

[54] ZINC PLATING PROCESS AND ELECTROLYTES THEREFOR

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Related U.S. Application Data

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[52] U.S. Cl. 204/55 R

[51] Int. Cl.² C25D 3/22

[58] Field of Search 204/55 R, 55 Y, 43 Z, 44

[56] References Cited

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Primary Examiner—G. L. Kaplan
Attorney, Agent, or Firm—Kenneth G. Wheelless;
Robert P. Auber

[57] ABSTRACT

This invention relates to a method of producing bright zinc electrodeposits over a wide current density range, free of "spores" and/or striations, which comprises passing current from an anode to a metal cathode for a time period sufficient to deposit a bright zinc electrodeposit upon said cathode; the current passing through an aqueous bath composition containing at least one zinc compound providing zinc ions for electroplating zinc.

- a. at least one bath soluble surfactant selected from the group consisting of bath soluble polyethers, substituted polyethers, and substituted non-aromatic nitrogen heterocyclic surfactants, and
- b. at least one aromatic, non-carbonyl containing nitrogen heterocyclic compound.

38 Claims, No Drawings

ZINC PLATING PROCESS AND ELECTROLYTES THEREFOR

This application is a divisional application of co-pending application Ser. No. 293,659 filed September 26 1972 and now U.S. Pat. No. 3821,7095

This invention relates to the electrodeposition of bright zinc, and is especially useful for plating from non-cyanide baths. More particularly this invention relates to improved zinc plating bath compositions, to methods of using and preparing such bath compositions and to improved surfaces having bright zinc electrodeposits thereon.

The enactment and enforcement of various environmental protection laws, especially those designed to improve water quality, have made it desirable to significantly reduce or eliminate the discharge of cyanides, phosphates, and a number of metal ions from the effluents of electroplating plants. As a result, non-polluting bright zinc plating processes have been sought as alternatives to the classical zinc cyanide baths.

Alkaline solutions containing complex compounds of zinc and alkaline metal pyrophosphates have been proposed as a replacement for cyanide baths and cyanide processes for the electrodeposition of bright zinc. The electrodeposition of zinc using a pyrophosphate bath, however, may give relatively poor low current density coverage, spore formation, roughness, insufficient brightness, and relatively non-uniform deposits. In addition, passivation of the anodes may produce undesirable precipitates which in turn can clog filter systems and sometimes results in intermittent operation necessitated by frequent changes of filter media.

The use of phosphates may also produce waste disposal problems since phosphates are not easily removed and may promote the growth of undesirable aquatic plant life if discharged into streams. These disposal disadvantages further limit the acceptance of pyrophosphate zinc plating bath compositions in industrial applications.

Non-cyanide zincate zinc plating baths have also been proposed as substitutes for cyanide containing systems. However, the bright plating current density range of these baths is quite limited, making the plating of articles of complex shape difficult, if not impossible. Since the addition of cyanide to these non-cyanide zincate baths greatly improves the bright plate current density range of the deposits, platers tend to add cyanides to their zincate systems, thus negating the non-cyanide feature of the original bath.

Highly acidic zinc plating baths have been known for some time and such baths are cyanide-free. These systems do not produce bright decorative deposits, (in the currently accepted usage of the word "bright"), have extremely poor low current density coverage and find their chief application in the strip line plating of wire and sheet steel using very high but narrow current density ranges. Thus, they are not suited for plating objects of complex shape or for normal decorative, or rust-proofing application.

More recently, neutral, mildly alkaline or mildly acidic non-cyanide zinc plating baths containing large amounts of buffering and complexing agents to stabilize both pH and solubilize the zinc ions at the pH values involved have been employed to overcome the objections of using cyanide-based zinc plating processes. In general these zinc baths consist of an aqueous solu-

tion containing at least one simple zinc salt, (for example zinc sulfate, zinc chloride, zinc acetate), and an ammonium salt (for example an ammonium halide, or ammonium sulfate). The zinc bath may additionally contain an organic zinc complexing agent such as a hydroxy carboxylic acid or salts thereof, ethylenediamine tetraacetic acid or salts thereof, and/or similar materials to prevent the precipitation of zinc from the bath as the insoluble hydroxide at higher values of pH, i.e. pH 5.5 and above. These baths are typically operated in the pH range of about 4 to 8.

Additions of suitable bath soluble surfactants such as polyoxyalkylene compounds to zinc baths of the foregoing type may result in improved throwing power, hardness, and luster of the zinc deposits. A representative bath composition may consist of:

ZnCl ₂	50 g/l
NH ₄ Cl	125 g/l
Citric Acid	60 g/l
NH ₄ OH to adjust the pH to some value between e.g. 4 and 8.	
Suitable bath soluble polyoxyalkylene surfactant	6 g/l

In order to improve and increase the brightness, luster and throwing power of zinc deposits from these baths, certain organic aromatic carbonyl compounds are generally used as brighteners. While these brighteners provide generally satisfactory zinc deposits from freshly prepared zinc baths, the deposits tend to be dull in low current density regions. In addition, because of the nature of the aromatic organic additives used as brighteners, highly objectionable oily decomposition products may form on prolonged bath electrolysis. These oily materials are not soluble in the bath and float on the surface where they adhere to parts as they are placed in and removed from the bath causing pitting problems during the plating cycle, with blotching and non-uniform results in subsequent chromate post-treatment of the zinc deposits. Removal of these oily decomposition products is difficult and troublesome, and as a result zinc electroplating processes of this type have found only limited acceptance in the plating industry.

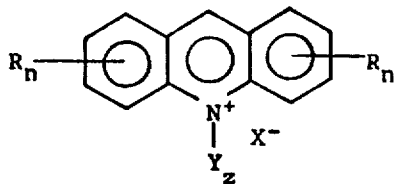
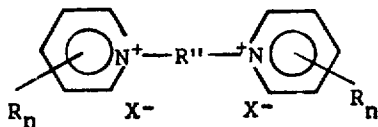
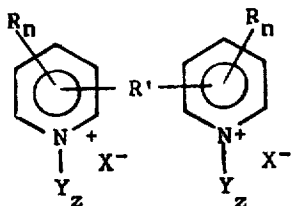
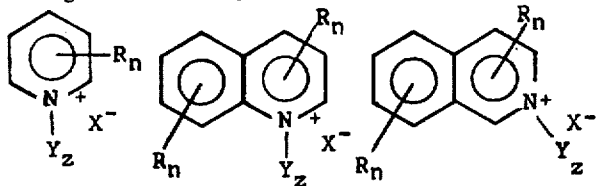
While mildly acidic, neutral, and/or mildly basic zinc plating baths of the type described above have the potential for producing suitable bright zinc deposits, the inclusion in their composition of organic complexing agents such as hydroxy carboxylic acids, and/or salts thereof, ethylenediamine tetraacetic acid and/or salts thereof, as well as other complexing agents makes it extremely difficult and expensive to remove zinc metal ions from these electroplating bath waste effluents. As a result, in the current state of the art of bright zinc electroplating from non-cyanide zinc baths, the use of organic complexing agents is avoided.

The exclusion of organic metal complexing agents from bright zinc electroplating baths has made it possible to effectively and easily remove zinc metal ions from plating plant waste effluents in compliance with anti-pollution laws. However, with the elimination of organic complexing agents it is desirable to operate the zinc bath in the mildly acidic pH range, and it is more difficult to produce satisfactory bright zinc deposits over a wide current density range from these complex-free baths using the previously effective bath additives.

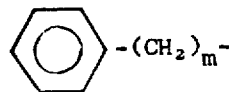
Additionally, the deposits from these baths are generally severely striated and/or covered with spores in the medium and high current density areas. Spores can best be described as very small, discrete, frosty-looking mounds, possibly an unique type of "burnt" deposit, often accompanied by gas pitting, and completely unacceptable in bright zinc deposits.

