



US 20100236936A1

(19) **United States**(12) **Patent Application Publication**
Brunner et al.(10) **Pub. No.: US 2010/0236936 A1**(43) **Pub. Date: Sep. 23, 2010**(54) **AQUEOUS, ALKALINE, CYANIDE-FREE BATH
FOR THE GALVANIC DEPOSITION OF ZINC
AND ZINC ALLOY COATINGS**(52) **U.S. Cl. 205/244; 205/312**(57) **ABSTRACT**(75) Inventors: **Heiko Brunner**, Berlin (DE); **Lars
Kohlmann**, Berlin (DE); **Ellen
Habig**, Berlin (DE); **Konstantin
Thom**, Berlin (DE); **Roland Vogel**,
Berlin (DE)

The invention relates to an aqueous, alkaline cyanide-free electrolyte bath for de-positing zinc and zinc alloy coatings on substrate surfaces comprising (a) a source for zinc ions and optionally a source for further metal ions, (b) hydroxide ions, (c) a polymer of general formula I which is soluble in the bath and (d) at least one pyridinium compound of general formula II or III. The electrolyte bath is suitable for the galvanic deposition of bright and even zinc and zinc alloy coatings.

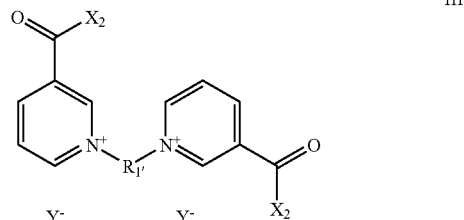
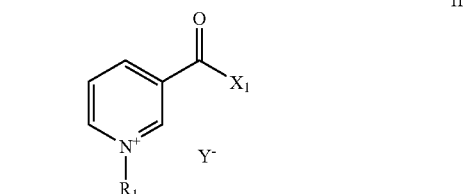
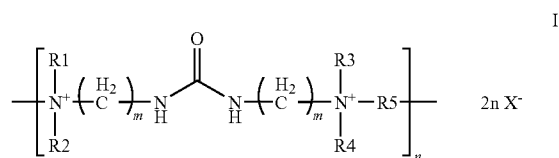
Correspondence Address:

**EDWARDS ANGELL PALMER & DODGE LLP
P.O. BOX 55874
BOSTON, MA 02205 (US)**(73) Assignee: **Atotech Deutschland GmbH**,
Berlin (DE)(21) Appl. No.: **12/308,615**(22) PCT Filed: **Jun. 21, 2007**(86) PCT No.: **PCT/EP2007/005490**

§ 371 (c)(1),

(2), (4) Date: **Feb. 9, 2009**(30) **Foreign Application Priority Data**

Jun. 21, 2006 (EP) 06012766.9

Publication Classification(51) **Int. Cl.**
C25D 3/56 (2006.01)
C25D 3/22 (2006.01)

AQUEOUS, ALKALINE, CYANIDE-FREE BATH FOR THE GALVANIC DEPOSITION OF ZINC AND ZINC ALLOY COATINGS

FIELD OF THE INVENTION

[0001] The present invention relates to an aqueous, alkaline galvanic bath without addition of cyanide ions as complexing agents for the deposition of zinc and zinc alloy coatings, which bath contains as additives bis-(N,N-diaminoalkyl) urea- α,ω -dihaloalkyl copolymers or oligomers and 3-carbamoyl pyridinium compounds quaternized in the 1-position. Furthermore, the invention relates to a process for the deposition of bright and even zinc and zinc alloy coatings in which the bath is used.

BACKGROUND OF THE INVENTION

[0002] The zinc deposition from cyanide-containing alkaline solution has had a significant market share for many years. However, increasingly stringent statutory requirements regarding the disposal of used zinc and zinc alloy electrolyte baths and the consequent strict control regarding waste water have resulted in increased interest in cyanide-free zinc and zinc alloy electrolytes.

[0003] Such metal coatings are used for improving corrosion properties and for achieving certain optical properties. Thus, the automotive industry has used electroplated zinc for decades in order to provide highly corrosion-resistant coatings at reasonable cost.

[0004] Cyanide-free zinc electrolytes and corresponding alloy baths can be classified into two types of baths, namely weakly acidic zinc electrolytes (containing zinc chloride or zinc sulfate) and alkaline zinc electrolytes. Weakly acidic zinc baths result in the deposition of a uniformly bright zinc layer. However, they have the disadvantage that their current efficiency is always 100% across a wide range of current densities. In the case of substrates having a simple shape, this may be advantageous since the electric current is used only for the deposition of zinc. However, in the case of substrates having a complex geometry, this results in excessively thick zinc layers in areas of high current density and to thin zinc layers in areas of low current density.

[0005] The ratio of the zinc layer thickness in the area of high current density to the zinc layer thickness in the area of low current density is referred to as layer thickness distribution and should ideally be 1 (scattering coefficient). From a technical and functional point of view, the zinc layer on the substrate should have the same or approximately the same layer thickness across the entire substrate and should have high brightness.

[0006] A good layer thickness distribution may be achieved by lowering the current efficiency in the area of high current density while the current efficiency is maintained in the area of low current density. So far, this kind of equalizing the zinc layer thickness across a wide range of current densities has been achieved in the deposition of zinc from alkaline, cyanide-free electrolytes.

[0007] Alkaline zinc electroplating baths are generally constituted on the basis of an aqueous solution of zincate ions in the presence of alkali metal hydroxides. DE 25 25 264 and U.S. Pat. No. 3,884,774 describe such electrolytes; however, the zinc layers obtained according to these documents do not show a uniform layer thickness distribution.

[0008] The state of the art contains numerous suggestions for improving the layer thickness distribution by addition of suitable additives.

[0009] Such additive systems are described in U.S. Pat. No. 5,405,523, U.S. Pat. No. 5,435,989, DE 19 50 9713 and U.S. Pat. No. 4,030,987.

[0010] EP 1 114 206 B1 describes a formulation consisting of quaternary derivatives of pyridinium-3-carboxylic acid, copolymers consisting of N,N-bis-[3-(dialkylamino)-alkyl] ureas with α,ω -dihaloalkanes and an aromatic aldehyde, which are characterized in that the formation of bubbles frequently described in connection of the deposition of zinc can be avoided. Further copolymers of the aforementioned type are described in U.S. Pat. No. 5,405,523, U.S. Pat. No. 5,435,898 and WO 2004/044269 A2. Apart from the aforementioned ingredients, WO 2004/044269 A2 uses reducing sugars in order to obtain bright depositions. A disadvantage of this method is the high concentration of reducing sugars which results in increased COD and TOC contents in the effluent water.

[0011] The copolymers described in EP 1 114 206 B1, U.S. Pat. No. 5,405,523 and U.S. Pat. No. 5,435,898 are used as brightening agents together with the commercially readily available quaternized derivatives of nicotinic acid, in particular, N-benzyl-nicotinate.

[0012] The use of 1-benzyl-3-carbamoyl-pyridinium-chloride for cyanide-containing alkaline zinc electrolytes is described in "Kinzoku Hyomen Gijutsu" (1980), 31, p. 244-248.

[0013] U.S. Pat. No. 4,071,418 describes a bath formulation consisting of a quaternary pyridinium derivative and a cationic copolymer of a diamine with 1,3-dihalopropane-2-ol.

[0014] Despite the aforementioned suggestions, the electroplating industry still has, in view of increasingly stringent economic and ecological requirements, a constant need for improved alkaline, cyanide-free zinc and zinc alloy electrolytes which are characterized, on one hand, by reduced amounts of additives and improved layer thickness distribution as well as, on the other hand, increased current efficiency and good brightness. Apart from the aforementioned aspect of layer thickness distribution, in times of steadily increasing energy costs, current efficiency plays an important role since it is inversely proportional to investment and operational costs.

