United States Patent Office 3,758,386 Patented Sept. 11, 1973

3,758,386

NOVEL ZINC PLATING PROCESS

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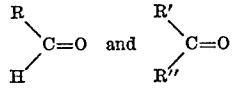
No Drawing. Filed Nov. 2, 1966, Ser. No. 591,412
Int. Cl. C23b 5/10
U.S. Cl. 204—55 26 Claims

ABSTRACT OF THE DISCLOSURE

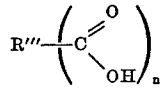
This invention relates to novel compositions and to a process of producing bright zinc deposits which comprises passing current from an anode to a metal cathode through an aqueous alkaline pyrophosphate solution containing at least one zinc compound providing zinc ions for electroplating zinc and at least one organic carrier compound selected from the group consisting of:

(a) bis[sulfonaphthyl] methane and salts thereof,
(b) naphthalene derivatives which contain substituents selected from the group consisting of sulfonic acids and their alkali metal salts, hydroxyl, amino, and imino radicals,
(c) benzene derivatives containing substituents selected from the group consisting of sulfonic acids and their salts with alkali metal, ammonium, alkyl, and imino radicals, and
(d) allyl sulfonic acid and its salts with alkali metals and ammonium;

at least one carbonyl compound having a structural formula selected from the group consisting of:



wherein R is selected from the group consisting of hydrogen, alkyl, aryl, and heterocyclic oxygen and sulfur radicals, and R′ and R″ are each selected from the group consisting of alkyl and aryl radicals; and at least one organic acid component of the formula:



and anhydrides thereof, wherein *n* is an integer 1–4 and R‴ is selected from the group consisting of a hydrocarbyl group and an inertly substituted hydrocarbyl group.

This invention relates to the electrodeposition of bright zinc from an alkaline pyrophosphate bath. More particularly, this invention relates to improved brightener compositions, bath compositions, and to methods of using and preparing such brightener compositions and bath compositions.

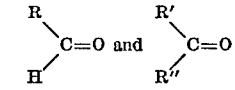
Alkaline solutions containing complex compounds of zinc and alkali metal pyrophosphates have been proposed as a replacement for the cyanide bath in processes for the electrodeposition of bright zinc due to the troublesome and costly disposal problems associated with the use of cyanide baths. However, the electrodeposition of zinc using a pyrophosphate bath may give relatively poor low current density coverage, spore formation, roughness, lack of brightness, and non-uniform deposits. Furthermore, anode corrosion may result in passivation of the anode. In addition, undesirable precipitates may form during operation which tend to clog filter systems and may result in intermittent operation due to frequent change of filter media. Attempts to overcome the deficiencies of the bath by the addition of certain expensive additives have met with only partial success and pyrophosphate zinc plating baths containing these additives have not attained widespread commercial acceptance.

It is an object of this invention to provide novel processes and compositions for electroplating of bright zinc plate. Other objects will be apparent to those skilled-in-the-art on inspection of the following description.

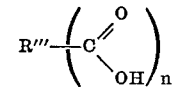
In accordance with certain of its aspects, this invention relates to a process of producing bright zinc deposits which comprises passing current from an anode to a metal cathode through an aqueous alkaline pyrophosphate solution containing at least one zinc compound providing zinc ions for electroplating zinc and at least one organic carrier compound selected from the group consisting of:

(a) bis[sulfonaphthyl] methane and salts thereof,
(b) naphthalene derivatives which contain substituents selected from the group consisting of sulfonic acids and their alkali metal salts, hydroxyl, amino, and imino radicals,
(c) benzene derivatives containing substituents selected from the group consisting of sulfonic acids and their salts with alkali metal, ammonium, alkyl, and imino radicals, and
(d) allyl sulfonic acid and its salts with alkali metals and ammonium;

at least one carbonyl compound having a structural formula selected from the group consisting of:



wherein R is selected from the group consisting of hydrogen, alkyl, aryl, and heterocyclic oxygen and sulfur radicals, and R′ and R″ are each selected from the group consisting of alkyl and aryl radicals; and at least one organic acid compound of the formula:



and anhydrides thereof, wherein *n* is an integer 1–4 and R‴ is selected from the group consisting of a hydrocarbyl group and inertly substituted hydrocarbyl group.

Examples of suitable organic carrier compounds (corresponding to groups (a)–(d) set forth above) which may be used according to the invention are set forth in Table I.