It is an object of this invention to provide novel processes and compositions for the electrodeposition of bright to brilliant zinc plate, over a wide current density range, especially from mildly acidic, neutral, or mildly alkaline zinc plating baths, which may or may not additionally contain organic complexing agents; said deposits being free of objectionable spores and/or striations. Other objects of the invention will be apparent to those skilled in the art of bright zinc plating upon inspection of the following detailed description.

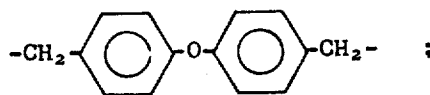
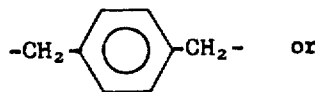
This invention relates to a method of producing bright to brilliant zinc electrodeposits over a wide current density range, free of spores and/or striations, which comprises passing current from an anode to a metal cathode for a time period sufficient to deposit a bright zinc electrodeposit upon said cathode; the current passing through an aqueous bath composition containing at least one zinc compound providing zinc ions for electroplating zinc, a suitable bath-soluble surfactant as a support or carrier and at least one compound selected from the class of compounds consisting of aromatic non-carbonyl nitrogen heterocycles. The following generalized formulae describe typical compounds falling within the scope of this invention:



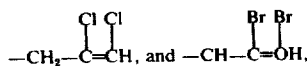
wherein each R is independently hydrogen, alkyl, alkenyl, alkoxy, alkylamine, alkylsulfonic acid and/or salt thereof, sulfonic acid and/or salt thereof, halogen, amine, hydroxyl, mercapto, nitrile, benzyl, or phenylalkyl



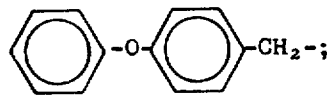
(where m is an integer 0 to 4); n is an integer 0 to 3; R' is a divalent alkylene, divalent alkenylene, secondary amine, or a direct bond between two heterocyclic rings; R'' is a bifunctional radical such as



z is 0 or 1; Y is oxygen, allyl, propargyl, benzyl, an alkoxy group, alkyl sulfonic acid $-(CH_2)_p-SO_3^-$ (where p is an integer of from 1 to 4), an oxyalkylsulfonic acid, quinaldiny, halogenated alkenyl radicals such as



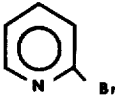
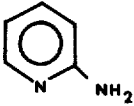
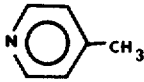
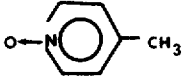
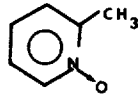
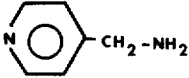
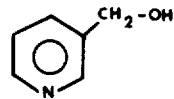
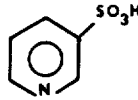
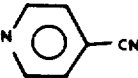

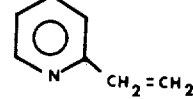
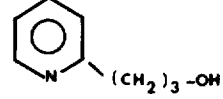
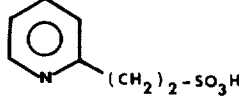
and the radical *p*-phenoxybenzyl



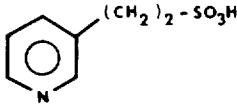
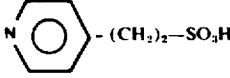
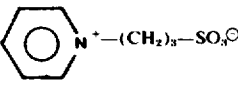
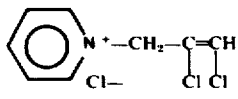
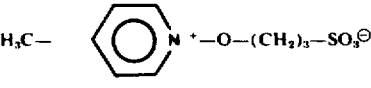
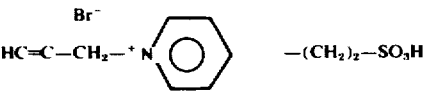
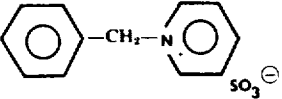
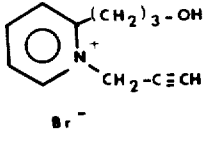
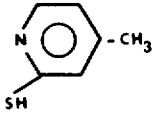
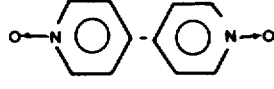
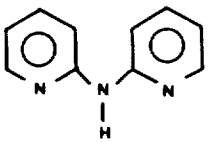
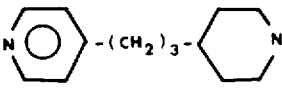
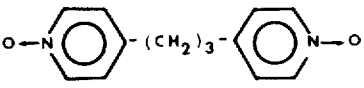
and X^- provides ionic charge neutrality where necessary and represents an anionic radical or the anionic moiety of Y (as for example $-(CH_2)_3-SO_3^-$), or the anionic moiety of R (as for example $-SO_3^-$), except that when Y represents the N-oxide or z is zero X^- is not required; and wherein it is understood that all unsatisfied valences of carbon atoms are attached to hydrogen atoms, and wherein each vertex of the formulae represents a carbon atom.

The following compounds are examples of typical aromatic non-carbonyl nitrogen heterocyclic compounds which may be employed according to this invention and which illustrate the generalized structural formulae given above.

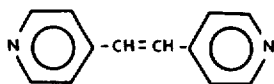
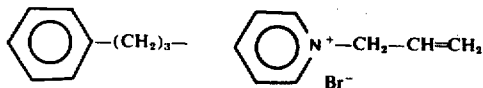
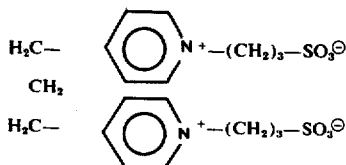
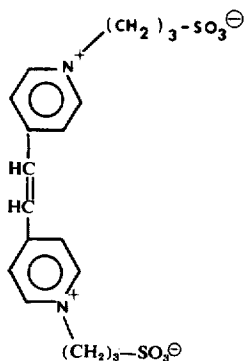
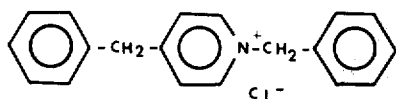
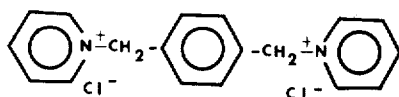
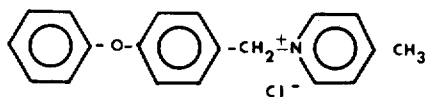
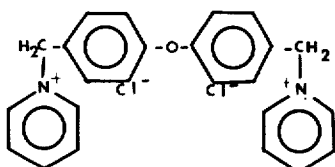
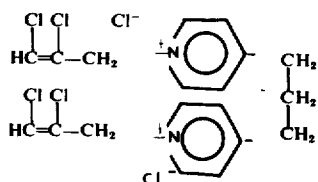
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	2-bromopyridine
	2-aminopyridine
	4-methylpyridine
	4-methylpyridine-N-oxide
	2-picoline-N-oxide
	4-picolyamine
	3-pyridylcarbinol
	3-pyridylsulfonic acid
	4-cyanopyridine
	4-cyanopyridine-N-oxide
	2-vinylpyridine
	2-propanolpyridine
	2-pyridyl-2-ethylsulfonic acid

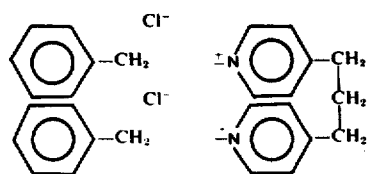
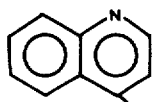
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	3-pyridyl-2-ethylsulfonic
	4-pyridyl-2-ethyl sulfonic acid
	pyridyl-N-propanesulfonic acid betaine
	N-(2,3-dichloro-2-propenyl)-pyridinium chloride
	4-methylpyridyl-N-oxypropanesulfonic acid betaine
	N-propargyl-4-(2-ethylsulfonic acid)-pyridinium bromide
	N-benzyl-3-pyridyl-sulfonic acid betaine
	N-propargyl-2-propanol-pyridinium bromide
	2-mercapto-4-methylpyridine
	4,4'-dipyridyl-N,N'-dioxide
	2,2'-dipyridylamine
	1,3-di-(4,4'-pyridyl)-propane
	1,3-di-(4-pyridyl)-propane N,N' dioxide