DESCRIPTION OF THE INVENTION

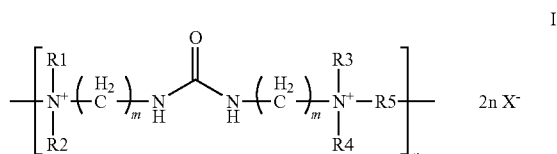
[0015] It is the object of the invention to provide zinc and zinc alloy electrolytes which result in zinc and zinc alloy layers having high brightness and good or improved layer thickness distribution at high current efficiency.

[0016] It has now been found that, by combination of the copolymers known from EP 1 114 206 B1, U.S. Pat. No. 5,405,523 and U.S. Pat. No. 5,435,898 with suitable brightening agents, it is possible to obtain electrolytes resulting in the deposition of zinc and zinc alloy layers with surprisingly improved layer thickness distribution, improved brightness and increased current efficiency. In particular, it has been found that the use of pyridine-3-carboxylic acid amides as brightening agents results in electrolyte compositions which are characterized by high brightness, improved layer thickness distribution and increased current efficiency.

[0017] Thus, the invention provides an aqueous, alkaline, cyanide-free electrolyte bath for the deposition of zinc and

zinc alloy coatings on substrate surfaces, which bath comprises the following components:

- a) a source of zinc ions and, optionally, a source of further metal ions,
- b) hydroxide ions,
- c) a polymer which is soluble in the bath of the general formula I



[0018] wherein

[0019] m represents an integer of 1 to 5, preferably 2 to 5, or 1 to 4, more preferably 2 to 3,

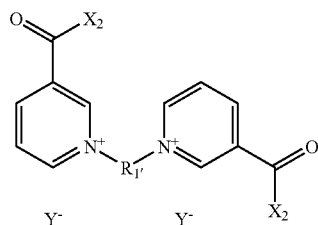
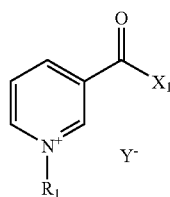
[0020] n represents an integer greater than 1, preferably greater than 2,

[0021] R1, R2, R3, R4 may be the same or different and each represents a substituted or unsubstituted hydrocarbon residue having 1 to 6 carbon atoms, preferably methyl, ethyl, hydroxyethyl or $\text{—CH}_2\text{CH}_2(\text{OCH}_2\text{CH}_2)_y\text{—OH}$, wherein y lies between 0 and 6,

[0022] R5 represents $(\text{CH}_2)_p$, wherein p represents an integer of 2 to 12, preferably a methylene or propylene group or a $\text{—(CH}_2)_2\text{—O—(CH}_2)_2\text{—}$ or $\text{—(CH}_2)_2\text{—O—(CH}_2)_2\text{—O—(CH}_2)_2\text{—O—(CH}_2)_2\text{—}$ group and

[0023] X^- represents a counter ion, preferably halide or pseudo-halide; and

d) at least one pyridinium compound of general formula II or III



[0024] wherein

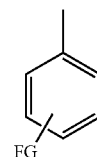
[0025] R1 represents a substituted or unsubstituted, saturated or unsaturated, aliphatic or araliphatic hydrocarbon residue having 1 to 12 carbon atoms,

[0026] R1' represents a divalent, substituted or unsubstituted, saturated or unsaturated, aliphatic or araliphatic hydrocarbon residue having 1 to 12 carbon atoms,

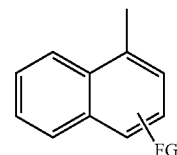
[0027] X_1 and X_2 represent NR_xR_y , wherein R_x and R_y may be the same or different and represent hydrogen or linear or branched alkyl groups having 1 to 12 carbon atoms, and

[0028] Y^- is a counter ion.

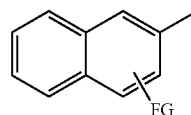
[0029] In a preferred embodiment, R1 in formula II represents substituted aryl of the following formulae R1a to R1I:



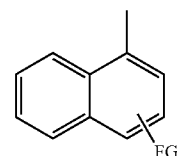
R1a



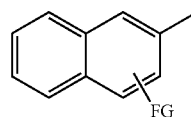
R1b



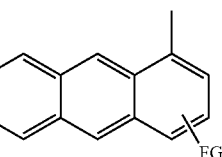
R1c



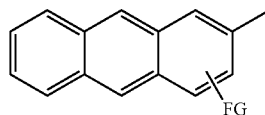
R1d



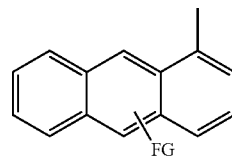
R1e



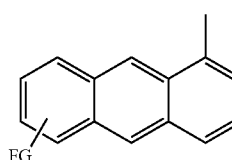
R1f



R1g

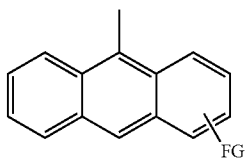


R1h

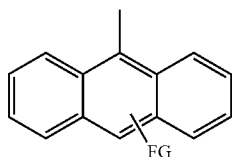


R1i

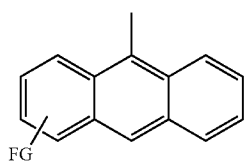
-continued



R1j



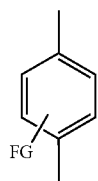
R1k



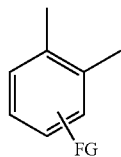
R1l

wherein FG represents a residue selected from the group consisting of carboxy, ester, sulfonic acid, carbamoyl, amino, cyano, alkyl, alkoxy, hydroxy, trifluoromethyl, allyl, propargyl-, 4-sulfobutyl, 3-sulfopropyl, 4-carboxybutyl, 3-carboxypropyl residues, hydrogen and halogens, selected from fluorine, chlorine and bromine,

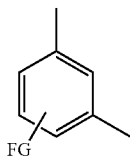
and R₁' in formula III represents but-2-enyl, but-2-ynyl or aryl of the following formulae R1'a to R1' r:



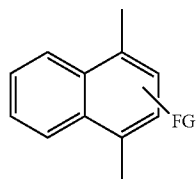
R1'a



R1'b

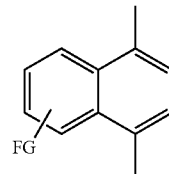


R1'c

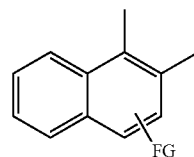


R1'd

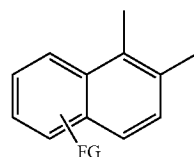
-continued



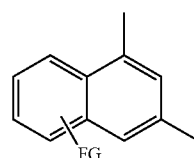
R1'e



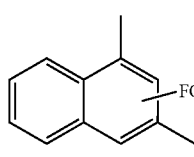
R1'f



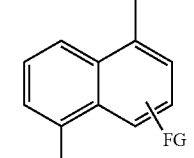
R1'g



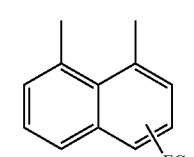
R1'e



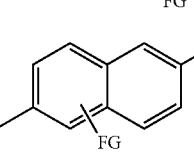
R1'f



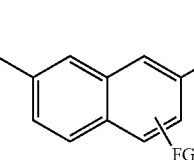
R1'g



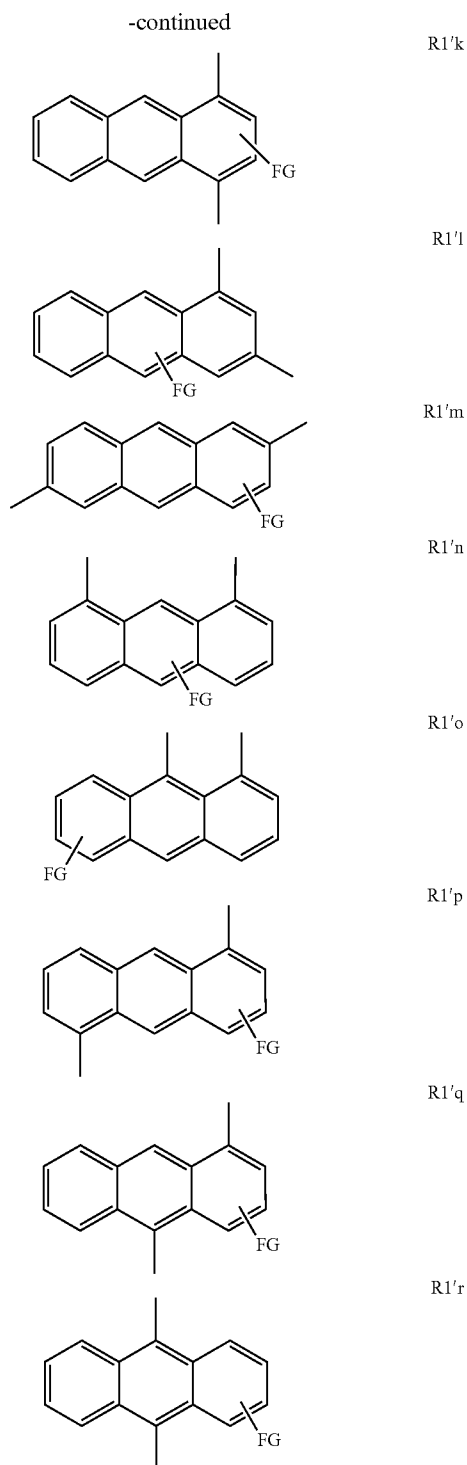
R1'h



R1'i



R1'j



wherein FG represents a residue selected from the group consisting of carboxy, ester, sulfonic acid, carbamoyl, amino, cyano, alkyl, alkoxy, trifluoromethyl residues, hydrogen and halogens, selected from fluorine, chlorine and bromine, wherein all rings or individual fused rings may be substituted.

[0030] Preferably, residues R_1 and R_1' in formulae II and III are bonded to the pyridinium residue via a methylene group.

[0031] Preferred araliphatic hydrocarbon residues are, for example, benzyl (R_{1a}) and naphthyl methyl (R_{1b}).

[0032] In the context of the present invention, fluorides, chlorides and bromides may be used as halides. Furthermore, the bath according to the invention may contain compounds, which are similar, with respect to their physical and chemical properties, to the halides, i.e., so-called pseudo-halides. Such pseudo-halides are known to the skilled person as such and are described, for example, in Römpp-Lexikon, Chemie, 10th edition, page 3609. In the context of the present invention, pseudohalides also comprise residues such as mesitylate and triflate.

[0033] The soluble polymers of general formula I contained in the bath may be obtained according to EP 1 114 206 B1 by reaction of N,N-bis-[(dialkylamino)-alkyl]-ureas with α,ω -dihaloalkanes. A particularly preferred copolymer of this class is, apart from the compounds described in EP 1 114 206 B1, Mirapol™ WT available from Rhodia or Lugalvan™ P available from BASF.

[0034] The polymer of formula I is contained in the bath according to the invention preferably in an amount of 0.1 to 50 g/l, more preferably 0.25 to 10 g/l. The bath may contain a combination of different soluble polymers of general formula I.

[0035] The electroplating baths according to the invention contain an inorganic alkaline component, preferably a hydroxide of an alkali metal and, particularly preferably, sodium hydroxide, potassium hydroxide and/or lithium hydroxide, in order to adjust the pH of the bath to at least 10 and preferably to at least 11. To this end, amounts of 50 to about 250 g/l, preferably 90 to 130 g/l of the alkaline component may be used.

[0036] The electroplating baths according to the invention generally contain zinc ions at concentrations ranging from about 0.1 to about 100 g/l, concentrations of 4 to 30 g/l being preferred. The zinc ion may be present in the bath according to the invention in the form of a soluble salt, for example zinc oxide, zinc sulfate, zinc carbonate, zinc acetate, zinc sulfamate, zinc hydroxide, zinc tartrate.

[0037] As alloying metal, the baths according to the invention contain about 0.1 to 50 g/l of metal ions, suitable metal salts are hydroxides, sulfates, carbonates, ammonium sulfates, sulfamates, acetates, formates and halides, preferably chloride and bromide. Suitable alloying metals are preferably cobalt, nickel, manganese and/or iron. The concentration of the alloying metal ions in the baths according to the invention may be varied across a wide range and preferably is 0.01 to 100 g/l. Since different types of alloys require different contents of alloying metals, for example in order to improve protection against corrosion, this concentration varies from metal ion to metal ion.

[0038] Preferably, the baths according to the invention contain about 0.1 to 50 g/l of nickel ions as alloying metal. Suitable nickel salts are nickel hydroxide, nickel sulfate, nickel carbonate, ammonium nickel sulfate, nickel sulfamate, nickel acetate, nickel formate and nickel halides.

[0039] In a preferred embodiment, the electrolyte bath contains zinc in an amount of 0.1 to 30 g/l and cobalt in an amount of 10 to 120 mg/l, nickel in an amount of 0.3 to 3 g/l, manganese in an amount of 10 to 100 g/l and/or iron in an amount of 10 to 120 mg/l.

[0040] The electrolyte baths according to the invention contain the aforementioned aromatic heterocyclic nitrogen-containing compounds of general formulae II and III for

substantial improvement of leveling and brightness properties of the deposited layers across a wide range of current densities. Therefore, the compounds of formulae II and III are hereinafter referred to as brightening agent according to the invention.

[0041] Preferred compounds of formulae II and III are 1-benzyl-3-carbamoyl-pyridinium-chloride, 1-(2'-chloro-benzyl)-3-carbamoyl-pyridinium-chloride, 1-(2'-fluoro-benzyl)-3-carbamoyl-pyridinium-chloride, 1-(2'-methoxy-benzyl)-3-carbamoyl-pyridinium-chloride, 1-(2'-carboxy-benzyl)-3-carbamoyl-pyridinium-chloride, 1-(2'-carbamoylbenzyl)-3-carbamoyl-pyridinium-chloride, 1-(3'-chloro-benzyl)-3-carbamoyl-pyridinium-chloride, 1-(3'-fluoro-benzyl)-3-carbamoyl-pyridinium-chloride, 1-(3'-methoxy-benzyl)-3-carbamoyl-pyridinium-chloride, 1-(3'-carboxy-benzyl)-3-carbamoyl-pyridinium-chloride, 1-(3'-carbamoylbenzyl)-3-carbamoyl-pyridinium-chloride, 1-(4'-chloro-benzyl)-3-carbamoyl-pyridinium-chloride, 1-(4'-fluoro-benzyl)-3-carbamoyl-pyridinium-chloride, 1-(4'-methoxy-benzyl)-3-carbamoyl-pyridinium-chloride, 1-(4'-carboxy-benzyl)-3-carbamoyl-pyridinium-chloride, 1-(4'-carbamoylbenzyl)-3-carbamoyl-pyridinium-chloride, (1'-methyl-naphthyl)-3-carbamoyl-pyridinium-chloride, 1-(1'-methyl-naphthyl)-3-carbamoyl-pyridinium-bromide, 1-(1'-methyl-naphthyl)-3-carbamoyl-pyridinium-fluoride, 1,1'-(but-2-enyl)-3,3'-biscarbamoyl-bispyridinium-dichloride, 1,1'-(but-2-enyl)-3,3'-bis-carboxy-bispyridinium-dichloride, 1-allyl-3-carbamoyl-pyridinium-chloride, 1-allyl-3-carboxypyridinium-chloride, 1-propargyl-3-carbamoyl-pyridinium-chloride, 1,1'-(but-2-ynyl)-3,3'-biscarbamoyl-bispyridinium-dichloride, 1,1'-(but-2-ynyl)-3,3'-bis-carboxy-bis-pyridinium-dichloride, 1,1'-(xylenyl)-3,3'-bis-carbamoyl-bis-pyridinium-dibromide, 1-(3'-sulfopropyl)-3-carbamoyl-pyridinium-betaine as well as the corresponding bromides, fluorides, iodides and pseudo-halides (for example, triflates, tosylates) of the aforementioned compounds.