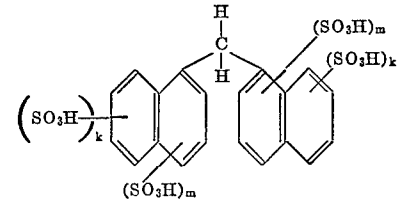
TABLE I

Organic carrier compounds

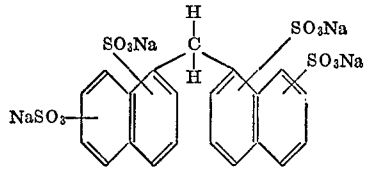
(a)

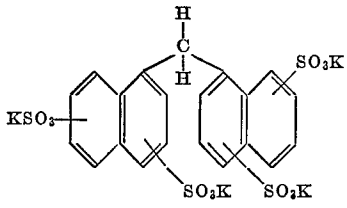
bis[sulfonaphthyl] methane,
sodium salt of bis[sulfonaphthyl] methane,
potassium salt of bis[sulfonaphthyl] methane,
ammonium salt of bis[sulfonaphthyl] methane;

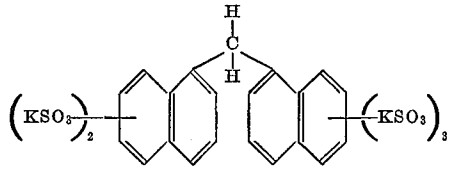
Typical bis[sulfonaphthyl] methane compounds (and salts thereof) which may be used include compounds of the formula:

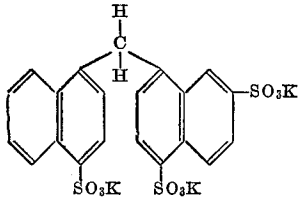


wherein each of m and k is an integer 0–3 such that the sum $m+k$ is at least one and preferably 1–6. Examples of salts of such compounds include:









etc.

In the above formulas, it is understood that all unsubstituted carbon atoms are bonded to hydrogen atoms.

(b)

naphthalene derivatives:
2,6-naphthalene-disulfonic acid
8-amino-1-naphthalene-2-sulfonic acid
6,6'-imino-bis-[1-naphthol-3] sulfonic acid
2-naphthol-6,8-disulfonic acid
2,3-dihydroxy-6-naphthalene sulfonate, sodium salt
1,5-dihydroxy-naphthalene
1,4-naphthalene diol;

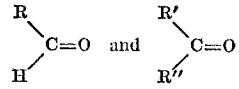
(c)

benzene derivatives:
sodium salt of benzene monosulfonate
benzene sulfonamide
sodium toluene sulfonate
o-sulfobenzimide

(d)

sodium allyl sulfonate

Suitable carbonyl compounds of the aldehyde and ketone type which cooperate effectively with the other additives of the invention and may be used in the processes and compositions of the invention have a structural formula selected from the group consisting of:



wherein R is selected from the group consisting of hydrogen, alkyl, aryl, and heterocylic radicals containing oxygen and/or sulfur as the hetero-atoms, and R' and R'' are each selected from the group consisting of alkyl and aryl radicals. Both the alkyl and the aryl radicals in

R, R', and R'' may contain substituents such as alkoxy or hydroxy radicals. Table II sets forth suitable examples of carbonyl compounds which may be used in combination with the other additives according to the invention:

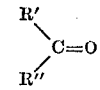
TABLE II

Aldehydes



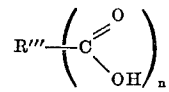
formaldehyde
benzaldehyde
meta-hydroxy-benzaldehyde
para-hydroxy-benzaldehyde
ortho-hydroxy-benzaldehyde
piperonal
veratraldehyde (i.e. 3,4-dimethoxy-benzaldehyde)
isovanillin (i.e. 3-hydroxy-4-methoxy-benzaldehyde)
vanillin ethyl ether
beta-methoxy-propionaldehyde
furfural
glyceraldehyde
ethyl vanillin
anisaldehyde
salicylaldehyde propyl sultone
thiophene-2-aldehyde

Ketones



acetophenone
acetylacetone
isophorone
dihydroxy acetone

Examples of suitable organic acid compounds of the formula



and anhydrides thereof, wherein n is an integer 1–4 and R''' may be selected from the group consisting of a hydrocarbyl radical and an inertly substituted hydrocarbyl radical, are provided in Table III.

In this compound, R''' may be a hydrocarbyl radical preferably selected from the group consisting of alkyl, alkenyl, cycloalkyl, aralkyl, aryl, alkaryl, including such radicals when inertly substituted. When R''' is alkyl, it may typically be straight chain alkyl or branched alkyl, including methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, n-amyl, neopentyl, isoamyl, n-hexyl, isohexyl, heptyls, octyls, decyls, dodecyls, tetradecyl, octadecyl, etc. Preferred alkyls includes lower alkyl i.e. having less than about 8 carbon atoms i.e. octyls and lower. When R''' is alkenyl, it may typically be vinyl, allyl, 1-propenyl, methallyl, buten-1-yl, buten-2-yl, buten-3-yl, penten-1-yl, hexenyl, heptenyl, octenyl, decenyl, dodecenyl, tetra-decenyl, octadecenyl, etc. When R''' is cycloalkyl, it may typically be cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, etc. When R''' is aralkyl, it may typically be benzyl, β-phenylethyl, γ-phenylpropyl, β-phenylpropyl, etc. When R''' is aryl, it may typically be phenyl, naphthyl, etc. When R''' is alkaryl, it may typically be tolyl, xylyl, p-ethylphenyl, p-nonylphenyl, etc. R''' may be inertly substituted e.g. may bear a non-reactive sub-