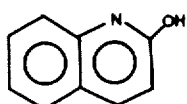
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1,2-di-(4,4'-pyridyl)
etheneN-allyl-4-phenylpropyl-
pyridinium bromide1,3-di-(4,4'-pyridyl-N,N'-
dipropanesulfonic acid
betaine)-propane1,2-di-(4,4'-pyridyl-N,N'-
dipropanesulfonic acid
betaine)-ethene4-benzyl-N-benzylpyrid-
inium chloridep-xylene- α,α' -di-(N,N'-
dipyridinium chloride)4-methyl-N-(4-oxyphenyl-
benzyl)-pyridinium
chloride4,4'-dibenzylether- α,α' -
di-(N,N'-pyridinium
chloride)1,3-di-(N,N'-2,3-dichloro-
2-propenyl-4,4'-pyridin-
ium chloride)-propane

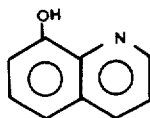
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1,3-di-(N,N'-benzyl-4,4'-
pyridinium chloride)-
propane

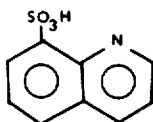
quinoline



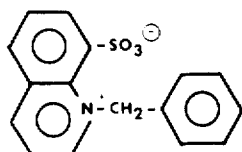
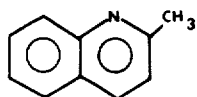
2-quinolinol



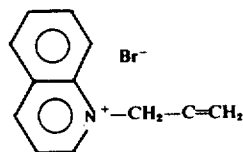
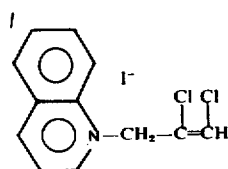
8-quinolinol



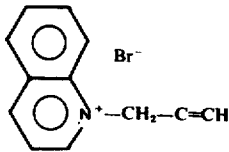
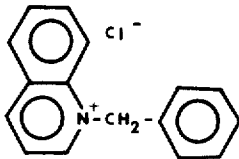
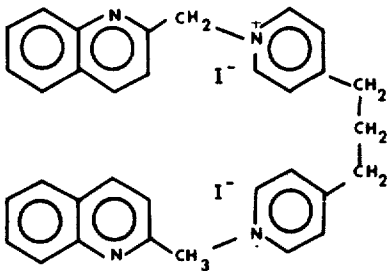
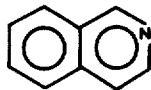
8-quinolinesulfonic acid

N-benzyl-8-quinoline-
sulfonic acid betaine

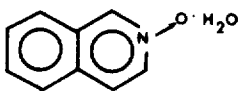
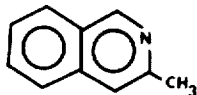
quinaldine

N-allylquinolinium
bromideN-(2,3-dichloro-2-
propenyl)-quinolinium
iodide

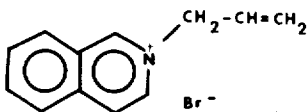
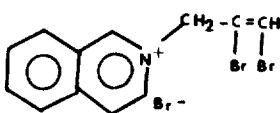
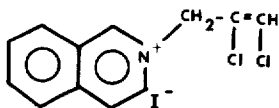
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N-propargylquinolinium
bromideN-benzylquinolinium
chloride1,3-di-(4,4'-pyridyl)-
propane -N,N'-di-
(quimaldinyl iodide)

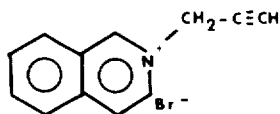
isoquinoline

isoquinoline-N-oxide
monohydrate

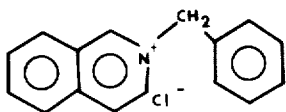
3-methylisoquinoline

N-allylisoquinolinium
bromideN-(2,3-dibromo-2-
propenyl)-isoquino-
linium bromideN-(2,3-dichloro-2-
propenyl)-isoquino-
linium iodide

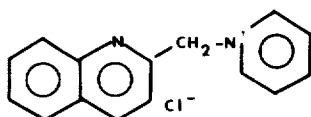
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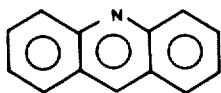
N-propargylisoquinolinium bromide



N-benzylisoquinolinium chloride



N-(quinaldinyl)pyridinium chloride



acridine

Some compounds which have given particularly outstanding results in fulfilling the objectives of this invention are:

4-cyanopyridine
 4-cyanopyridine-N-oxide
 3-pyridylsulfonic acid
 2-mercapto-4-methylpyridine
 1,3-di-(4,4'-pyridyl)-propane
 1,3-di-(4,4'-pyridyl-N,N'-oxide)-propane 4,4'
 p-xylene- α,α' -di-(N,N'-pyridinium chloride)
 N-(2,3-dichloro-2-propenyl)-pyridinium chloride
 N-propargyl-2-(n-propan-3-ol)-pyridinium bromide
 quinoline
 N-allylquinolinium bromide
 N-(2,3-dichloro-2-propenyl)-quinolinium iodide
 isoquinoline
 isoquinoline-N-oxide
 N-allylisoquinolinium bromide
 N-benzylisoquinolinium chloride
 N-(2,3-dichloro-2-propenyl)isoquinolinium iodide
 acridine

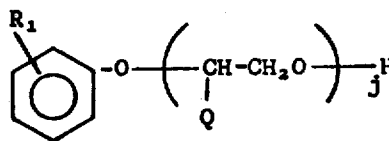
A single compound of mixtures of the nitrogen heterocyclic compounds of this invention may be used in combination with other additives known to those skilled in the art of bright zinc plating to overcome deposit striations and/or spores and to generally increase the brightness and enhance the overall appearance and luster of the zinc deposit.

The amount of heterocyclic nitrogen compound or mixtures thereof employed in the compositions of this invention is an amount sufficient to provide improved bright zinc electroplate when compared with a bath composition which is identical in all respects save that said bath composition contains no heterocyclic nitrogen compounds of the invention herein. The improved bright zinc electroplate deposits of the invention herein are generally characterized as showing improvement in at least one of the properties such as freedom from dullness or skip in lower current density areas, improved ductility, uniformity of lustrous deposit throughout the plating current density range and free-

dom from spores and/or striations. In general, amounts of heterocyclic nitrogen compounds of about 0.001 g/l - 4.0 g/l (preferably about 0.005 - 0.25 g/l) may be used.

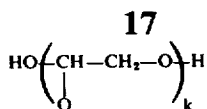
When the aromatic non-carbonyl containing nitrogen heterocyclic compounds of this invention are employed in mildly acidic, neutral, or mildly basic zinc electroplating baths, they are preferably used in combination with carrier and/or support compounds known to those skilled in the art of zinc plating. These carrier and/or support compounds are typically bath soluble polyethers, substituted polyethers and/or substituted non-aromatic nitrogen heterocyclic surfactants.

A bath soluble surfactant which may be employed in amounts of about 1.0-2.5 g/l (preferably about 2-10 g/l) in combination with the nitrogen heterocyclic compounds in amounts of about 0.001 g/l - 4.0 g/l (preferably about 0.005 - 0.25 g/l) may include aromatic ethers of aliphatic polyethers. Preferably the polyether is a polyalkoxylated alkyl phenol. Typical polyalkoxylated alkyl phenols include polyethoxylated alkyl phenols having the formula:



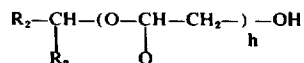
wherein R_1 represents an alkyl group of from 8 to 16 carbon atoms (preferably 8 or 9 carbon atoms) and j is an integer of from 5 to 50 (preferably from about 10 to 30), and Q is hydrogen or methyl.