[0042] The brightening agents can be readily prepared by reacting the corresponding nicotinic acid amide derivatives with the corresponding benzyl halides in a suitable solvent, such as ethanol, propanol, iso-propanol, butanol, iso-butanol, methanol or their mixtures, DMF, DMAc; NMP, NEP, in substance or in an aqueous medium, while heating under

normal or increased pressure. The reaction times required range from 1 to 48 hours, depending on the starting material used. In this connection, apart from conventional sources of heat, a microwave oven may be used. The pyridinium compounds obtained can either be used directly as the aqueous or alcoholic reaction solution or they can be isolated after cooling by filtration or by removal of the corresponding solvent. The compounds can be purified by recrystallization from a suitable solvent such as ethanol, precipitation or column chromatography.

[0043] The bis-pyridinium compounds of general formula II can be prepared according to U.S. Pat. No. 6,652,728.

[0044] The compounds of formula II or III can be used alone or as a mixture at a concentration of 0.001 to 20 Wt, preferably of 0.001 to 10 g/l. The bath may contain a combination of pyridinium compounds of formulae II and III.

[0045] The baths according to the invention may be prepared according to conventional methods, for example by adding the specific amounts of the aforementioned components to water. The amount of the basic component, such as sodium hydroxide, should be sufficient to achieve the desired pH of the bath of at least 10 and preferably above 11.

[0046] The baths according to the invention deposit a bright, even and ductile zinc or zinc alloy layer at any conventional temperature of about 15° C. to 50° C., preferably 20° C. to 30° C., more preferably about 25° C. At these temperatures, the baths according to the invention are stable and effective over a wide range of current densities of 0.01 to 10 A/dm², preferably 0.5 to 4 A/dm².

[0047] The baths according to the invention can be used in continuous or batch-wise mode and the components will have to be replaced from time to time. The components of the bath can be added alone or in combination. Moreover, depending on the type and the properties of the zinc and the zinc alloy baths to which the substances are added, they may be varied across a wide range.

[0048] Table 1 shows, according to a particularly preferred embodiment, the influence with respect to the layer thickness (and thus current efficiency), brightness and layer thickness distribution in the electrolytes according to the invention for deposition of a zinc layer (using 10⁻⁴ mmol/l of pyridinium compound and a polymeric additive according to Preparation Example 2.2 of EP 1 114 206 B1):

TABLE 1

Ex. Pyridinium compound	Brightness	Layer thickness	Layer thickness	Layer thickness coefficient
		j = 3.0 A/dm ² [μm]	j = 0.5 A/dm ² [μm]	
1 1-benzyl-3-carboxy-pyridinium-chloride*	+++	3.84	2.41	1.59
2 1-benzyl-3-carbamoyl-pyridinium-chloride	+++	4.74	3.76	1.26
3 1-(4'-methoxy-benzyl)-3-carbamoyl-pyridinium-chloride	+++	4.20	3.18	1.32
4 1-(4'-trifluoromethyl-benzyl)-3-carbamoyl-pyridinium-chloride	+++	4.98	3.71	1.34
5 1,1'-(xylenyl)-3,3'-biscarbamoyl-bispyridinium-chloride	++	4.80	3.18	1.51
6 1-(4'-chloro-benzyl)-3-carbamoyl-pyridinium-chloride	+++	4.20	3.15	1.33

TABLE 1-continued

Ex. Pyridinium compound	Brightness	Layer thickness	Layer thickness	Layer thickness coefficient
		$j = 3.0 \text{ A/dm}^2$ [μm]	$j = 0.5 \text{ A/dm}^2$ [μm]	
7 1-benzyl-3-N,N-dimethylcarbamoyl-pyridinium-chloride	+++	4.15	2.99	1.39

*Comparative Example according to Example 13 of EP 1 114 206 B1

[0049] As Table 1 clearly shows, the novel electrolytes according to the invention show markedly better layer thickness distributions while the current efficiency is increased at the same time. In the areas of both high and low current density, there are achieved current efficiencies which are 10 to 30% (in the area of high current density) or 30 to 50% (in the area of low current density) higher compared to the classic pyridinium compound. Especially the much higher current efficiencies in the area of low current density are very interesting in connection with applications using drum electroplating methods.

[0050] The formulation according to the invention of the aforementioned pyridinium compounds (which are known from U.S. Pat. No. 4,071,418) with the aforementioned copolymers of general formula I results in unexpected advantageous properties of the deposited layers. Table 2 shows these synergistic effects of the electrolyte compositions according to the invention:

brightening agent in the electrolytes according to the invention is significantly lower and thus more economical than the conventionally used pyridinium derivatives based on nicotinic acid.

[0053] Apart from the additives mentioned above, the baths according to the invention may contain known levelling agents such as 3-mercapto-1,2,4-triazole and/or thiourea, thiourea frequently being preferred.

[0054] In principle, the electrolyte bath according to the invention may contain additional brightening agents from the group of sulphur compounds, aldehydes or bisulfite adducts thereof, ketons, amines, polyvinyl alcohol, polyvinyl pyrrolidone, proteins or reactions products of halohydrines with aliphatic or aromatic amines, polyamines or heterocyclic nitrogen compounds and mixtures thereof. As additional brightening agents, there may be used, in particular, aromatic aldehydes from the group of 4-hydroxybenzaldehyde, 4-hydroxy-3-methoxy-benzaldehyde, 3,4-dimethoxy-benzalde-

TABELLE 2

Ex. Formulation	Brightness	Layer thickness	Layer thickness	Layer thickness coefficient
		$j = 3.0 \text{ A/dm}^2$ [μm]	$j = 0.5 \text{ A/dm}^2$ [μm]	
8 Formulation according to the invention with 100 mg/l of 1-benzyl-3-carbamoyl-pyridinium-chloride	+++	4.9	3.7	1.32
9 Formulation according to Example 6 of U.S. Pat. No. 4,071,418 with 100 mg/l 1-benzyl-3-carbamoyl-pyridinium-chloride instead of sodium nicotinate	+	5.4	2.3	2.35
10 Formulation according to Example 6 of U.S. Pat. No. 4,071,418	+	6.1	3.3	1.85

[0051] As Table 2 shows, the formulations according to U.S. Pat. No. 4,071,418 do achieve high current efficiencies at high current density; however, both the brightness and the layer thickness distribution coefficient obtained with these electrolytes are significantly worse than with the formulations according to the invention. Actually, the pyridinium compounds of general formula II and III give worse results in combination with the cationic polymers described in U.S. Pat. No. 4,071,418 than the classic, widely used benzyl nicotinate.