stituent such as alkyl, aryl, cycloalkyl, aralkyl, alkaryl, alkenyl, ether, halogen, nitro, ester, etc. Typical substituted alkyls include 3-chloropropyl, 2-ethoxyethyl, carboethoxy-methyl, etc. Substituted alkenyls include 4-chlorobutyl, γ-phenyl-propenyl, chloroallyl, etc. Substituted cycloalkyls include 4 - methyl-cyclohexyl 4-chlorocyclohexyl, etc. Inertly substituted aryl includes chlorophenyl, anisyl, biphenyl, etc. Inertly substituted aralkyl includes chlorobenzyl, p-phenylbenzyl, p-methylbenzyl, etc. Inertly substituted alkaryl includes 3-chloro-5-methylphenyl, 2,6-di-tert-butyl-4-chlorophenyl, etc. Other suitable R''' groups include alkoxyalkyl, alkoxyaryl, aryloxyalkyl, alkylene, alkenylene, alkynyl, as well as trivalent and tetravalent hydrocarbyl and inertly substituted hydrocarbyl groups.

TABLE III

Organic acids (and anhydrides)

acetic acid
acetic anhydride
chloroacetic acid
chloroacetic anhydride
dichloroacetic acid
dichloroacetic anhydride
trichloroacetic acid
trichloroacetic anhydride
bromoacetic acid
bromoacetic anhydride
dibromoacetic acid
dibromoacetic anhydride
tribromoacetic acid
tribromoacetic anhydride
iodoacetic acid
iodoacetic anhydride
methoxyacetic acid
methoxyacetic anhydride
ethoxyacetic acid
ethoxyacetic anhydride
phenoxyacetic acid
phenoxyacetic anhydride
2-hydroxyethoxyacetic acid
malonic acid
malonic anhydride
succinic acid
succinic anhydride
glutaric acid
glutaric anhydride
adipic acid
adipic anhydride
pimelic acid
pimelic anhydride
fumaric acid
fumaric anhydride

The halogenated organic carboxylic acids which may be added, either as such or e.g. as their anhydrides or salts (typically the sodium salt), to zinc plating baths in practice of this invention may typically include:

(a) Monohalogenated aliphatic monocarboxylic acids having at least two carbon atoms,

(b) Polyhalogenated aliphatic monocarboxylic acids having at least two carbon atoms,

(c) Monohalogenated aliphatic polycarboxylic acids having at least two carbon atoms,

(d) Polyhalogenated aliphatic polycarboxylic acids having at least two carbon atoms,

(e) Monohalogenated aromatic monocarboxylic acids having at least two carbon atoms,

(f) Monohalogenated aromatic polycarboxylic acids having at least two carbon atoms,

(g) Polyhalogenated aromatic monocarboxylic acids having at least two carbon atoms, and

(h) Polyhalogenated aromatic polycarboxylic acids having at least two carbon atoms.

Typical illustrative monohalogenated aliphatic monocarboxylic acids having at least three carbon atoms which may be employed may include:

2-chloropropionic acid
3-bromopropionic acid
3-iodopropionic acid
2-chlorobutanoic acid
chloropivalic acid (monochlorinated tertiary pentanoic acid)
2-chloropentanoic acid

Typical illustrative polyhalogenated aliphatic monocarboxylic acids having at least three carbon atoms which may be employed may include:

2,2-dichloropropionic acid
2,2,3-trichloropropionic acid

Typical illustrative monohalogenated aliphatic polycarboxylic acids having at least three carbon atoms which may be employed may include:

chloromalonic acid
2-chlorosuccinic acid
2-bromosuccinic acid
2-chloroadipic acid

Typical illustrative polyhalogenated aliphatic polycarboxylic acids which may be employed may include:

2,2-dichlorosuccinic acid
2,2-dichloroadipic acid
tetrachlorosuccinic acid
2,3-dibromosuccinic acid
3,3-diiodosuccinic acid
3,4-dichloroadipic acid

Typical illustrative monohalogenated aromatic monocarboxylic acids which may be employed may include:

3-chloro-4-sulfobenzoic acid
3-bromo-4-sulfobenzoic acid

Typical illustrative monohalogenated aromatic polycarboxylic acids which may be employed may include:

4-chlorophthalic acid
2-bromoterephthalic acid

Typical illustrative polyhalogenated aromatic monocarboxylic acids which may be employed may include:

3,5-dichloro-4-sulfobenzoic acid
3,6-dibromo-4-sulfobenzoic acid

Typical illustrative polyhalogenated aromatic polycarboxylic acids which may be employed may include:

3,4-dichlorophthalic acid
3,4-dibromophthalic acid
4,5-dichlorophthalic acid

Other acids falling within the scope of this invention will be apparent to those skilled-in-the-art.