Other polyethers which may be employed in amounts of about 1.0 - 25 g/l (preferably about 2-10 g/l) in combination with the nitrogen heterocyclic compounds in amounts of about 0.001 - 4.0 g/l (preferably about 0.005 - 0.25 g/l) may include aliphatic polyethers characterized by the following general formula:



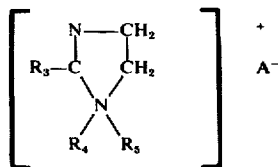
wherein Q represents hydrogen or methyl and k is an integer of from about 7 to 100 (preferably from about 12 to 50).

Other polyethers which may be employed include alkyl polyethers of the general formula:



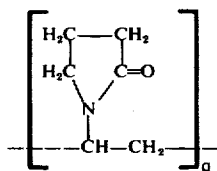
wherein Q represents hydrogen or methyl and R₂ is an alkyl group of from about 5 to 25 carbon atoms and h is an integer from about 10 to 50 (preferably about 12 to 25).

Other bath soluble surfactants which may be employed include quaternary imidazolium compounds with the following generalized structural formula:



where R₃ is a saturated or unsaturated fatty acid radical, R₄ is an alkyl carboxylate radical or alkali metal carboxylate, R₅ is an alkyl alcohol, alkyl alcoholate, or ethoxylated alkyl carboxylic acid or alkalie salt thereof, and A⁻ is a hydroxyl ion or long chain alkyl sulfate or sulfamate anion.

Other surfactants which may be employed in amounts of about 1.0 - 25 g/l (preferably about 2 to 10 g/l) in combination with the nitrogen heterocyclic compounds in amounts of about 0.001 - 4.0 g/l (preferably about 0.005 - 0.25 g/l) include polyvinylpyrrolidone polymers characterized by the following general formula:



where q is an integer of from about 50 to 5000 (preferably from about 90 to 3500).

The nitrogen heterocyclic compounds and the polyether compounds used in combination in the novel bright zinc electroplating baths of the invention may contain inert substituents. By an inert substituent as the term is used herein is meant any bath compatible group which does not destroy, reduce, interfere with, or hinder the formation of the bright zinc electrodeposits described herein. Typical examples of inert substituents include the halogens (chloride, bromide, iodide, and fluoride); hydroxy groups, alkoxy groups (such as methoxy, ethoxy, propoxy, etc.), alkyl groups, sulfate, etc.

According to a particular aspect of the invention, a mixture of the nitrogen heterocyclic compounds and the carrier and/or support compounds (preferably a polyether) may be employed in combination with other additives. Examples of such cooperating mixtures in-

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clude a 50:1 (parts by weight) combination of the reaction products of nonyl phenol with about 15 moles of ethylene oxide and a nitrogen-containing heterocyclic compound. Other suitable weight ratios of carrier and/or support compounds (polyether) and nitrogen-containing heterocyclic compounds include weight ratios of about 100:1 to 1/2:1, respectively. Mixtures of nitrogen heterocyclic compounds may also be used and wherever mixtures of nitrogen heterocyclic compounds are employed, the weight ratios referred to herein refer to the total weight of all of the nitrogen heterocyclic compounds combined.

The basis metal onto which the bright zinc deposits of this invention may be applied may include ferrous metals such as steel and cast iron; copper including its alloys such as brass, bronze, etc.; die cast metals which may bear a plate of another metal such as copper; thin coatings, e.g. of silver, nickel, or copper, on a non-conductive article (such as a rigid or flexible plastic) which coating may be applied by chemical reductive techniques, such as electroless plating, etc.

According to another aspect of the invention the preferred operating conditions, such as pH, temperature, and current density may vary depending upon the particular bath composition and the nature of the article receiving the layer of bright zinc electrodeposit. In general, good, bright zinc electrodeposits may be obtained within a specific range of operating conditions. For example, in mildly acid, neutral, or mildly basic zinc baths, when the pH is within the desired range (i.e. about 1.0 - 10.0, preferably about 4.0 - 8.0) a zinc electrodeposit may attain maximum brightness and the current efficiency may also be optimized.

The bright zinc electroplating processes using the compositions of the invention may be carried out at temperatures of about 10°C. - 60°C. (preferably 15°C. - 35°C.) either with or without agitation. Using average current densities of 0.5 - 5.0 amperes per square decimeter (ASD), bright zinc electrodeposits having average thicknesses of 0.25 - 25 microns may be obtained using plating times which may average 0.5 - 120 minutes.

If necessary, agitation of the plating bath composition may be provided either by mechanical movement of the article being plated or by solution agitation during the electrodeposition. Such agitation may permit the use of high plating current densities on the article being plated.

During the plating operation, it is desirable to keep metallic contaminants at very low concentration levels in order to insure a bright zinc electrodeposit. Such contamination from metal ions, (such as cadmium, copper, iron, and lead) may be reduced or eliminated through conventional purification methods. Other types of contaminants (such as organic contaminants) may also be eliminated or reduced by circulation of the zinc electroplating solution through a suitable filter media such as activated carbon or types of ion exchange or absorption media.

Some of the nitrogen heterocyclic compounds of this invention may have only limited solubility in aqueous solutions. In order to introduce the required amount of these materials into the plating bath, it is most advantageous to first dissolve the appropriate nitrogen heterocyclic compounds in a suitable bath soluble solvent. Such solvents include methanol, ethanol, isopropanol, ethylene glycol-monoethyl ether (i.e., cellosolve), acetone, etc. A concentration of about 25 to 50 g/l of the

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nitrogen heterocyclic compounds in a suitable solvent provides a satisfactory stock solution for addition to the plating bath. In this manner the nitrogen heterocyclic compounds of this invention can be easily added to the plating solution while obtaining rapid dispersion and optimum miscibility.

The following examples are submitted for the purpose of illustration only, so that those skilled in the art of zinc plating may better understand the operation of the invention. These examples are not to be construed as limiting the scope of the invention in any way.

EXAMPLE I

A four liter aqueous bright zinc electroplating bath composition containing the following ingredients in the amounts indicated was prepared:

ZnCl ₂	40 g/l
NH ₄ Cl	125 g/l
citric acid monohydrate	75 g/l
NH ₄ OH to give a pH of	4.8
Reaction product of nonyl-phenol and 15 moles of ethylene oxide	4 g/l
3-pyridylsulfonic acid	0.3 g/l

Using mild cathode rod agitation, parts were plated in the above bath at an average current density of about 2.5 asd. Excellent, uniformly bright deposits were obtained which easily accepted a subsequent clear chromate conversion coating.

EXAMPLE II

An aqueous bright zinc electroplating bath composition was prepared using the following ingredients in the amounts indicated:

ZnCl ₂	32 g/l
NH ₄ Cl	200 g/l
pH	5
Reaction product of a mixture of linear secondary alcohols exhibiting 11 to 16 carbon atoms with 12 moles of ethylene oxide	4 g/l
2-mercapto-4-methylpyridine	0.04 g/l
N-(2,3-dichloro-2-propenyl)-isoquinolinium iodide	0.025 g/l

This bath composition was operated in a 267 ml Hull cell at room temperature, using 1 ampere cell current, a plating time of 5 minutes, mild agitation provided by a small magnetic stirrer, buffed brass cathodes and a sheet zinc anode. The resultant zinc deposit was bright across the entire current density range of the panel (0-6.0 asd.) and was free of high current density spores and/or striations.

EXAMPLE III

An aqueous bright zinc electroplating bath composition was prepared using the following ingredients in the amounts indicated:

ZnCl ₂	40 g/l
NH ₄ Cl	125 g/l
citric acid monohydrate	75
NH ₄ OH to give pH	4.5
Reaction product of nonyl-phenol and 15 moles of ethylene oxide	4 g/l
3-pyridyl-2-ethylsulfonic acid	0.4 g/l
4-pyridyl-2-ethylsulfonic	

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-continued

acid 0.4 g/l

Using a 267 ml Hull cell and the operating procedure given in Example II, the resulting zinc deposit was brilliant in the high current density areas, very bright in the medium current density areas and was bright in the low current density areas.