[0052] A further advantage of the electrolytes according to the invention, compared to the electrolyte of EP 1 114 206 B1 is the surprisingly lower consumption of the quaternized nicotinamide derivatives according to the invention, compared to the N-benzyl-nicotinate. As Application Example 12 shows, the consumption of pyridinium compounds acting as

hyde, 3,4-methylenedioxy-benzaldehyde, 2-hydroxy-benzaldehyde and mixtures as well as bisulfite adducts thereof, in an amount of 0.001 to 1.0 g/l.

[0055] Surprisingly, it was found that, with the electrolytes according to the invention, the conventional use of aromatic aldehydes or their bisulfite adducts as additional brighteners, for example 4-hydroxybenzaldehyde, 4-hydroxy-3-methoxybenzaldehyde, 3,4-dimethoxybenzaldehyde, 3,4-methylenedioxybenzaldehyde, 2-hydroxybenzaldehyde or mixtures thereof as well as bisulfite adducts thereof, is unnecessary.

[0056] In a preferred embodiment, the electrolyte bath according to the invention thus contains no aromatic aldehydes or their bisulfite adducts as additional brighteners, in particular, it contains no 4-hydroxybenzaldehyde, 4-hydroxy-3-methoxybenzaldehyde, 3,4-dimethoxybenzaldehyde,

hyde, 3,4-methylenedioxybenzaldehyde or 2-hydroxybenzaldehyde or bisulfite adduct thereof.

[0057] The electrolyte bath according to the invention may contain a complexing agent or a water softening agent. The complexing agent is preferably a chelate forming agent, which is preferably present in an amount of 2 to 200 g/l.

[0058] The electrolyte bath according to the invention can also contain, as leveling agent, a sulfur compound, for example, 3-mercapto-1,2,4-triazole and/or thiourea, preferably in an amount of 0.01 to 0.50 g/l.

[0059] The aqueous, alkaline baths according to the invention can generally be used for all types of substrates on which zinc and zinc alloys can be deposited. Examples of suitable substrates are soft steel, spring steel, chromium steel, chromiummolybdenum steel, copper, copper/zinc alloys.

[0060] Therefore, the invention also provides a process for the galvanic deposition of zinc and zinc alloy coatings on conventional substrates, wherein the electrolyte bath according to the invention is used. In the process according to the invention, the deposition of coatings is preferably carried out at a current density of 0.01 A/dm² to 10 A/dm² and at a temperature in the range of 15 to 50° C., preferably 20 to 30° C., more preferably about 25° C.

[0061] The process according to the invention may be carried out, for example, as barrel electroplating process when applied to small pieces and as a rack electroplating process when applied to larger pieces. The process involves the use of anodes, which may be soluble, for example, zinc anodes, which may serve as zinc ion source at the same time so that the zinc deposited on the cathode is replaced by dissolution of zinc from the anode.

[0062] However, insoluble anodes (for example, platinized titanium mixed oxide anodes) may also be used, in which case the zinc ions and/or further metal ions removed from the electrolyte by deposition of the alloy have to be added to the electrolyte in other ways, for example by using a zinc dissolution container.

[0063] As generally possible in electroplating, the process according to the invention, too, can be carried out with injection of air, with or without agitation of the substrate, which has no negative effects on the coatings obtained. In order to avoid or reduce the oxidation of additives, the electrode regions may be separated or membrane anodes may be used.

[0064] The current source may be a conventional rectifier or pulse rectifier.

EXAMPLES

[0065] The following examples illustrate the invention, but the invention is not limited thereto.

Preparation Example 1

Synthesis of 1-(4'-methoxy-benzyl)-3-carbamoyl-pyridinium-chloride

[0066] In a 100 ml round-bottom flask with reflux condenser, 60 ml of water, 9.2 g of nicotinic acid amide (98%) (0.0738 mol), 11.68 g of 4-methoxybenzylchloride (99%) (0.07378 mol) are heated under reflux for 24 hours. After completion of the reaction, the water is removed in vacuo and the residue is taken up in 200 ml of ethanol and heated under reflux for another hour. The reaction mixture is then cooled to

4° C. and the white solid obtained is removed by filtration and dried in vacuo. This yielded 16.92 g of a white solid (82.26% of the theoretical yield).

Preparation Example 2

Synthesis of 1-(4'-chloro-benzyl)-3-carbamoyl-pyridinium-chloride

[0067] In a 100 ml round-bottom flask with reflux condenser, 60 ml of ethanol, 10 g of nicotinic acid amide (98%) (0.0802 mol), 13.05 g of 4-chloro-benzylchloride (99%) (0.0802 mol) are heated under reflux for 24 hours. After completion of the reaction, the solid residue is heated in an ethanol/methanol mixture for another 15 minutes and then cooled to 4° C. The solid obtained is removed by filtration and dried in vacuo. This yielded 18.82 g of a white solid (82.87% of the theoretical yield).

Preparation Example 3

Synthesis of 1,1'-(xylenyl)-3,3'-bis-carbamoyl-bis-pyridinium-dichloride

[0068] In a 100 ml round-bottom flask with reflux condenser, 60 ml of ethanol, 10 g of nicotinic acid amide (98%) (0.0802 mol), 7.16 g of α,α' -dichloro-p-xylene (98%) (0.0401 mol) are heated under reflux for 24 hours. After completion of the reaction, the solid residue is heated in 200 ml of an ethanol/methanol mixture for another 15 minutes and then cooled to 4° C. The resulting solid is removed by filtration and dried in vacuo. This yielded 12.29 g of a white solid (73.13% of the theoretical yield).

Preparation Example 4

Synthesis of 1-(4'-trifluoromethyl-benzyl)-3-carbamoyl-pyridinium-chloride

[0069] In a 100 ml round-bottom flask with reflux condenser, 80 ml of water, 3.11 g of nicotinic acid amide (98%) (24.93 mmol), 4.95 g of α -chloro- α,α,α -trifluoro-paraxylene (98%) (24.93 mmol) are heated under reflux for 24 hours. After completion of the reaction, the reaction mixture is concentrated in vacuo and the resulting solid is dried in vacuo. This yielded 5.99 g of a white solid (75.82% of the theoretical yield).

Preparation Example 5

Synthesis of benzyl-3-carbamoyl-pyridinium-chloride

[0070] In a 100 ml round-bottom flask with reflux condenser, 60 ml of ethanol, 10 g of nicotinic acid amide (98%) (0.0802 mol), 10.252 g of benzyl chloride (99%) (0.0802 mol) are heated under reflux for 24 hours. After completion of the reaction, the reaction mixture is cooled to 4° C. and the resulting solid is removed by filtration and re-crystallized from 1 liter of ethanol. This yielded 19.00 g of a white solid (95.33% of the theoretical yield).

Preparation Example 6

Synthesis of 1-benzyl-3-N,N-dimethylcarbamoyl-pyridinium-chloride

[0071] Into a 50 ml round bottom flask with reflux condenser are charged 1 g of pyridine-3-N,N-dimethyl-carboxylic acid amide (6.658 mmol), 0.841 g of benzylchloride (99%)

(6.658 mmol) in 10 ml of DMF and heated for 12 hours at 120° C. After completion of the reaction, the excess solvent is removed in vacuo and the crude product is extracted for a prolonged time with water/ethyl acetate. The resulting ethyl acetate phase is discarded and the aqueous phase is concentrated in vacuo. The resulting solid is dried in oil pump vacuum. This yielded 1.8 g of a caramel color product (97.7% of the theoretical yield).

Application Example 1

Comparative Example according to EP 1 114 206 B1

[0072] An electrolyte having the following composition is used:

12.5 g/l	Zn(OH) ₂
120 g/l	NaOH
25 mg/l	1-benzyl-3-carboxy-pyridinium-chloride
1 g/l	a polymeric additive according to Preparation Example 2.2 of EP 1 114 206 B1 (amount stated is relative to solid content)

[0073] 250 ml of the electrolyte are filled into a Hull cell. A steel anode is used. The cathode sheet is coated for 15 minutes at 1 A. After completion of the reaction, the sheet is rinsed and dried with compressed air. The measurement of layer thickness is carried out at two points (3 cm from the bottom edge and 2.5 cm from the right- and left-hand edge) at high (3 A/dm²) and low current density (0.5 A/dm²).