According to another aspect of the invention, a mixture of organic acids may be employed in combination with the other additives. Examples of such mixtures include acetic and chloroacetic acid, acetic acid and hydroxyacetic acid, trichloroacetic acid and hydroxyacetic acid, dihloroacetic acid and bromoacetic acid, etc. Preferred mixtures of acids which may be used include mixtures of hydroxyacetic acid and at least one other acid such as acetic acid, iodoacetic acid, chloroacetic acid, bromoacetic acid, etc. The use of hydroxyacetic acid in combination with at least one other acid (such as acetic acid, a haloacetic acid, or a polyhaloacetic acid) results in further improved reduction and/or inhibition of undesirable precipitate formation in alkaline pyrophosphate plating baths containing zinc ions. Alkoxy and aryloxy acids,

including methoxyacetic acid, phenoxyacetic acid, etc. may be employed.

According to still another aspect of the invention, a used pyrophosphate zinc plating bath which is contaminated with undesirable precipitate may be regenerated by the addition of suitable quantities of organic carrier, carbonyl compound, and organic acid compound.

The basis metal onto which the bright zinc deposits of this invention may be applied may include ferrous metals such as steel; copper, including its alloys such as brass, bronze, etc.; die cast metals which may bear a plate of another metal such as copper; thin metal coating, 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, etc.

According to another aspect of the process of the invention, the preferred operating conditions such as pH, temperature, and current density may vary depending upon the paticular bath composition and the nature of the article being plated. In general, good bright zinc deposits can be obtained within a specific range of operating conditions. For example, when the pH is within the desired range a zinc deposit may attain maximum brightness and when the pH is within the desired range the current efficiency may be optimum.

Table IV sets forth the ranges and conditions suitable for the bath compositions which may be used according to the process of this invention.

TABLE IV

Composition and/or conditions	Broad range	Preferred range
Zinc metal concentration (g./l.)	10–60	20–32
Pyrophosphate/zinc (P_2O_7/Zn) weight ratio	6.5:1–8.0:1	7.0:1–8.0:0
pH	10.5–12.0	11.2–11.7
Temperature	40–55	45–41
Current density-amp. per decimeter (ASD)	0.2–0	0.4–5
Organic carrier compound (g./l.)	0.5–18.0	4.0–14.0
Carbonyl compound (g./l.)	0.025–0.2	0.05–0.1
Organic acid compound (g./l.)	4.0–50	12.0–22.0

Vigorous and uniform agitation of the plating bath may be provided, if necessary, either by mechanical or solution agitation during the electrodeposition. Such agitation may permit the use of higher plating current densities on the article being plated. During the plating operation, it is desirable to remove or eliminate metal and other contaminants to insure a bright metal zinc deposit. Such contamination from metal ions (such as cadmium, copper, iron, and lead) may be the most troublesome, and conventional purification methods may be used to eliminate or reduce the amounts of such contaminants. Other types of contaminants (such as organic contaminants) may also be eliminated or reduced by circulation of the pyrophosphate solution using a suitable filter media such as activated carbon or other types of exchange or absorption media.

Although numerous combinations of organic carrier compounds, carbonyl compounds, and organic acid compounds may be used according to the invention, a particularly preferred embodiment of the invention comprises the utilization of an alkaline pyrophosphate zinc plating bath containing organic carrier bis[sulfonaphthyl] methane (or the alkali metal salts thereof), furfuraldehyde as the carbonyl compound, and an aqueous mixture containing acetic acid and hydroxyacetic acid as the organic acid component. This composition may give particularly good results with respect to reduction of roughness, increase in brightness of the zinc deposit, reduction of spore formation, and elimination or reduction of excessive precipitate formation.

Thus, according to a preferred embodiment, the invention relates to a process for the production of bright zinc deposits which may comprise electrodepositing bright zinc by passing current from an anode to a metal cathode through an aqueous alkaline pyrophosphate solution containing at least one zinc compound providing zinc ions for electroplating zinc and about 0.5 to about 18.0 grams per liter of an organic carrier compound, from about 0.025 to about 0.2 gram per liter of a carbonyl compound selected from the group consisting of aldehydes and ketones, and about 4.0 g./l. to about 50.0 g./l. of at least one organic acid selected from the group consisting of acetic acid, haloacetic acids, alkoxyacetic acids, phenoxyacetic acid, and hydroxyacetic acids (preferably a mixture of acetic acid and hydroxyacetic acid).