EXAMPLE IV

An aqueous bright zinc electroplating bath composition was prepared using the following ingredients in the amounts indicated:

ZnCl ₂	32 g/l
NH ₄ Cl	200 g/l
pH	4.8
Reaction product of nonyl-phenol and 15 moles of ethylene oxide	4 g/l
Acridine	0.05 g/l
4-cyanopyridine-N-oxide	0.4 g/l

Using a 267 ml Hull cell and the operating procedure given in Example II, the resulting zinc deposit was bright across the entire current density range of the test panel, and was also free of spores and/or striations.

EXAMPLE V

An aqueous bright zinc electroplating bath composition was prepared using the following ingredients in the amounts indicated:

ZnCl ₂	40 g/l
NH ₄ Cl	125 g/l
citric acid monohydrate	75 g/l
NH ₄ OH sufficient to give pH	4.5
Reaction product of nonyl-phenol and 15 moles of ethylene oxide	4 g/l
1,2-di-(4,4'-pyridyl)-ethene	0.04 g/l
N-(2,3-dichloro-2-propenyl)-isoquinolinium iodide	0.01 g/l

Using a 267 ml Hull cell and the operating conditions given in Example II, the resulting zinc deposit was uniformly bright, spore free and generally excellent across the entire current density range of the test panel.

EXAMPLE VI

An aqueous bright zinc electroplating bath composition was prepared using the following ingredients in the amounts indicated:

ZnCl ₂	40 g/l
NH ₄ Cl	125 g/l
citric acid monohydrate	75 g/l
NH ₄ OH sufficient to give pH	7.5
Reaction product of nonyl-phenol and 15 moles of ethylene oxide	8 g/l
N-benzylisoquinolinium chloride	0.025 g/l

Using a 267 ml Hull cell and the operating conditions given in Example II, the resulting zinc deposit was bright and free of spores across the entire current density range of the test panel.

EXAMPLE VII

A four liter aqueous bright zinc electroplating bath composition containing the following ingredients in the amounts indicated was prepared:

ZnCl ₂	40	g/l
NH ₄ Cl	125	g/l
citric acid monohydrate	75	g/l
NH ₄ OH to adjust pH	4.5	
Reaction product of nonyl-phenol and 15 moles of ethylene oxide	4	g/l
1,3-(4,4'-dipyridyl)-propane-N,N'-dioxide	0.4	g/l
N-(2,3-dichloro-2-propenyl)-isoquinolinium iodide	0.01	g/l

A large number of parts were plated from this bath at average current densities ranging up to 6.0 asd. The resulting deposits were consistently brilliant and free of any haze, spores or striations. The deposits were of such a degree of brightness as plated that even a subsequent bright chromate conversion coating did not significantly increase the brightness further, although the conversion coating does retard eventual tarnishing and dulling due to normal corrosion.

EXAMPLE VIII

An aqueous bright zinc electroplating bath composition was prepared using the following ingredients in the amounts indicated:

ZnCl ₂	32	g/l
NH ₄ Cl	200	g/l
pH as prepared	4.5	
Quaternary imidazolium compound sold as "Miranol C2M-SF" by the Miranol Chemical Company, Inc.	20	g/l
N-(2,2-dichloro-2-propenyl)-isoquinolinium iodide	0.025	g/l

Using a 267 ml Hull cell and the operating conditions given in Example II, the resulting zinc deposit was uniformly brilliant across the entire current density range of the test panel and was free of spores and/or striations.

EXAMPLE IX

A four liter aqueous bright zinc electroplating bath composition containing the following ingredients in the amounts indicated was prepared:

ZnCl ₂	32	g/l
NH ₄ Cl	200	g/l
pH	4.8	
Reaction product of nonyl-phenol and 15 moles of ethylene oxide	4	g/l
Polyvinylpyrrolidone (M. wt. avg. 40,000)	2	g/l
N-(2,3-dichloro-2-propenyl)-isoquinolinium iodide	0.02	g/l

Using a small plexiglass, horizontal, hexagonal plating barrel, 12.5 cm. long by 10 cm. diameter, rotating at about 5 rpm, a large number of barrel loads of steel nails (approximately 1000 sq. cm. surface area per load) were plated in the above bath composition at 10 to 20 amperes cell current for 30 minutes. The resulting zinc deposits were brilliant and lustrous as plated, free of any haziness, spores and/or striations. The deposits were subsequently rinsed and given a clear chromate conversion coating to improve their corrosion resistance as is normal in the zinc plating industry.

EXAMPLE X

A four liter aqueous bright zinc electroplating bath composition was prepared using the following ingredients in the amounts indicated:

ZnCl ₂	32	g/l
NH ₄ Cl	200	g/l
pH	4.8	
Polyvinylpyrrolidone (M. wt. avg. 40,000)	2	g/l
Reaction product of nonyl-phenol and 15 moles of ethylene oxide	4	g/l
N-allylisoquinolinium bromide	0.025	g/l

A large number of parts were rack plated in this bath using cathode rod agitation of about 7 meters/min. and an average current density of about 2.0 to 3.0 asd. Plating time ranged from about 30 minutes to 2 hours. Excellent, uniformly brilliant, lustrous zinc deposits, free of haziness, spores or striations were consistently obtained from this system.

EXAMPLE XI

A four liter aqueous bright zinc electroplating bath composition containing the following ingredients in the amounts indicated was prepared:

ZnCl ₂	32	g/l
NH ₄ Cl	200	g/l
pH	4.8	
Reaction product of a mixture of linear secondary alcohols exhibiting 11 to 16 carbon atoms with 12 moles of ethylene oxide	4	g/l
Polyvinylpyrrolidone	2	g/l
N-benzylisoquinolinium chloride	0.01	g/l

A number of parts were plated in this bath and the resulting deposits were brilliant, lustrous and free of haze, spores or striations. The average current densities were about 2.0 to 3.0 asd.

EXAMPLE XII

A four liter aqueous bright zinc electroplating bath composition containing the following ingredients in the indicated amounts was prepared:

ZnCl ₂	40	g/l
NH ₄ Cl	125	g/l
citric acid monohydrate	75	g/l
NH ₄ OH sufficient to give pH	4.5	
Reaction product of 1 mole nonylphenol and 15 moles ethylene oxide	4	g/l
4-picolylamine	0.2	g/l
N-(2,3-dichloro-2-propenyl)-isoquinolinium iodide	0.01	g/l

A number of parts were plated in the above bath at average current densities ranging from about 1.2 to 3.6 amp. per sq. decimeter. After plating, the parts were water rinsed and given a clear chromate conversion coating as is the normal practice in the zinc plating industry. The resulting zinc deposits were uniformly bright and lustrous.

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EXAMPLE XIII

An aqueous bright zinc electroplating bath composition was prepared using the following ingredients in the amounts indicated:

Zn(SO ₃ NH ₂) ₂	28	g/l
NH ₄ SO ₃ NH ₂	185	g/l
NH ₄ OH sufficient to give pH	4.5	
Reaction product of nonylphenol and 15 moles of ethylene oxide	4	g/l
Polyvinylpyrrolidone (Molecular weight avg. 40,000)	2	g/l
N-(2,3-dichloro-2-propenyl)-isoquinolinium iodide	0.025	g/l

Using a 267 ml Hull cell and the operating conditions given in Example II, the resulting zinc deposit was uniformly bright across the entire test panel and was free of spores and/or striations.

EXAMPLE XIV

An aqueous bright zinc electroplating bath composition was prepared using the following ingredients in the amounts listed:

ZnSO ₄ ·7H ₂ O	100	g/l
NH ₄ Cl	100	g/l
Citric acid monohydrate	100	g/l
NH ₄ OH sufficient to give pH	8.0	
Reaction product of nonylphenol and 15 moles of ethylene oxide	4	g/l
Isoquinoline-N-oxide monohydrate	0.025	g/l

Using a 267 ml Hull cell and the operating conditions given in Example II, the resulting zinc deposit was lustrous and bright as well as free of striations or spores across the entire current density range of the test panel.