[0074] The thickness layer coefficient is the ratio of the layer thickness at high current density and the layer thickness at low current density.

[0075] A very bright deposition with the following layer thicknesses was obtained:

Brightness	Layer thickness [μm] j = 3 A/dm ²	Layer thickness [μm] j = 0.5 A/dm ²	Layer thickness coefficient
+++	3.84	2.41	1.59

Application Example 2

[0076] Application Example 1 is repeated with the exception that an electrolyte having the following composition is used:

12.5 g/l	Zn(OH) ₂
120 g/l	NaOH
25 mg/l	1-benzyl-3-carbamoyl-pyridinium-chloride
1 g/l	a polymeric additive according to Preparation Example 2.2 of EP 1 114 206 B1 (amount stated is relative to solid content)

A very bright deposition with the following layer thicknesses was obtained:

Brightness	Layer thickness [μm] j = 3 A/dm ²	Layer thickness [μm] j = 0.5 A/dm ²	Layer thickness coefficient
+++	4.74	3.76	1.26

Application Example 3

[0077] Application Example 1 is repeated with the exception that an electrolyte having the following composition is used:

12.5 g/l	Zn(OH) ₂
120 g/l	NaOH
27.8 mg/l	1-(4'-methoxy-benzyl)-3-carbamoyl-pyridinium-chloride
1 g/l	a polymeric additive according to Preparation Example 2.2 of EP 1 114 206 B1 (amount stated is relative to solid content)

A very bright deposition with the following layer thicknesses was obtained:

Brightness	Layer thickness [μm] j = 3 A/dm ²	Layer thickness [μm] j = 0.5 A/dm ²	Layer thickness coefficient
+++	4.20	3.18	1.32

Application Example 4

[0078] Application Example 1 is repeated with the exception that an electrolyte having the following composition is used:

12.5 g/l	Zn(OH) ₂
120 g/l	NaOH
31.7 mg/l	1-(4'-trifluoromethyl-benzyl)-3-carbamoyl-pyridinium-chloride
1 g/l	a polymeric additive according to Preparation Example 2.2 of EP 1 114 206 B1 (amount stated is relative to solid content)

A very bright deposition with the following layer thicknesses was obtained:

Brightness	Layer thickness [μm] j = 3 A/dm ²	Layer thickness [μm] j = 0.5 A/dm ²	Layer thickness coefficient
+++	4.98	3.71	1.34

Application Example 5

[0079] Application Example 1 is repeated with the exception that an electrolyte having the following composition is used:

12.5 g/l	Zn(OH) ₂
120 g/l	NaOH
41.9 mg/l	1,1'-(xylene)-3,3'-biscarbamoyl-bispyridinium-dichloride
1 g/l	a polymeric additive according to Preparation Example 2.2 of EP 1 114 206 B1 (amount stated is relative to solid content)

A very bright deposition with the following layer thicknesses was obtained:

Brightness	Layer thickness [μm] j = 3 A/dm ²	Layer thickness [μm] j = 0.5 A/dm ²	Layer thickness coefficient
++	4.80	3.18	1.51

Application Example 6

[0080] Application Example 1 is repeated with the exception that an electrolyte having the following composition is used:

12.5 g/l	Zn(OH) ₂
120 g/l	NaOH
28.3 mg/l	1-(4'-chloro-benzyl)-3-carbamoyl-pyridinium-chloride
1 g/l	a polymeric additive according to Preparation Example 2.2 of EP 1 114 206 B1 (amount stated is relative to solid content)

A very bright deposition with the following layer thicknesses was obtained:

Brightness	Layer thickness [μm] j = 3 A/dm ²	Layer thickness [μm] j = 0.5 A/dm ²	Layer thickness coefficient
+++	4.20	3.15	1.33

Application Example 7

[0081] Application Example 1 is repeated with the exception that an electrolyte having the following composition is used:

12.5 g/l	Zn(OH) ₂
120 g/l	NaOH
27 mg/l	1-benzyl-3-N,N-dimethylcarbamoyl-pyridinium-chloride
1 g/l	a polymeric additive according to Preparation Example 2.2 of EP 1 114 206 B1 (amount stated is relative to solid content)

A very bright deposition with the following layer thicknesses was obtained:

Brightness	Layer thickness [μm] j = 3 A/dm ²	Layer thickness [μm] j = 0.5 A/dm ²	Layer thickness coefficient
+++	4.15	2.99	1.39

Application Example 8

[0082] Application Example 1 is repeated with the exception that an electrolyte having the following composition is used:

12.5 g/l	Zn(OH) ₂
120 g/l	NaOH
100 mg/l	1-benzyl-3-carbamoyl-pyridinium-chloride
1 g/l	a polymeric additive according to Preparation Example 2.2 of EP 1 114 206 B1 (amount stated is relative to solid content)

A very bright deposition with the following layer thicknesses was obtained:

Brightness	Layer thickness [μm] j = 3 A/dm ²	Layer thickness [μm] j = 0.5 A/dm ²	Layer thickness coefficient
+++	4.90	3.70	1.32

Application Example 9

Comparative Example according to U.S. Pat. No. 4,071,418 with 1-benzyl-3-carbamoyl-pyridinium-chloride

[0083] Application Example 1 is repeated with the exception that an electrolyte having the following composition is used:

12.5 g/l	Zn(OH) ₂
120 g/l	NaOH
100 mg/l	1-benzyl-3-carbamoyl-pyridinium-chloride
1 g/l	a polymeric additive according to Preparation Example 1 of U.S. Pat. No. 4,071,418 (amount stated is relative to solid content)

A bright deposition with the following layer thicknesses was obtained:

Brightness	Layer thickness [μm] j = 3 A/dm ²	Layer thickness [μm] j = 0.5 A/dm ²	Layer thickness coefficient
+	5.40	2.30	2.35

Application Example 10

Comparative Example according to U.S. Pat. No.
4,071,418

[0084] Application Example 1 is repeated with the exception that an electrolyte having the following composition is used:

12.5 g/l	Zn(OH) ₂
120 g/l	NaOH
200 mg/l	1-benzyl-3-carboxy-pyridinium-chloride (N-benzyl nicotinate)
1 g/l	a polymeric additive according to Preparation Example 1 of U.S. Pat. No. 4,071,418 (amount stated is relative to solid content)

A bright deposition with the following layer thicknesses was obtained:

Brightness	Layer thickness [μm] j = 3 A/dm ²	Layer thickness [μm] j = 0.5 A/dm ²	Layer thickness coefficient
+	6.10	3.30	1.85

Application Example 11

[0085] Application Example 1 is repeated with the exception that an electrolyte having the following composition is used:

12.5 g/l	Zn(OH) ₂
120 g/l	NaOH
25 mg/l	1-benzyl-3-carbamoyl-pyridinium-chloride
1 g/l	Mirapol™ WT (rel. 100%)

A very bright deposition with the following layer thicknesses was obtained:

Brightness	Layer thickness [μm] j = 3 A/dm ²	Layer thickness [μm] j = 0.5 A/dm ²	Layer thickness coefficient
+++	4.70	3.60	1.305

Application Example 12

Long-Term Experiment with a 5 Liter Bath for
Determining the Additive Consumption

[0086] In a comparative experiment, electrolytes having the following composition are used:

12.5 g/l	zinc oxide
130 g/l	NaOH
20 g/l	sodium carbonate

-continued

1 g/l	1 g/l of a polymeric additive according to Preparation Example 2.2 of EP 1 114 206 B1 (amount stated is relative to solid content)
25 mg/l	a pyridinium compound (N-benzyl nicotinate or 1-benzyl-3-carbamoyl-pyridinium-chloride)
100 mg/l	3-mercaptoptriazol
50 mg/l	p-hydroxybenzaldehyde (active substance as bisulfite adduct)

[0087] The use of N-benzyl nicotinate corresponds to the teaching of the prior art (Example 14 of EP 1 114 206 B1).