While the additives and carriers of this invention may be used at any concentrations within the broad ranges stated above, it is generally preferable to employ the organic carriers in concentration of from about 4.0 to about 14.0 grams per liter, the most preferable concentration being about 9–10 g./l.; the carbonyl compounds in concentrations of from about 0.05 to about 0.1 gram per liter, and the organic acids in concentrations of from about 12.0 grams per liter to about 22.0 grams per liter, and most preferably about 16 grams per liter.

The additives and carriers may be added either separately or simultaneously to the zinc plating bath. For the carbonyl compound, it is often most convenient to incorporate the compound into the bath in the form of dilute aqueous solution. Aqueous solutions containing alkali metal hydroxide may be used for the preparation of baths with higher concentrations of carbonyl compounds. To prepare solutions of carbonyl compounds which have longer shelf lives, the carbonyl compounds may be dissolved in the form of an aqueous-alcoholic solution. The organic acid additive may similarly be added to the zinc plating bath, preferably in the form of an aqueous solution. When a mixture of acids (e.g. acetic acid and hydroxyacetic acid) is used, the mixture may contain suitable amounts of water as a diluent. Concentrated solutions may be diluted directly in the bath.

The zinc plating operation may be carried out at a temperature at which the bath remains a liquid. Generally, temperatures of from about 20° C. to 65° C. may be employed, typically temperatures of from 45° C. to 55° C. and preferably temperatures of from 50° C. to 52° C.

The following examples are submitted for the purpose of illustration only and are not to be construed as limiting the scope of the invention in any way. The compositions of the metal panels used in these plating experiments were as follows.

(I) STEEL PANEL

Type: Low carbon cold rolled steel
SAE number: 1010

Element:	Percent by weight
Carbon	0.08–0.13.
Manganese	0.30–0.60.
Phosphorus	0.040 (maximum).
Sulfur	0.050 (maximum).
Iron	Remainder.

Impurities

Element:	Percent by weight
Silicon	0.08
Nickel	0.07
Chromium	0.04
Molybdenum	0.02
Aluminum	0.002
Arsenic	0.032
Copper	Trace

(II) BRASS PANEL

Type: 70% copper and 30% zinc; half-hard brass (ingot not sand cast)

Element:	Percent by weight
Copper	65.00 (min.)–69.00 (max.).
Tin	1.50 (max.).
Lead	1.50 (min.)–3.5 (max.).
Zinc	Remainder.

Impurities

Element:	Percent by weight
Nickel	0.5.
Iron	0.5.
Silicon	0.05 (max.)

EXAMPLE 1

A pyrophosphate stock solution designated Zinc-Plating Solution A may be prepared containing the following components:

Zn	g./l.	22.8–27.0
$K_4P_2O_7$	g./l.	273.6–350
K/Zn ratio		12–31:1
PO_4	g./l.	7.5 max.
SO_4	g./l.	<0.38
pH		10.3–11.5

To 3.5 liters of Solution A may be added about 3.8 grams of the sodium salt of bis[sulfonaphthyl] methane, 0.44 gram of furfuraldehyde, and 6.3 grams of hydroxyacetic acid, the electrometeric pH of the solution being approximately 11.2. The temperature of the bath may be held at about 25° C. and a 6.25 cm. x 10 cm. x 0.15 cm. half-hard brass panel (70% by weight copper and 30% zinc) of the same composition as brass panel II as previously described may be immersed in the bath and zinc plated using a current of three amperes for a time period of ten minutes. An excellent bright zinc-plated panel was obtained. The anodes remained clean and no spores were formed on the zinc-plated panel. Similar results are obtained using steel panels.

EXAMPLE 2

This example illustrates the regeneration of a deteriorated zinc plating bath. 3.5 liters of a pyrophosphate stock Solution A containing 0.1 g./l. of furfuraldehyde and 1.2 g./l. of the sodium salt of bis[sulfonaphthyl] methane may be used for several days. At the end of this time, a crust of precipitate may have formed at the bottom of the bath and the bath may no longer produce satisfactory bright zinc deposits. To a sample of 3.5 liters of this spent bright zinc plating bath may be added sufficient hydroxyacetic acid to dissolve the precipitate in the bath (approximately 15–25 grams). Glacial acetic acid (0.5 g./l.) may be added, the anodes were bagged, and several brass panels were plated using a current of 4 amperes for twenty minutes. Excellent bright zinc plated brass panels may be obtained and it may be noted that the andoes remained clean even at current densities in the range of 30 amperes per square decimeter (ASD).

EXAMPLE 3

This example may illustrate the advantage of the use of an organic acid in combination with a bis[sulfonaphthyl] methane compound (including salts thereof) and a carbonyl compound.

In a control experiment, 300 milliliters of pyrophosphate zinc plating Solution A as described in Example 1 may be added to 0.36 gram of the sodium salt of bis[sulfonaphthyl] methane and 0'03 gram of furfuraldehyde. The resulting solution (pH 11.3) may be heated to 50° C. and a steel panel was plated in a standard Hull cell at 1 ampere for ten minutes. The resulting zinc plated control panel may contain black spore-deposits. Repetition of this control plating procedure using the same bath with another steel panel at 1.5 amperes for ten minutes may give a zinc-plated steel panel which was disfigured with unsightly black spores on the surface of the zinc plate.

