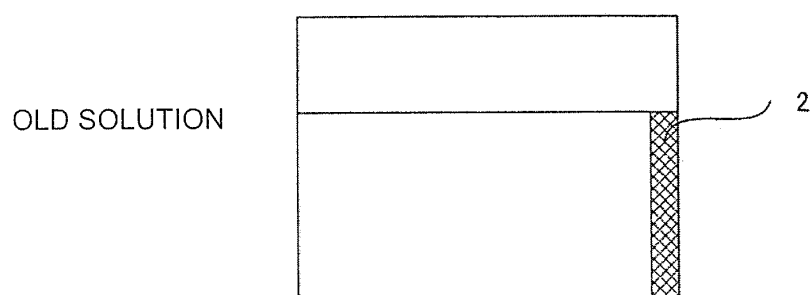
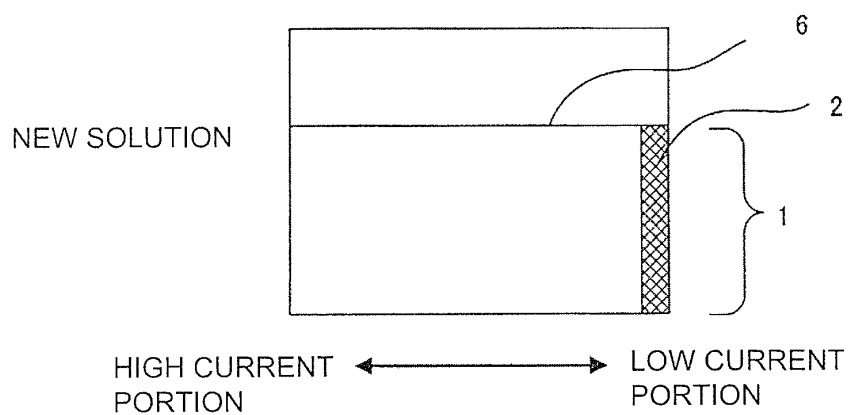


FIG.2

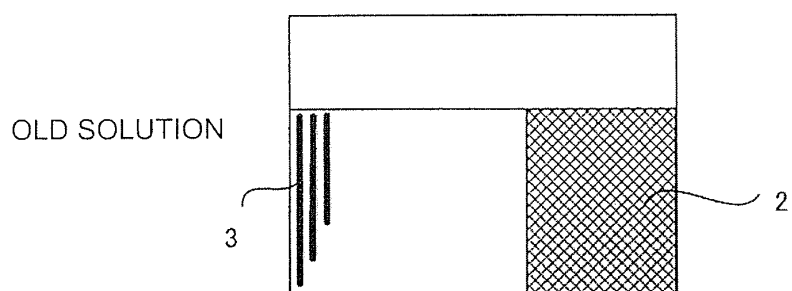
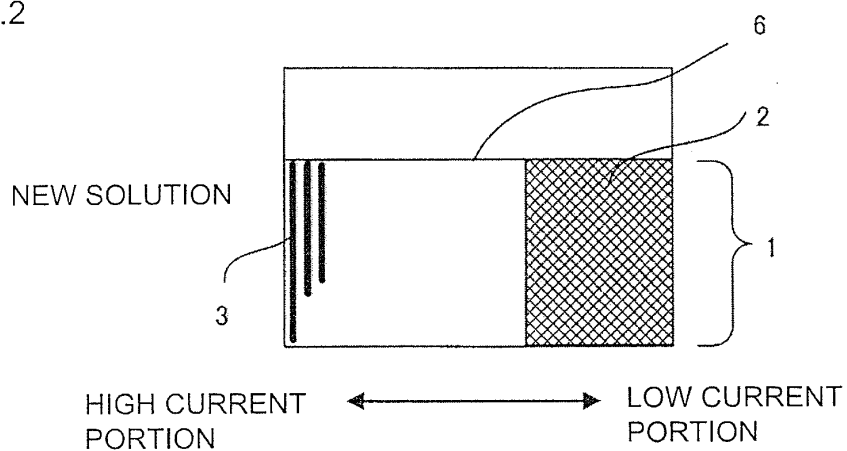