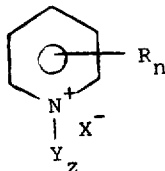
Although this invention has been illustrated by reference to specific embodiments, modifications thereof which are clearly within the scope of the invention will be apparent to those skilled-in-the-art.

I claim:

1. A method of producing bright, or brilliant zinc electrodeposits free of spores and/or striations over a wide current density range which comprises passing current from an anode to a metal cathode through an aqueous bath composition having a pH of 1.0 to 10.0 and containing at least one zinc compound providing zinc ions for electroplating zinc,

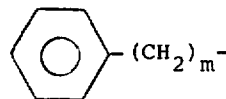
a. 1.0 gram per liter to 25 grams per liter of at least one bath soluble surfactant selected from the group consisting of bath soluble polyethers, substituted polyethers; and

b. 0.001 gram per liter to 4.0 grams per liter of at least one aromatic, non-carbonyl, non-nitrile, nitrogen-containing heterocyclic compound of the formula



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wherein each R is independently hydrogen, alkyl, alkenyl, alkoxy, alkylamino, alkylsulfonic acid or salts thereof, sulfonic acid or salts thereof, halogen amino, hydroxyl, mercapto, benzyl, or phenylalkyl



(where m is an integer 0 to 4); n is an integer 0 to 3; z is 0 or 1; Y is oxygen, allyl, propargyl, benzyl, an alkoxy group, alkyl sulfonic acid $-(CH_2)_p-SO_3^-$ (where p is an integer of from 1 to 4), an oxyalkylsulfonic acid, quinaldiny, p-phenoxybenzyl or a halogenated alkenyl radical in the absence of carbonyl and nitrile groups and X⁻ represents an anionic radical or the anionic moiety of Y or R provided that when Y is N-oxide X⁻ is absent.

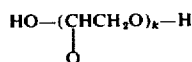
2. The method as claimed in claim 1 wherein at least one nitrogen-containing heterocyclic compound is N-(2,3-dichloro-2-propenyl)-pyridinium chloride.

3. The method as claimed in claim 1 wherein at least one nitrogen-containing heterocyclic compound is N-propargyl-2-(n-propan-3-ol)-pyridinium bromide.

4. The method as claimed in claim 1 wherein at least one nitrogen-containing heterocyclic compound is 2-mercapto-4-methylpyridine.

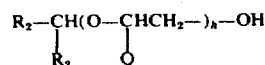
5. The method as claimed in claim 1 wherein at least one nitrogen-containing heterocyclic compound is 3-pyridylsulfonic acid.

6. The method as claimed in claim 1 wherein at least one bath-soluble surfactant is a polyether of the formula



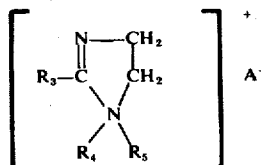
wherein Q is hydrogen or a methyl group and k is an integer of about 7-100.

7. The method as claimed in claim 1 wherein at least one bath-soluble surfactant is a polyether of the formula



wherein Q is hydrogen or methyl, R₂ is alkyl of from 5 to 25 carbon atoms, and h is an integer of from 10 to 50.

8. The method as claimed in claim 1 wherein at least one bath-soluble surfactant is a quaternary imidazolinium of the formula:



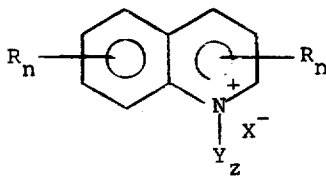
wherein R₃ is a saturated or unsaturated fatty acid radical, R₄ is an alkyl carboxylate or alkali metal carboxylate, R₅ is selected from the group consisting of alkyl alcoholate, alkyl alcohol, ethoxylated alkyl carboxylic

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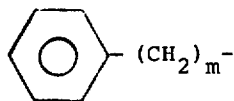
acid and alkali metal salts of ethoxylated alkyl carboxylic acids, and A^- is a hydroxyl ion or long chain alkyl sulfate or sulfamate anion.

9. A method of producing bright, or brilliant zinc electrodeposits free of spores and/or striations over a wide current density range which comprises passing current from an anode to a metal cathode through an aqueous bath composition having a pH of 1.0 to 10.0 and containing at least one zinc compound providing zinc ions for electroplating zinc,

- a. 1.0 gram per liter to 25 grams per liter of at least one bath soluble surfactant selected from the group consisting of bath soluble polyethers, substituted polyethers, and substituted non-aromatic nitrogen heterocyclic surfactants; and
- b. 0.001 gram per liter to 4.0 grams per liter of at least one aromatic, non-carbonyl, non-nitrile, nitrogen-containing heterocyclic [is] compound of the formula



wherein each R is independently hydrogen, alkyl, alkenyl, alkoxy, alkylamino, alkylsulfonic acid or salts thereof, sulfonic acid or salts thereof, halogen, amino, hydroxyl, mercapto, benzyl, or phenylalkyl



(where m is an integer 0 to 4); n is an integer 0 to 3; z is 0 or 1; Y is oxygen, allyl, propargyl, benzyl, an alkoxy group, alkyl sulfonic acid $-(CH_2)_p-SO_3^-$ (where p is an integer of from 1 to 4), an oxyalkylsulfonic acid, quinaldiny, p-phenoxybenzyl, or a halogenated alkenyl radical and X^- represents an anionic radical or the anionic moiety of Y or R provided that when Y is N-oxide X^- is absent.

10. The method as claimed in claim 9 wherein at least one nitrogen-containing heterocyclic compound is quinoline.

11. The method as claimed in claim 9 wherein at least one nitrogen-containing heterocyclic compound is N-allylquinolinium bromide.

12. The method as claimed in claim 9 wherein at least one nitrogen-containing heterocyclic compound is N-(2,3-dichloro-2-propenyl)-quinolinium iodide.

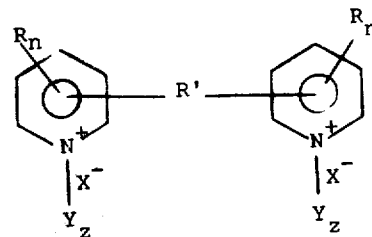
13. A method of producing bright, or brilliant zinc electrodeposits free of spores and/or striations over a wide current density range which comprises passing current from an anode to a metal cathode through an aqueous bath composition having a pH of 1.0 to 10.0 and containing at least one zinc compound providing zinc ions for electroplating zinc,

- a. 1.0 gram per liter to 25 grams per liter of at least one bath soluble surfactant selected from the group consisting of bath soluble polyethers, substituted

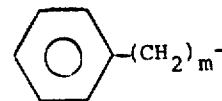
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polyethers, and substituted non-aromatic nitrogen heterocyclic surfactants; and

- b. 0.001 gram per liter to 4.0 grams per liter of at least one aromatic, non-carbonyl, non-nitrile, nitrogen-containing heterocyclic compound of the formula



wherein each R is independently hydrogen, alkyl, alkenyl, alkoxy, alkylamino, alkylsulfonic acid or salts thereof, sulfonic acid or salts thereof, halogen, amino, hydroxyl, mercapto, benzyl, or phenylalkyl



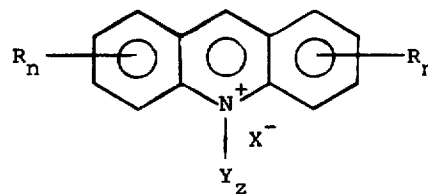
(where m is an integer 0 to 4); n is an integer 0 to 3; R' is a divalent alkylene, divalent alkenylene, secondary amine, or a direct bond between two heterocyclic rings; z is 0 or 1; Y is oxygen, allyl, propargyl, benzyl, an alkoxy group, alkyl sulfonic acid $-(CH_2)_p-SO_3^-$ (where p is an integer of from 1 to 4), an oxyalkylsulfonic acid, quinaldiny, p-phenoxybenzyl or a halogenated alkenyl radical and X^- represents an anionic radical or the anionic moiety of Y or R provided that when Y is N-oxide X^- is absent.