In a process carried out in accordance with this invention, the same solution as employed in the preceding experiment but with the addition of 2.5 grams of a mixture of 0.1 gram of glacial acetic acid and 2.4 grams of hydroxyacetic acid may be employed to plate an identical steel panel at 1.5 amperes for ten minutes at 50° C. in a standard Hull cell, the pH of the solution being 11.3, as in the preceding experiment. No spores may be formed on the experimental zinc-plated steel panel. Repetition of the experiment using the same zinc plating solution but at 1.0 ampere for 10 minutes may give a zinc-plated steel panel free of spores.

EXAMPLES 4–13

Table V gives examples of various combinations of carbonyl compound, organic carrier compound, and organic acid compound which may produce significantly improved spore-free bright zinc plate with reduced anode deterioration and reduced sludge or precipitate formation in the plating bath. A typical basic zinc plating bath which may be used in combination with the ingredients of Table V may be composed as follows:

Zinc (as the metal)	g./l.	22.8–27.0
$K_4P_2O_7$	g./l.	273.6–350
Total P_2O_7	g./l.	approx. 188
$K_4P_2O_7$/Zn weight ratio		12:1–13:1
PO_4	g./l.	7.5 max.
SO_4	g./l.	<0.38
pH		10.3–11.5
Temperature (° C.)		45–55

In the examples of Table V, the bath temperature may be maintained at about 50° C., the pH may be approximately 11.3 and mild agitation may be employed. The zinc-plating experiments may be carried out in a Hull cell for 10 minutes at 1 ampere, using steel panels as previously described.

TABLE V

Ex. No.	Carbonyl compound	G./l.	Organic carrier compound	G./l.	Organic acid compound
4	p-Hydroxy benzaldehyde	0.25	bis(sulfonaphthyl)methane*	1.2	Iodoacetic acid, 0.2 (g./l.).
5	Veratraldehyde	0.1	do	1.2	Glacial acetic acid, 0.2 (g./l.).
6	Benzaldehyde	0.4	do	1.2	Hydroxyacetic acid, 8 (g./l.).
7	Furfural	0.1	do	1.2	0.2 g./l. glacial acetic acid plus 8 g./l. hydroxyacetic acid.
8	Glyceraldehyde	0.1	do	1.2	Trichloroacetic acid, 0.32 (g./l.).
9	Anisaldehyde	0.6	do	1.2	Bromoacetic acid, 0.75 (g./l.).
10	Salicylaldehyde propyl sultone	0.05	do	1.2	Trichloroacetic acid, 0.32 (g./l.).
11	Ethyl vanillin	0.4	do	1.2	0.2 g./l. glacial acetic acid plus 8 g./l. hydroxyacetic acid.
12	Thiophene-2-aldehyde	0.2	do	1.2	Bromoacetic acid, 0.75 (g./l.).
13	Acetylacetone	0.4	do	1.2	Iodoacetic acid, 0.2 (g./l.).

*As sodium salt.

EXAMPLES 14–23

Improved results may be obtained in a similar manner when steel panels are zinc plated in a standard Hull cell using the same plating conditions as in the preceding

Examples 4–13, but employing the following acids at a concentration of 0.2 g./l. in combination with 3.4 g./l. of the sodium salt of bis[sulfonaphthyl]methane and 2.03 g./l. of furfuraldehyde.

Example No. —	Organic acid
14	Butyric acid.
15	2-bromobutyric acid.
16	Propionic acid.
17	α-Chloropropionic acid.
18	Succinic acid.
19	Benzoic acid.
20	Glutaric acid.
21	Adipic acid.
22	Succinic anhydride.
23	Phthalic acid.

Similar results may be obtained using sodium pyrophosphate in place of potassium pyrophosphate in the pyrophosphate zinc plating Solution A.

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

I claim:

1. The process of producing bright zinc deposits which comprises passing current from an anode to a metal cathode through an aqueous alkaline pyrophosphate solution containing

at least one zinc compound providing zinc ions for electroplating zinc and at least one organic carrier compound selected from the group consisting of:

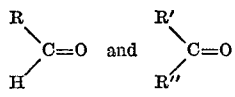
(a) bis(sulfonaphthyl) methane and salts thereof;

(b) naphthalene derivatives wherein each substituent is selected from the group consisting of sulfonic acids and their alkali metal salts, a hydroxyl radical, an amino radical, and an imino radical;

(c) benzene derivatives containing substituents selected from the group consisting of sulfonic acids and their alkali metal and ammonium salts, an alkyl radical, and an imino radical; and

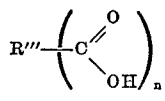
(d) allyl sulfonic acid and its alkali metal and ammonium salts;

at least one carbonyl compound having a structural formula selected from the group consisting of



wherein R is selected from the group consisting of hydrogen, an alkyl radical, an aryl radical, and heterocyclic radicals containing oxygen and sulfur as the hetero-atoms, and R′ and R″ are each selected from the group consisting of alkyl and aryl radicals;

and at least one organic acid compound and anhydrides thereof of the formula:



wherein *n* is one and R‴ is selected from the group consisting of methyl, hydroxymethyl, halomethyl groups, and haloethyl groups.