FIG.3

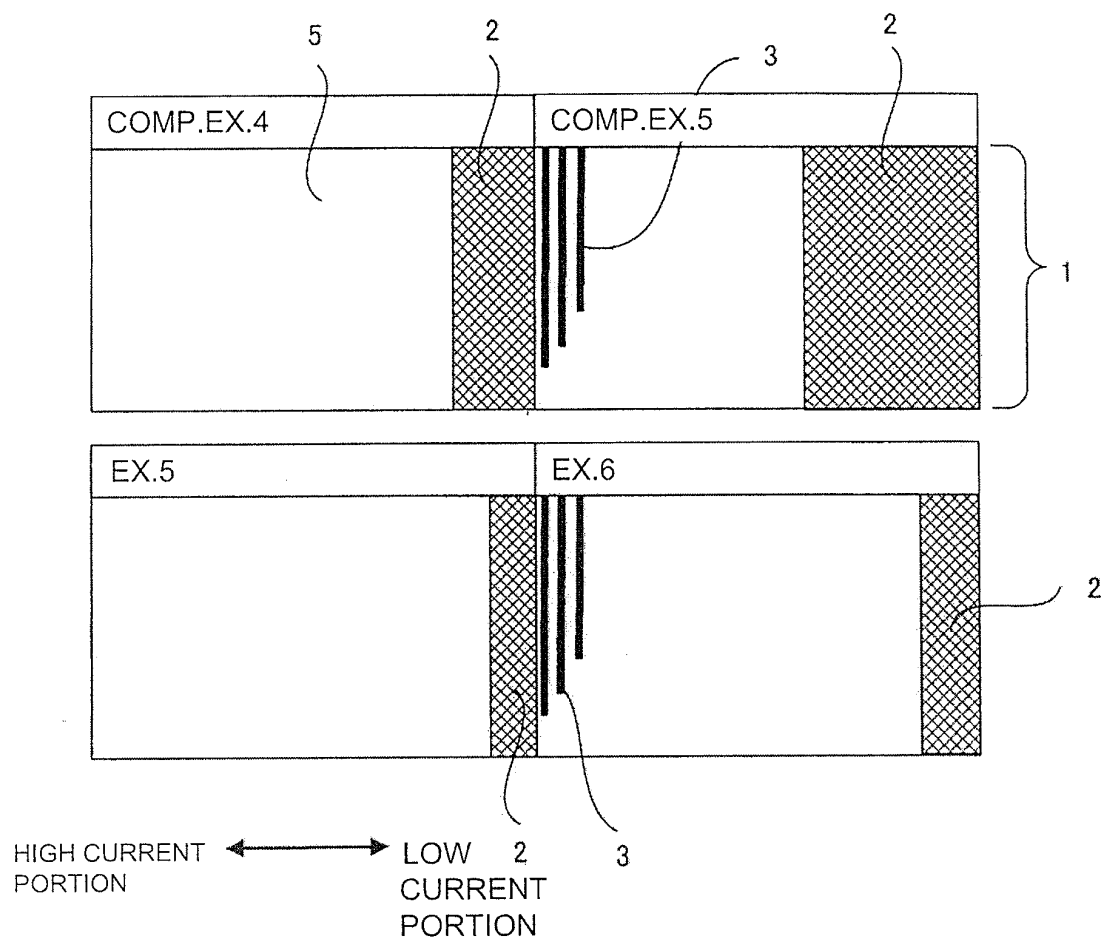


FIG.4

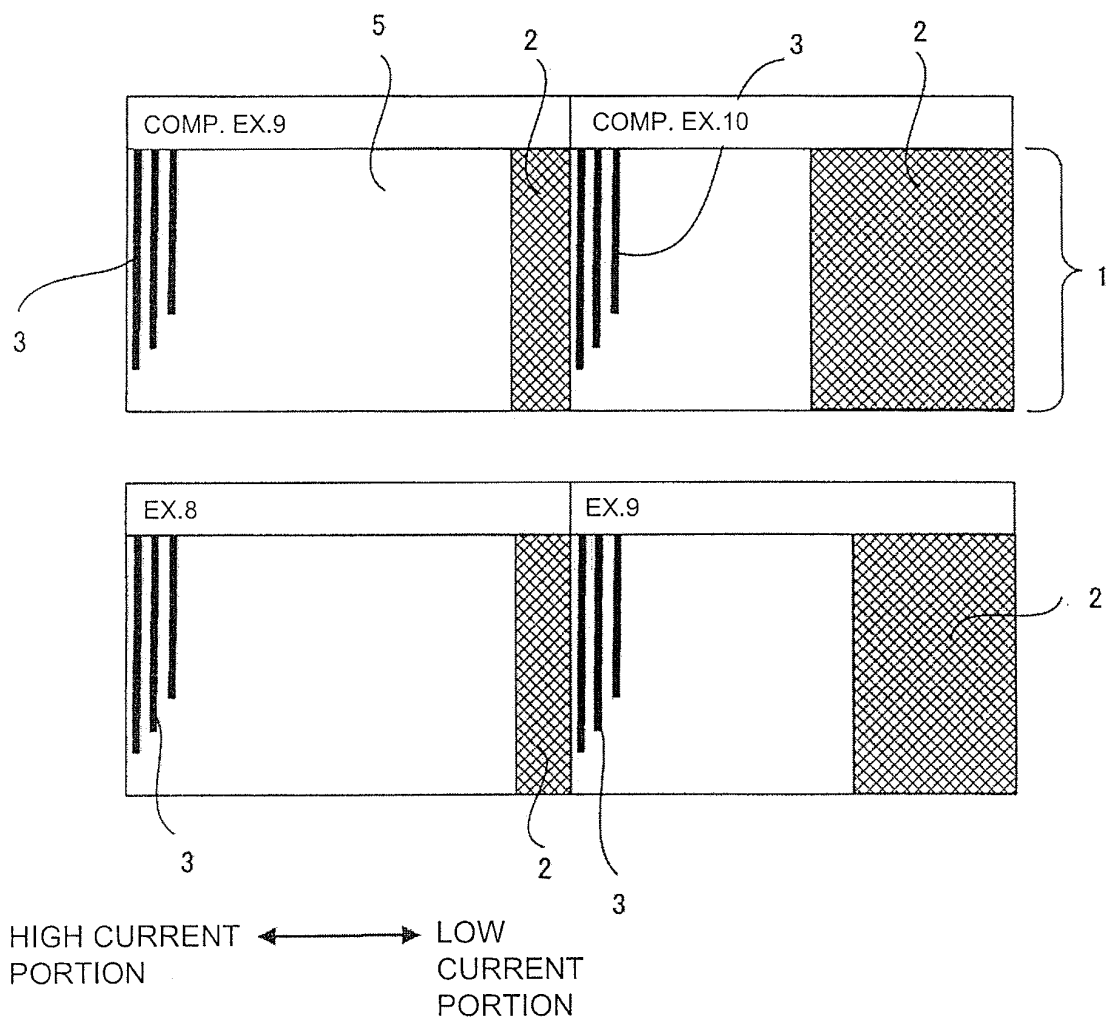


FIG.5

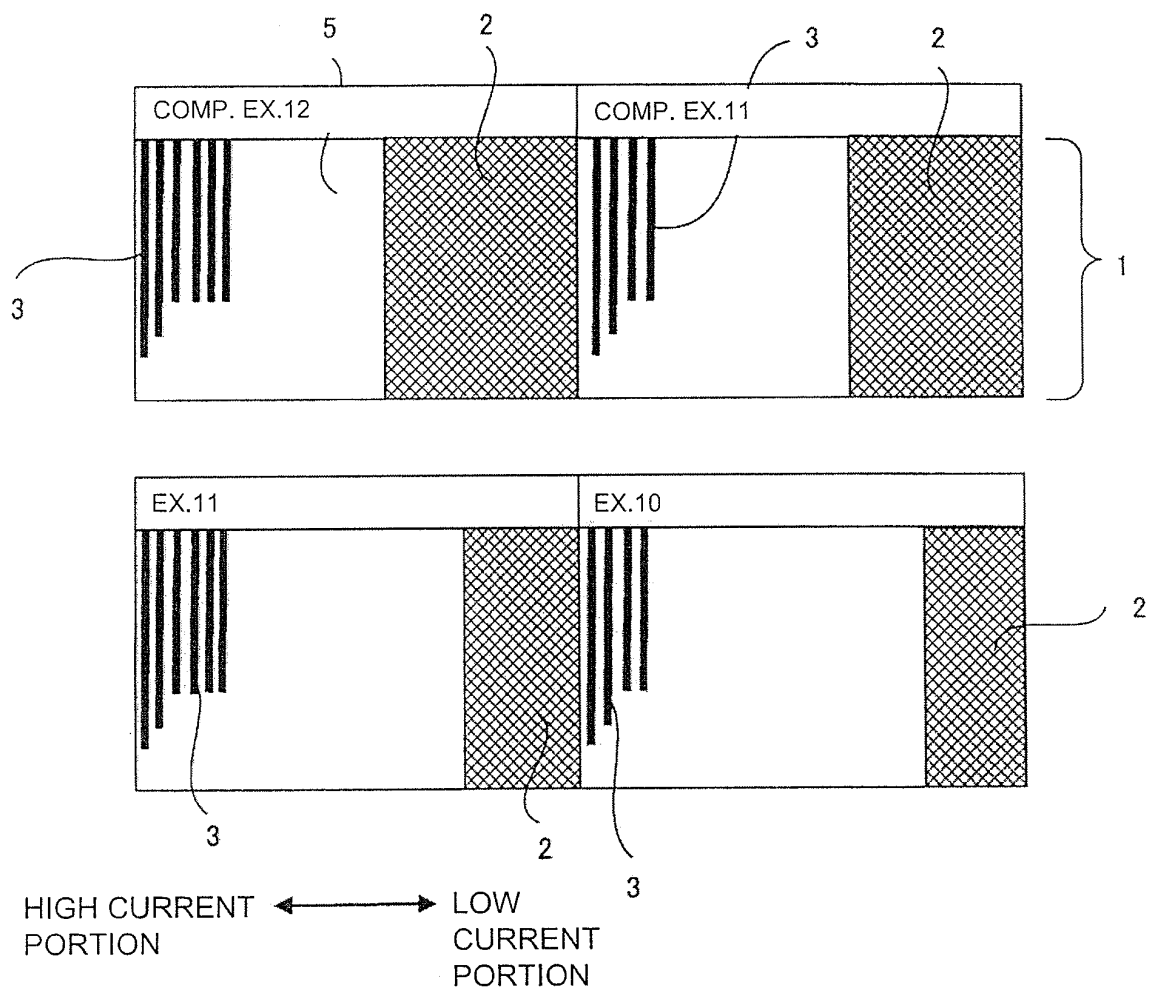


FIG.6

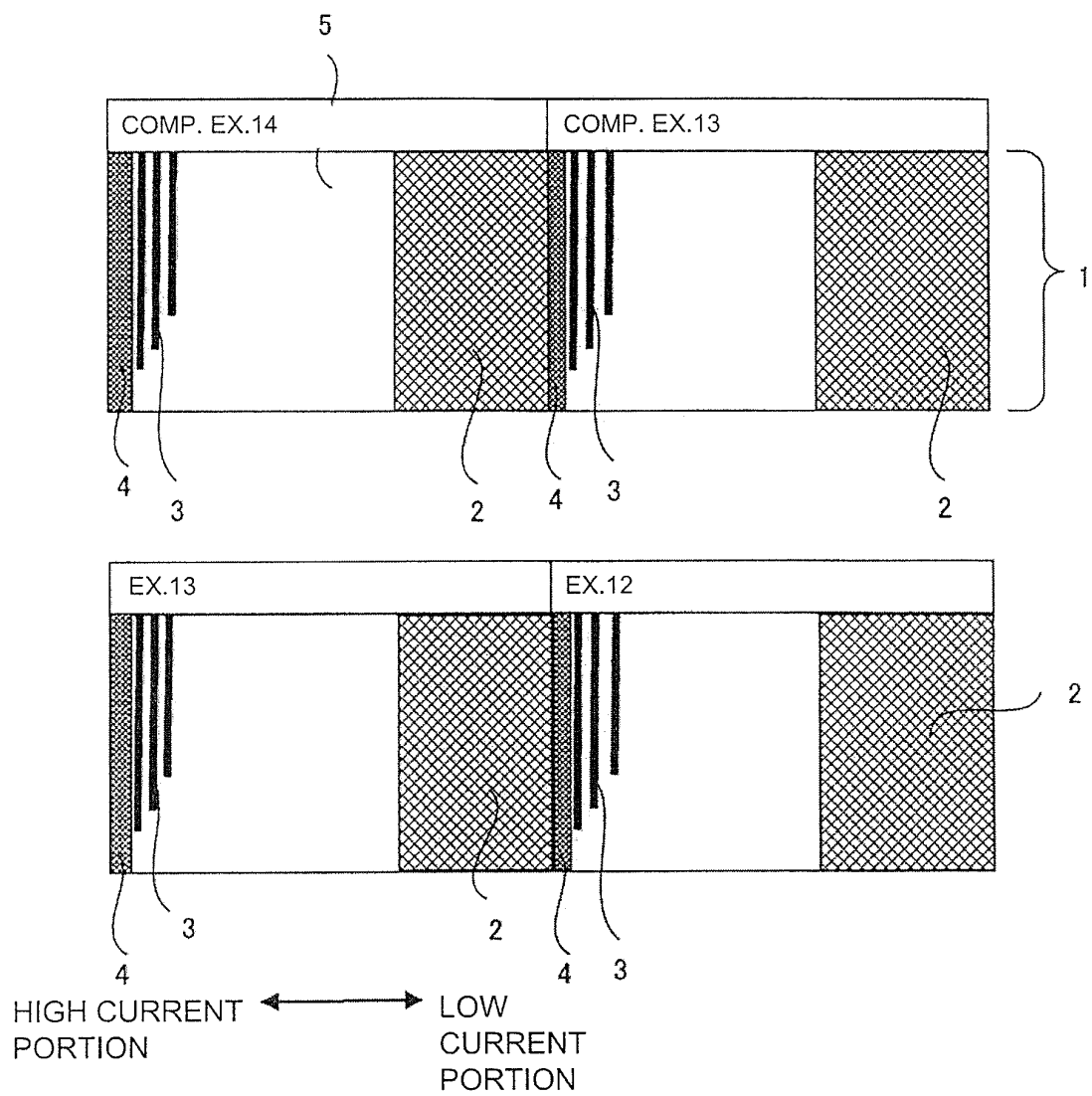
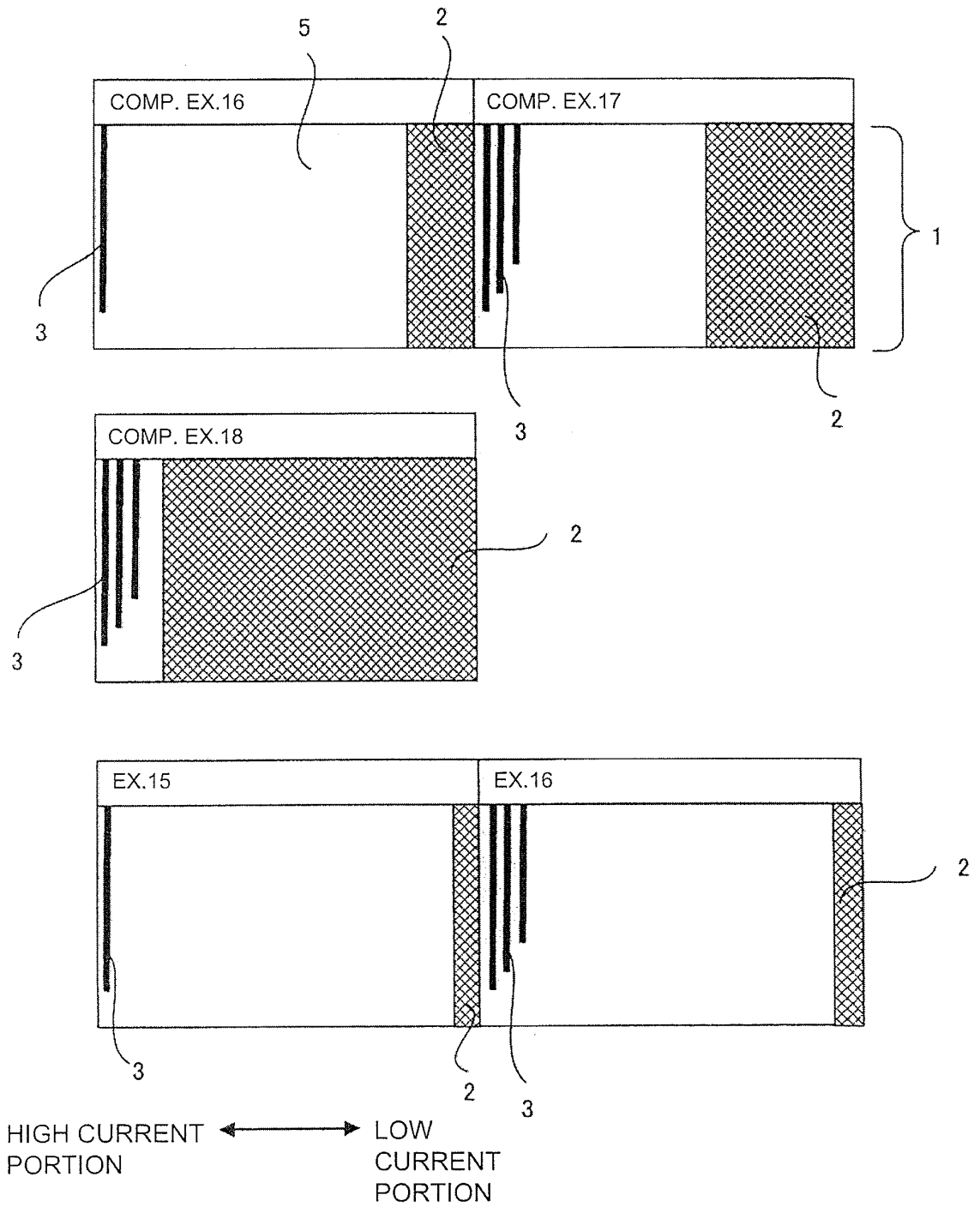


FIG.7



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2009/069372

A. CLASSIFICATION OF SUBJECT MATTER

C25D3/22 (2006.01) i

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)

C25D1/00-3/66, C25D5/00-7/12

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

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2009
Kokai Jitsuyo Shinan Koho	1971-2009	Toroku Jitsuyo Shinan Koho	1994-2009

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.
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A	JP 05-171489 A (Yuken Industry Co., Ltd.), 09 July 1993 (09.07.1993), entire text (Family: none)	1-5
A	JP 03-094094 A (Toppan Printing Co., Ltd.), 18 April 1991 (18.04.1991), entire text (Family: none)	1-5

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

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Date of the actual completion of the international search
08 December, 2009 (08.12.09)Date of mailing of the international search report
15 December, 2009 (15.12.09)Name and mailing address of the ISA/
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