14. The method as claimed in claim 13 wherein at least one nitrogen-containing heterocyclic compound is 1,3-di-(4,4'-pyridyl-N,N'-oxide)-n-propane.

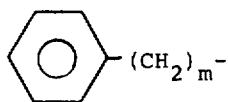
15. The method as claimed in claim 13 wherein at least one nitrogen-containing heterocyclic compound is 1,3-di-(4,4'-pyridyl)propane.

16. A method of producing bright, or brilliant zinc electrodeposits free of spores and/or striations over a wide current density range which comprises passing current from an anode to a metal cathode through an aqueous bath composition having a pH of 1.0 to 10.0 and containing at least one zinc compound providing zinc ions for electroplating zinc,

- a. 1.0 gram per liter to 25 grams per liter of at least one bath soluble surfactant selected from the group consisting of bath soluble polyethers, substituted polyethers, and substituted non-aromatic nitrogen heterocyclic surfactants; and
- b. 0.001 gram per liter to 4.0 grams per liter of at least one aromatic, non-carbonyl, non-nitrile, nitrogen-containing heterocyclic compound of the formula



wherein each R is independently hydrogen, alkyl, alkenyl, alkoxy, alkylamino, alkylsulfonic acid or salts thereof, sulfonic acid or salts thereof, halogen, amino, hydroxyl, mercapto, benzyl, or phenylalkyl

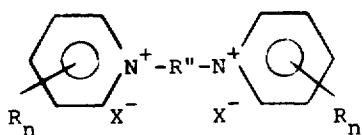


(where m is an integer 0 to 4); n is an integer 0 to 3; z is 0 or 1; Y is oxygen, allyl, propargyl, benzyl, an alkoxy group, alkyl sulfonic acid $-(CH_2)_p-SO_3^-$ (where p is an integer of from 1 to 4), an oxyalkylsulfonic acid, quinaldiny, p-phenoxybenzyl or a halogenated alkenyl radical and X^- represents an anionic radical or the anionic moiety of Y or R provided that when Y is N-oxide X^- is absent.

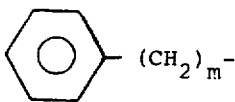
17. The method as claimed in claim 16 wherein at least one nitrogen-containing heterocyclic compound is acridine.

18. A method of producing bright, or brilliant zinc electrodeposits free of spores and/or striations over a wide current density range which comprises passing current from an anode to a metal cathode through an aqueous bath composition having a pH of 1.0 to 10.0 and containing at least one zinc compound providing zinc ions for electroplating zinc,

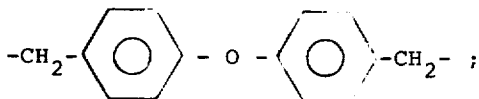
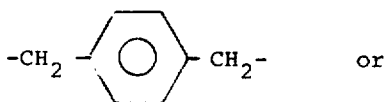
- a. 1.0 gram per liter to 25 grams per liter of at least one bath soluble surfactant selected from the group consisting of bath soluble polyethers, substituted polyethers, and substituted non-aromatic nitrogen heterocyclic surfactants; and
- b. 0.001 gram per liter to 4.0 grams per liter of at least one aromatic, non-carbonyl, non-nitrile, nitrogen-containing heterocyclic compound of the formula



wherein each R is independently hydrogen, alkyl, alkenyl, alkoxy, alkylamino, alkylsulfonic acid or salts thereof, sulfonic acid or salts thereof, halogen, amino, hydroxyl, mercapto, benzyl, or phenylalkyl



(where m is an integer 0 to 4); n is an integer 0 to 3; R'' is a bifunctional radical

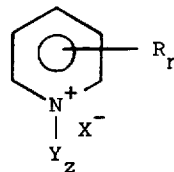


and X^- represents an anionic radical or the anionic moiety of R.

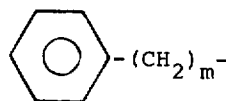
19. The method as claimed in claim 18 wherein at least one nitrogen-containing heterocyclic compound is p-xylene- α,α' -di-(N,N'-pyridinium chloride).

20. A composition for providing bright, or brilliant zinc electrodeposits free of spores and/or striations over a wide current density range which comprises an aqueous bath composition having a pH of 1.0 to 10.0 and containing at least one zinc compound providing zinc ions for electroplating zinc,

- a. 1.0 gram per liter to 25 grams per liter of at least one bath soluble surfactant selected from the group consisting of bath soluble polyethers, substituted polyethers; and
- b. 0.001 gram per liter to 4.0 grams per liter of at least one aromatic, non-carbonyl, non-nitrile, nitrogen-containing heterocyclic compound of the formula:



wherein each R is independently hydrogen, alkyl, alkenyl, alkoxy, alkylamino, alkylsulfonic acid or salts thereof, sulfonic acid or salts thereof, halogen, amino, hydroxyl, mercapto, benzyl, or phenylalkyl



(where m is an integer 0 to 4); n is an integer 0 to 3; z is 0 or 1; Y is oxygen, allyl, propargyl, benzyl, an alkoxy group, alkyl sulfonic acid $-(CH_2)_p-SO_3^-$ (where p is an integer of from 1 to 4), an oxyalkylsulfonic acid, quinaldiny, p-phenoxybenzyl or a halogenated alkenyl radical in the absence of carbonyl and nitrile groups and X^- represents an anionic radical or the anionic moiety of Y or R provided that when Y is N-oxide X^- is absent.

21. A composition as claimed in claim 20 wherein at least one nitrogen-containing heterocyclic compound is N-(2,3-dichloro-2-propenyl)-pyridinium chloride.

22. A composition as claimed in claim 20 wherein at least one nitrogen-containing heterocyclic compound is N-propargyl-2-(n-propan-3-ol)-pyridinium bromide.

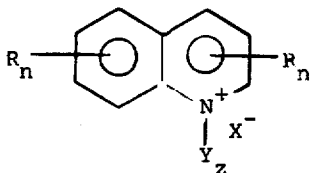
23. A composition as claimed in claim 20 wherein at least one nitrogen-containing heterocyclic compound is 2-mercapto-4-methylpyridine.

24. A composition as claimed in claim 20 wherein at least one nitrogen-containing heterocyclic compound is 3-pyridylsulfonic acid.

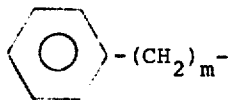
25. A composition for providing bright, or brilliant zinc electrodeposits free of "spores" and/or striations over a wide current density range which comprises an aqueous bath composition having a pH of 1.0 to 10.0 and containing at least one zinc compound providing zinc ions for electroplating zinc,

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- a. 1.0 gram per liter to 25 grams per liter of at least one bath soluble surfactant selected from the group consisting of bath soluble polyethers, substituted polyethers, and substituted non-aromatic nitrogen heterocyclic surfactants; and
- b. 0.001 gram per liter to 4.0 grams per liter of at least one aromatic, non-carbonyl, non-nitrile, nitrogen-containing heterocyclic compound of the formula:



wherein each R is independently hydrogen, alkyl, alkenyl, alkoxy, alkylamino, alkylsulfonic acid or salts thereof, sulfonic acid or salts thereof, halogen, amino, hydroxyl, mercapto, benzyl, or phenylalkyl



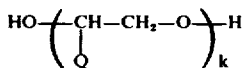
(where m is an integer 0 to 4); n is an integer 0 to 3; z is 0 or 1; Y is oxygen, allyl, propargyl, benzyl, an alkoxy group, alkyl sulfonic acid $-(CH_2)_p-SO_3^-$ (where p is an integer of from 1 to 4), an oxyalkylsulfonic acid, quinaldiny, p-phenoxybenzyl, or a halogenated alkenyl radical and X^- represents an anionic radical or the anionic moiety of Y or R provided that when Y is N-oxide X^- is absent.