2. The process of producing bright zinc deposits as claimed in claim **1** wherein the organic acid is a mixture of glacial acetic acid and hydroxyacetic acid.

3. The process of producing bright zinc deposits as claimed in claim **1** wherein the carbonyl compound is furfuraldehyde and the organic acid is a mixture of glacial acetic acid and hydroxyacetic acid.

4. The process of producing bright zinc deposits as claimed in claim **1** wherein the carbonyl compound is acetylacetone and the organic acid is iodoacetic acid.

5. The process of producing bright zinc deposits as claimed in claim **1** wherein the carbonyl compound is benzaldehyde and the organic acid is hydroxyacetic acid.

6. The process of producing bright zinc deposits as claimed in claim **1** wherein the carbonyl compound is furfuraldehyde and the organic acid is chloropropionic acid.

7. A zinc plating composition comprising

at least one organic carrier compound selected from the group consisting of:

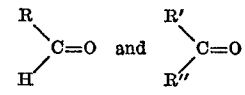
(a) bis(sulfonaphthyl) methane and salts thereof;

(b) naphthalene derivatives wherein each substituent is selected from the group consisting of sulfonic acids and their alkali metal salts, a hydroxyl radical, an amino radical, and an imino radical;

(c) benzene derivatives containing substituents selected from the group consisting of sulfonic acids and their alkali metal and ammonium salt, an alkyl radical, and an imino radical; and

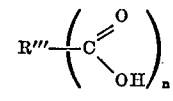
(d) allyl sulfonic acid and its alkali metal and ammonium salts;

at least one carbonyl compound having a structural formula selected from the group consisting of



wherein R is selected from the group consisting of hydrogen, an alkyl radical, an aryl radical, and heterocyclic radicals containing oxygen and sulfur as the hetero-atoms, and R′ and R″ are selected from the group consisting of alkyl and aryl radicals;

and at least one organic acid compound of the formula (and anhydrides thereof):



wherein *n* is one and R‴ is selected from the group consisting of methyl, hydroxymethyl, halomethyl groups, and haloethyl groups.

8. The zinc plating composition according to claim **7** wherein the organic acid is a mixture of glacial acetic acid and hydroxyacetic acid.

9. The zinc plating composition according to claim **7** wherein the carbonyl compound is furfuraldehyde and the organic acid is a mixture of glacial acetic acid and hydroxyacetic acid.

10. The zinc plating composition according to claim **7** wherein the carbonyl compound is acetylacetone and the organic acid is iodoacetic acid.

11. The zinc plating composition according to claim **7** wherein the carbonyl compound is benzaldehyde and the organic acid is hydroxyacetic acid.

12. The zinc plating composition according to claim **7** wherein the carbonyl compound is furfuraldehyde and the organic acid is α-chloropropionic acid.

13. The process of producing bright zinc deposits which comprises passing current from an anode to a metal cathode through an aqueous alkaline pyrophosphate solution containing

at least one zinc compound providing zinc ions for electroplating zinc and at least one organic carrier

compound which is selected from the group consisting of:

(a) bis(sulfonaphthyl) methane and the sodium, potassium, or ammonium salts thereof;

(b) naphthalene derivatives selected from the group consisting of:

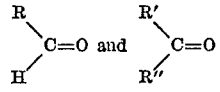
2,6-naphthalene-disulfonic acid;
8-amino-1-naphthalene-2-sulfonic acid;
6,6'-imino-bis-(1-naphthol-3) sulfonic acid;
2-naphthol-6,8-disulfonic acid;
2,3 - dihydroxy - 6 - naphthalene sulfonate, sodium salt;
1,5-dihydroxy-naphthalene;
1,4-naphthalene diol;

(c) benzene derivatives selected from the group consisting of:

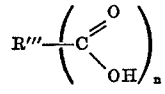
sodium salt of benzene monosulfonate;
benzene sulfonamide;
sodium toluene sulfonate;
o-sulfobenzimide; and

(d) sodium allyl sulfonate;

at least one carbonyl compound having a structural formula selected from the group consisting of



wherein R is selected from the group consisting of hydrogen, an alkyl radical, an aryl radical, and heterocyclic radicals containing oxygen and sulfur as the hetero-atoms, and R' and R'' are each selected from the group consisting of alkyl and aryl radicals; and at least one organic acid compound and anhydrides thereof of the formula:



wherein *n* is 1 and R''' is selected from the group consisting of methyl, hydroxymethyl, halomethyl and haloethyl groups.