[0088] In order to compare the consumption of additives of the electrolyte according to the invention and the electrolyte according to the prior art, both electrolytes are used in a 5 liter bath as in the Application Examples described above in order to electroplate Norton sheets. In this experiment, a Norton sheet is electroplated at 6 A for 30 minutes, whereafter the layer thickness and the visual appearance are evaluated. When the zinc and nickel contents which could be determined by titration with EDTA solution, were sufficient and the visual appearance of the Norton sheets was good and bright, the electroplating is continued. At intervals of 50 Ah (10 Ah/l), a complete bath test is carried out, consisting of the Hull cell test (as described above) and the determination of the zinc and NaOH concentration. If too little zinc (target value: 10 g/l zinc oxide) or NaOH is present, the missing amount is added. After the brightness has decreased, the corresponding pyridinium compound is replenished.

[0089] Relative to 10,000 Ah, the following additive consumption of pyridinium compounds used as brightening agents was determined:

Entry	Pyridinium compound	Consumption/ 10 kAh	Percent consumption
1	N-benzyl nicotinate (comparison)	20 g	100% (reference)
2	1-benzyl-3-carbamoyl-pyridinium-chloride	3.5 g	17.5%

Application Example 13

[0090] An electrolyte having the following composition is used:

12 g/l	ZnO
9.5 g/l	nickel sulphate hexahydrate
120 g/l	NaOH
30 g/l	tetraethylenepentamine
0.1 g/l	a polymeric additive according to Preparation Example 2.2 of EP 1 114 206 B1 (amount stated is relative to solid content)
50 mg/l	1-benzyl-3-carbamoyl-pyridinium-chloride

[0091] 250 ml of the electrolyte are filled into a Hull cell. A nickel anode is used. The cathode is electroplated at 1 A for 15 minutes. After completion of the electroplating, the metal sheet is rinsed and dried with compressed air. The layer thickness is measured at two points (3 cm from the bottom edge and 2.5 cm from the right- and left-hand edge) at high (3 A/dm²) and low current density (0.5 A/dm²). The measure-

ment of the nickel content is carried out at the same places. The measurement is done by XRF and four points in each position so as to minimize measurement errors. The coating obtained was highly bright.

[0092] The following layer thicknesses and nickel contents were obtained:

Current density [A/dm ²]	Layer thickness [μm]	Ni conc. [%]
3.0	6.7	15.1
0.5	2.6	13.1

Application Example 14

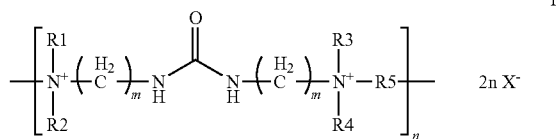
[0093] An electrolyte suitable for deposition of a zinc iron layer was prepared. The electrolyte had the following composition:

12.5 g/l	ZnO
120 g/l	NaOH
50 mg/l	iron (in the form of FeSO ₄ •7 H ₂ O)
25 g/l	sodium gluconate
1 g/l	a polymeric additive according to Preparation Example 2.2 of U.S. Pat. No. 6,652,728 (rel. 100%)
100 mg/l	1-benzyl-3-carbamoyl-pyridinium-chloride

[0094] A Hull cell sheet was coated for 10 minutes at 1 ampere. A very bright deposition is obtained. The Hull cell sheet was rinsed and chromated in a commercially available black chromation for zinc iron layers (Tridur™ black liquid ZnFe, Atotech). The chromated sheet showed good black coloration.

1. Aqueous, alkaline, cyanide-free electrolyte bath for the deposition of zinc and zinc alloy coatings on substrate surfaces, which bath comprises the following components:

- a source of zinc ions and, optionally, a source of further metal ions,
- hydroxide ions,
- a polymer which is soluble in the bath of the general formula I



wherein

m represents an integer of 1 to 5,

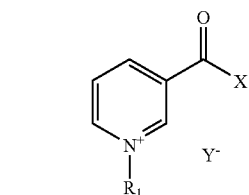
n represents an integer greater than 1,

R1, R2, R3, R4 may be the same or different and each represents a substituted or unsubstituted hydrocarbon residue having 1 to 6 carbon atoms or —CH₂CH₂(OCH₂CH₂)_y—OH, wherein y lies between 0 and 6,

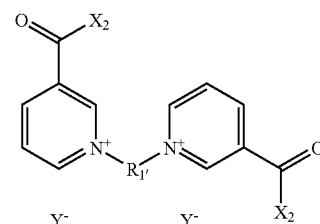
R5 represents (CH₂)_p, wherein p represents an integer of 2 to 12 or a —(CH₂)₂—O—(CH₂)₂— or —(CH₂)₂—O—(CH₂)₂—O—(CH₂)₂— group and

X[−] represents a counter ion, and

d) at least one pyridinium compound of general formula II or III



II



III

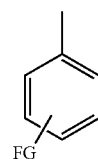
wherein

R₁ represents a substituted or unsubstituted, saturated or unsaturated, aliphatic or araliphatic hydrocarbon residue having 1 to 12 carbon atoms,

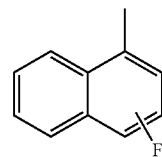
R₁' represents a divalent, substituted or unsubstituted, saturated or unsaturated, aliphatic or araliphatic hydrocarbon residue having 1 to 12 carbon atoms,

X₁ and X₂ represent NR_xR_y, wherein R_x and R_y may be the same or different and represent hydrogen or linear or branched alkyl groups having 1 to 12 carbon atoms, and Y[−] is a counter ion.

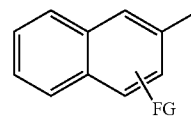
2. Electrolyte bath according to claim 1, wherein R₁ in formula II represents a substituted aryl residue of the following formulae R1a to R1I:



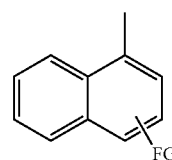
R1a



R1b

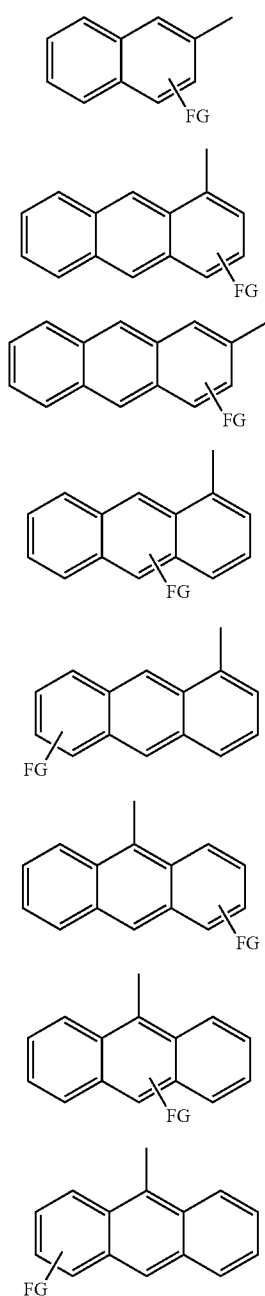


R1c



R1d

-continued



R1e

R1f

R1g

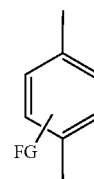
R1h

R1i

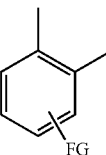
R1j

R1k

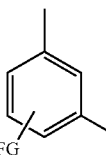
R1l



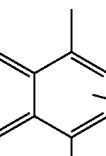
R1'a



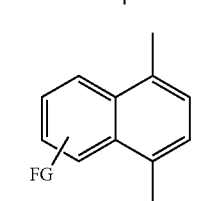
R1'b



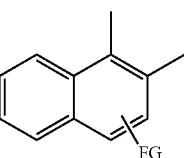
R1'c



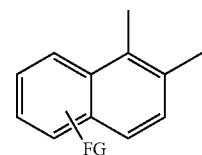
R1'd



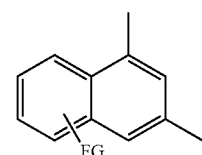
R1'e



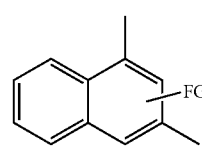
R1'f



R1'g



R1'e

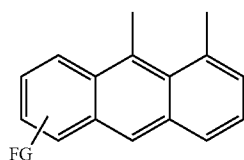
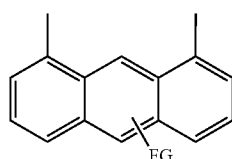
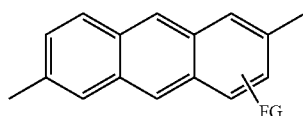
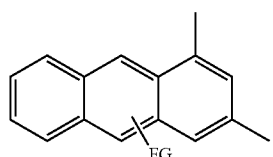
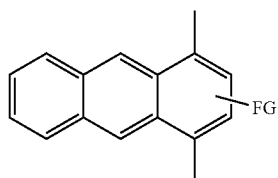
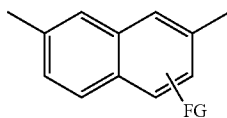
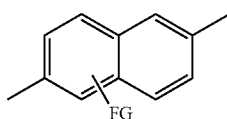
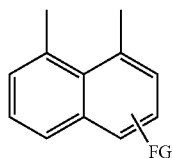
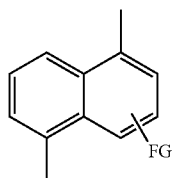


R1'f

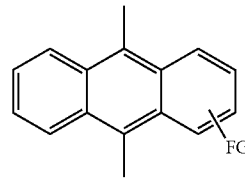
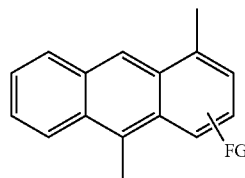
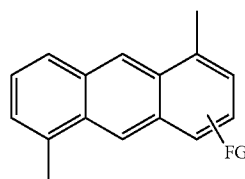
wherein FG represents a residue selected from the group consisting of carboxy, ester, sulfonic acid, carbamoyl, amino, cyano, alkyl, alkoxy, hydroxy, trifluoromethyl, allyl, propargyl-, 4-sulfobutyl, 3-sulfopropyl, 4-carboxybutyl, 3-carboxypropyl residues, hydrogen and halogens, selected from fluorine, chlorine and bromine wherein all rings or individual fused rings may be substituted.

3. Electrolyte bath according to claim 1, wherein R_1' in formula III represents but-2-enyl, but-2-ynyl or an aryl residue of the following formulae R_1' a to R_1' r:

-continued



-continued



wherein FG represents a residue selected from the group consisting of carboxy, ester, sulfonic acid, carbamoyl, amino, cyano, alkyl, alkoxy, trifluoromethyl residues, hydrogen and halogens, selected from fluorine, chlorine and bromine, wherein all rings or individual fused rings may be substituted.

4. Electrolyte bath according to claim 1, wherein R_1 in Formula II and/or R_1' in Formula III is/are bound to the pyridinium residue via a methylene group.

5. Electrolyte bath according to claim 1, wherein Y^- in Formula II or III is a halide or pseudo-halide.

6. Electrolyte bath according to claim 1, wherein the polymer of general formula I which is soluble in the bath is present in an amount of 0.1 to 50 g/l.

7. Electrolyte bath according to claim 6, wherein the polymer of general formula I which is soluble in the bath is present in an amount of 0.25 to 10 g/l.

8. Electrolyte bath according to claim 1, wherein the at least one pyridinium compound of formula II or III is present in an amount of 0.001 to 20 g/l.

9. Electrolyte bath according to claim 8, wherein the at least one pyridinium compound of formula II or III is present in an amount of 0.001 to 10 g/l.

10. Electrolyte bath according to claim 1, containing a combination of pyridinium compounds of formulae II and III.

11. Electrolyte bath according to claim 1, containing a combination of different soluble polymers of general formula I.

12. Electrolyte bath according to claim 1, wherein the source of zinc ions is zinc oxide or zinc hydroxide.

13. Electrolyte bath according to claim 1, wherein the concentration of zinc ions is from 0.1 to 100 g/l.

14. Electrolyte bath according to claim 13, wherein the concentration of zinc ions is from 0.1 to 30 g/l.

15. Electrolyte bath according to claim 1, wherein the further metal ions are cobalt, nickel, manganese and/or iron ions.

16. Electrolyte bath according to claim 15, wherein the zinc is present in an amount of 0.1 to 30 g/l and the cobalt is present in an amount of 10 to 120 mg/l, the nickel is present in an amount of 0.3 to 3 g/l, the manganese is present in an amount of 10 to 100 g/l and/or the iron is present in an amount of 10 to 120 mg/l.

17. Electrolyte bath according to claim 1, containing alkali metal hydroxide as base.

18. Electrolyte bath according to claim 17, wherein the alkali metal hydroxide is lithium hydroxide, sodium hydroxide and/or potassium hydroxide and is present in an amount of 50 to 250 g/l.

19. Electrolyte bath according to claim 1, wherein the pH of the bath is at least 10.

20. Electrolyte bath according to claim 1, wherein the bath does not contain additional brightening agents.

21. Electrolyte bath according to claim 1, containing a complexing agent or a water-softening agent.

22. Electrolyte bath according to claim 21, wherein the complexing agent is a chelate-forming agent.

23. Electrolyte bath according to claim 21, wherein the complexing agent is present in an amount of 2 to 200 g/l.

24. Electrolyte bath according to claim 1, wherein the bath contains a sulfur compound as leveling agent.

25. Electrolyte bath according to claim 24, wherein the leveling agent contains 3-mercapto-1,2,4-triazole and/or thiourea.

26. Electrolyte bath according to claim 24, wherein the sulfur compound is present in an amount of 0.01 to 0.50 g/l.

27. Process for the galvanic deposition of bright and even zinc and zinc alloy coatings, comprising the step of immersing the substrate to be coated into a bath according to claim 1.

28. Process according to claim 27, wherein the bath is operated at a current density of 0.01 to 10 A/dm².

29. Process according to claim 27, wherein the bath is operated at a temperature of 15 to 50° C.

30. Process according to claim 29, wherein the bath is operated at a temperature of 25 to 35° C.

31. Process according to claim 27, wherein the coatings are deposited on a conductive substrate by using a drum electroplating process.

32. Process according to claim 27, wherein the coatings are deposited on a conductive substrate by using a rack electroplating process.

33. Process according to claim 27, wherein a zinc coating is deposited on the substrate.

34. Process according to claim 27, wherein a zinc alloy coating is deposited on the substrate.

35. Process according to claim 34, wherein a coating of a zinc alloy with one or more metals from the group consisting of cobalt, nickel, manganese and/or iron is deposited on the substrate.

* * * * *