26. A composition as claimed in claim 25 wherein at least one nitrogen-containing heterocyclic compound is quinoline.

27. A composition as claimed in claim 25 wherein at least one nitrogen-containing heterocyclic compound is N-allylquinolinium bromide.

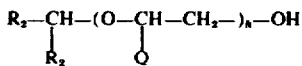
28. A composition as claimed in claim 25 wherein at least one nitrogen-containing heterocyclic compound is N-(2,3-dichloro-2-propenyl)-quinolinium iodide.

29. A composition as claimed in claim 25 wherein at least one bath-soluble surfactant is a polyether of the formula:



wherein Q is hydrogen or a methyl group and k is an integer of about 7-100.

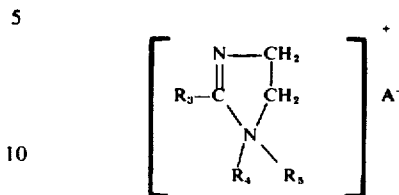
30. A composition as claimed in claim 25 wherein at least one bath-soluble surfactant is a polyether of the formula:



wherein Q is hydrogen or methyl, R_2 is alkyl of from 5 to 25 carbon atoms, and h is an integer of from 10 to 50.

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31. A composition as claimed in claim 25 wherein at least one bath-soluble surfactant is a quaternary imidazolium of the formula

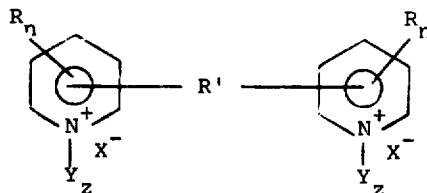


wherein R_3 is a saturated or unsaturated fatty acid radical, R_4 is an alkyl carboxylate or alkali metal carboxylate, R_5 is selected from the group consisting of alkyl alcoholate, alkyl alcohol, ethoxylated alkyl carboxylic acid and alkali metal salts of ethoxylated alkyl carboxylic acids, and A^- is a hydroxyl ion or long chain alkyl sulfate or sulfamate anion.

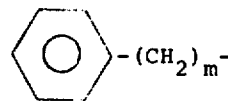
32. A composition for providing bright, or brilliant zinc electrodeposits free of spores and/or striations over a wide current density range which comprises an aqueous bath composition having a pH of 1.0 to 10.0 and containing at least one zinc compound providing zinc ions for electroplating zinc,

a. 1.0 gram per liter to 25 grams per liter of at least one bath soluble surfactant selected from the group consisting of bath soluble polyethers, substituted polyethers, and substituted non-aromatic nitrogen heterocyclic surfactants; and

b. 0.001 gram per liter to 4.0 grams per liter of at least one aromatic, non-carbonyl, non-nitrile, nitrogen-containing heterocyclic compound of the formula:



wherein each R is independently hydrogen, alkyl, alkenyl, alkoxy, alkylamino, alkylsulfonic acid or salts thereof, sulfonic acid or salts thereof, halogen, amino, hydroxyl, mercapto, benzyl, or phenylalkyl



(where m is an integer 0 to 4); n is an integer 0 to 3; R' is a divalent alkylene, divalent alkenylene, secondary amine, or a direct bond between two heterocyclic rings; z is 0 or 1; Y is oxygen, allyl, propargyl, benzyl, an alkoxy group, alkyl sulfonic acid $-(CH_2)_p-SO_3^-$ (where p is an integer of from 1 to 4), an oxyalkylsulfonic acid, quinaldiny, p-phenoxybenzyl or a halogenated alkenyl radical and X^- represents an anionic radical or the anionic moiety of Y or R provided that when Y is N-oxide X^- is absent.

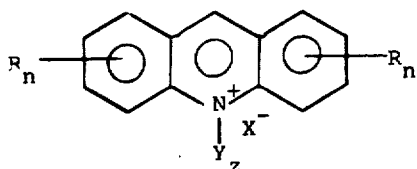
33. A composition as claimed in claim 32 wherein at least one nitrogen-containing heterocyclic compound is 1,3-di-(4,4'-pyridyl-N,N'-oxide)-n-propane.

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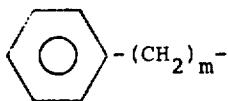
34. A composition as claimed in claim 32 wherein at least one nitrogen-containing heterocyclic compound is 1,3-di-(4,4'-pyridyl)propane.

35. A composition for providing bright, or brilliant zinc electrodeposits free of spores and/or striations over a wide current density range which comprises an aqueous bath composition having a pH of 1.0 to 10.0 and containing at least one zinc compound providing zinc ions for electroplating zinc,

- a. 1.0 gram per liter to 25 grams per liter of at least one bath soluble surfactant selected from the group consisting of bath soluble polyethers, substituted polyethers, and substituted non-aromatic nitrogen heterocyclic surfactants; and
- b. 0.001 gram per liter to 4.0 grams per liter of at least one aromatic, non-carbonyl, non-nitrile, nitrogen-containing heterocyclic compound of the formula:



wherein each R is independently hydrogen, alkyl, alkenyl, alkoxy, alkylamino, alkylsulfonic acid or salts thereof, sulfonic acid or salts thereof, halogen, amino, hydroxyl, mercapt, benzyl, or phenylalkyl



(where m is an integer 0 to 4); n is an integer 0 to 3; z is 0 or 1; Y is oxygen, allyl, propargyl, benzyl, an alkoxy group, alkyl sulfonic acid $-(CH_2)_p-SO_3^-$ (where p is an integer of from 1 to 4), an oxyalkylsulfonic acid, quinaldinyl, p-phenoxybenzyl or a halogenated alkenyl radical and X^- represents an anionic radical or the anionic moiety of Y or R provided that when Y is N-oxide X^- is absent.

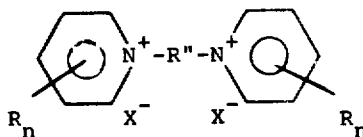
36. A composition as claimed in claim 35 wherein at least one nitrogen-containing heterocyclic compound is acridine.

37. A composition for providing bright, or brilliant zinc electrodeposits free of spores and/or striations over a wide current density range which comprises an

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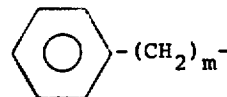
aqueous bath composition having a pH of 1.0 to 10.0 and containing at least one zinc compound providing zinc ions for electroplating zinc,

- a. 1.0 gram per liter to 25 grams per liter of at least one bath soluble surfactant selected from the group consisting of bath soluble polyethers, substituted polyethers, and substituted non-aromatic nitrogen heterocyclic surfactants; and
- b. 0.001 gram per liter to 4.0 grams per liter of at least one aromatic, non-carbonyl, non-nitrile, nitrogen-containing heterocyclic compound of the formula:



- wherein each R is independently hydrogen, alkyl, alkenyl, alkoxy, alkylamino, alkylsulfonic acid or salts thereof, sulfonic acid or salts thereof, halogen, amino, hydroxyl, mercapto, benzyl, or phenylalkyl

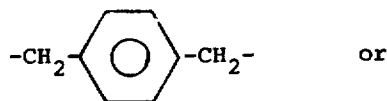
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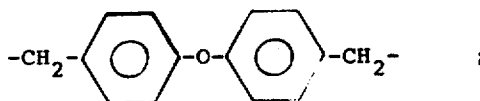
(where m is an integer 0 to 4); n is an integer 0 to 3; R'' is a bifunctional radical such as

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or

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and X^- represents an anionic radical or the anionic moiety of R.

38. A composition as claimed in claim 37 wherein at least one nitrogen-containing heterocyclic compound is p-xylene- α, α' -di-(N,N'-pyridinium chloride).

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