14. The process of producing bright zinc deposits as claimed in claim **13** wherein the carbonyl compound is furfuraldehyde and the organic acid is a mixture of glacial acetic acid and hydroxyacetic acid.

15. The process of producing bright zinc deposits as claimed in claim **13** wherein the carbonyl compound is acetylacetone and the organic acid is iodoacetic acid.

16. The process of producing bright zinc deposits as claimed in claim **13** wherein the carbonyl compound is benzaldehyde and the organic acid is hydroxyacetic acid.

17. The process of producing bright zinc deposits as claimed in claim **13** wherein the carbonyl compound is furfuraldehyde and the organic acid is chloropropionic acid.

18. A zinc plating composition comprising an aqueous alkaline pyrophosphate solution containing

at least one zinc compound providing zinc ions for electroplating zinc and containing in combination at least one organic carrier compound selected from the group consisting of:

(a) bis(sulfonaphthyl) methane and the sodium, potassium, or ammonium salts thereof;

(b) naphthalene derivatives selected from the group consisting of:

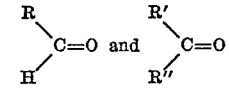
2,6-naphthalene-disulfonic acid;
8-amino-1-naphthalene-2-sulfonic acid;
6,6'-imino-bis-(1-naphthol-3) sulfonic acid;
2-naphthol-6,8-disulfonic acid;
2,3-dihydroxy-6-naphthalene sulfonate sodium salt;
1,5-dihydroxy-naphthalene;
1,4-naphthalene diol;

(c) benzene derivatives selected from the group consisting of:

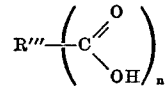
sodium salt of benzene monosulfonate;
benzene sulfonamide;
sodium toluene sulfonate;
o-sulfobenzimide; and

(d) sodium allyl sulfonate;

at least one carbonyl compound having a structural formula selected from the group consisting of



wherein R is selected from the group consisting of hydrogen, an alkyl radical, an aryl radical, and heterocyclic radicals containing oxygen and sulfur as the hetero-atoms, and R' and R'' are each selected from the group consisting of alkyl and aryl radicals; and at least one organic acid compound and anhydrides thereof of the formula:



wherein *n* is 1 and R''' is selected from the group consisting of methyl, hydroxymethyl, halomethyl and haloethyl groups.

19. The zinc plating composition according to claim **18** wherein the carbonyl compound is furfuraldehyde and the organic acid is a mixture of glacial acetic acid and hydroxy acetic acid.

20. The zinc plating composition according to claim **18** wherein the carbonyl compound is acetylacetone and the organic acid is iodoacetic acid.

21. The zinc plating composition according to claim **18** wherein the carbonyl compound is benzaldehyde and the organic acid is hydroxyacetic acid.

22. The zinc plating composition according to claim **18** wherein the carbonyl compound is furfuraldehyde and the organic acid is α-chloropropionic acid.

23. A process of producing bright zinc electrodeposits which comprises passing current from an anode to a metal cathode through an aqueous alkaline pyrophosphate solution containing at least one zinc compound providing zinc ions for electroplating zinc and containing in combination about:

0.5–18.0 g./l. of the sodium salt of bis(sulfonaphthyl) methane;
0.025–0.2 g./l. of furfuraldehyde; and
4.0–50 g./l. of hydroxyacetic acid.

24. A process of producing bright zinc electrodeposits which comprises passing current from an anode to a metal cathode through an aqueous alkaline pyrophosphate solution containing at least one zinc compound providing zinc ions for electroplating zinc and containing in combination about:

0.3–18.0 g./l. of the sodium salt of bis(sulfonaphthyl) methane;
0.025–0.2 g./l. of furfuraldehyde; and
4.0–50.0 g./l. of a mixture of acetic acid and hydroxyacetic acid.

25. A zinc plating composition comprising an aqueous alkaline pyrophosphate solution containing at least one

zinc compound providing zinc ions for electroplating zinc and containing in combination about:

0.5–18.0 g./l. of the sodium salt of bis(sulfonaphthyl) methane;
0.025–0.2 g./l. of furfuraldehyde; and
4.0–50 g./l. of hydroxyacetic acid.

26. A zinc plating composition consisting essentially of an aqueous alkaline pyrophosphate solution containing at least one zinc compound providing zinc ions for electroplating zinc and containing in combination about:

0.5–18.0 g./l. of the sodium salt of bis(sulfonaphthyl) methane;
0.025–0.2 g./l. of furfuraldehyde; and
4.0–50 g./l. of a mixture of acetic acid and hydroxyacetic acid.

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U.S. Cl. X.R.

204—114