

1

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**ZINC PLATING BATHS AND ADDITIVES THEREFOR**

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9 Claims

**ABSTRACT OF THE DISCLOSURE**

This invention relates to novel method of improving the brightness of zinc which is electrodeposited from aqueous zinc cyanide plating baths. More particularly, the invention comprises adding to the plating baths to improve the brightness of zinc deposited therefrom, an azomethine of the general formula  $RCH=NX$  wherein R and X are selected from the group consisting of phenyl, naphthyl and pyridyl and at least one of the groups R and X has substituted therein at least one substituent selected from the group consisting of  $-NH_2$ ,  $-COOH$ ,  $-OH$ ,  $-SO_3H$  and alkoxy. In addition, another part of the invention comprises adding to the plating baths organic polymers such as polyvinyl alcohol along with the defined azomethines to further improve the brightness and luster of the deposited zinc.

**BACKGROUND OF THE INVENTION**

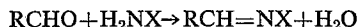
The use of brightening agents in the electrodeposition of zinc from alkaline cyanide plating baths is well known. Aromatic aldehydes, usually in the form of an aldehyde bisulfite addition compound, have been used extensively as brightening agents in commercial zinc plating. The use of the bisulfite addition compounds is necessary to effect sufficient solubility of the aromatic aldehyde in the plating bath to achieve beneficial plating results. Other brightening agents are also employed, with the type of brightening agent used generally depending on whether the plating bath is acid, containing zinc sulfate, chloride, or fluoroborate; or alkaline, containing zinc cyanide. This invention is concerned with alkaline zinc cyanide plating baths and improved brightening agents therefor.

One of the principal brightening agents used in zinc cyanide plating baths has been aromatic aldehydes. The problem with the use of these compounds is their instability in the cyanide plating bath, causing rapid decomposition during use and storage, and resulting in a high use cost. Consequently, efforts have been made to discover compositions which are more stable in the plating bath than aromatic aldehydes and which have equivalent or better brightening activity.

**DESCRIPTION OF THE INVENTION**

It has been discovered that azomethines are effective brightening agents for use in an aqueous zinc cyanide plating bath and that they have a much higher stability, with lower use cost than the aromatic aldehydes presently used. It has also been discovered that the brightness of the deposited zinc can be further improved by adding an organic polymer such as polyvinyl alcohol to the plating bath.

One way to prepare the azomethines used in this invention is to condense an aldehyde with a primary amine:

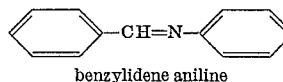


where both R and X may be either aryl or alkyl. The R and X can be substituted or unsubstituted with various substituents to be described more fully later herein. For the purpose of practicing this invention it is preferred

2

that R be aryl while X may be either aryl or alkyl. The condensation reaction may be effected by mixing the aldehyde and amine together in a suitable solvent such as methyl alcohol, the azomethine crystallizing out on standing. Of course, it may be more desirable from an economic viewpoint in practicing this invention to use a commercially available azomethine rather than preparing the azomethine as shown above.

From a practical standpoint the particular azomethine which is chosen to practice the invention should be soluble in the plating bath. (By the term "soluble" it is meant having a solubility of at least about 0.1 gram per liter at a temperature of about 25° C. in an alkaline cyanide zinc plating bath.) Azomethines which do not have the required solubility but which might otherwise be anticipated as being effective zinc brighteners, such as benzylidene aniline.



can be rendered useful by incorporating an alkali solubilizing group such as  $-OH$ ,  $-COOH$ , or  $-SO_3H$  into the molecule. One way of adding the alkali solubilizing group to the azomethine molecule is to start with the appropriately substituted aldehyde or amine.

Specifically the invention comprises an aqueous cyanide zinc electroplating bath containing a brightening agent therefor an azomethine, the azomethine being soluble in the bath. There should be a sufficient amount of azomethine present in the bath to yield a zinc electrodeposit of improved brightness. It is preferred that the azomethine used have at least one aromatic group as part of the molecule, and be present in the bath in an amount from about 0.1 to 10 grams per liter.

In the azomethine molecule, having the general formula  $RCH=NX$ , it is preferred that R be aryl and X be either aryl or alkyl. Some of the aryl groups that are satisfactory for use in the R and X positions are phenyl, pyridyl, naphthyl, quinolyl, and isoquinolyl. It is usually preferred that the alkyl group contain from about 1 to 6 carbon atoms. It is also possible to use certain heterocyclic groups having a partial aromatic nature such as pyrrole and furan in one or both of the R and X positions.

Organic polymers may be added to the plating bath along with aromatic azomethines to further improve brightness and luster of deposited zinc. Polyvinyl alcohols, natural polymers such as gelatin, peptone, gum tragacanth and agar-agar, as well as other synthetic polymers such as polyethyleneimine and the glyceryl ethers of polyvinyl alcohols are satisfactory for this purpose. Polyvinyl alcohols having molecular weights from about 5,000 to 20,000 work well as additives to improve brightness and in addition exhibit outstanding tolerance to sodium carbonate which builds up in the plating bath and which tends to salt out polyvinyl alcohols of higher molecular weight. A preferred polymer is polyvinyl alcohol which has a molecular weight of about 16,800 and which has been found to improve zinc brightness and exhibit excellent resistance to carbonate.

The optimum amount of the azomethine brightening agent will depend upon the specific compound used, the current density employed, and the type of plate desired. This optimum amount will generally range from about 0.1 to 10 g./l. of bath. When the azomethine is used in combination with an organic polymer, the polymer concentration should be from about 0.01 to 10 grams per liter of bath, preferably about 0.05 to 0.5 gram per liter of bath. The azomethine and organic polymer may be added separately but are preferably added together in the form of a concentrated aqueous brightener additive solution. This solution may contain from 1:1 to 50:1 parts

by weight of azomethine to polymer. Polyvinyl alcohol, as the preferred organic polymer, improves brightness when added in concentrations from about 0.01 to 10 grams/l. of bath. Other polymers suitable for use in the additive solution are gelatin, peptone, gum tragacanth, agar-agar, polyethyleneimine and the glyceryl ethers of polyvinyl alcohols.

A better understanding of the invention will be gained from the following examples illustrating the use of azomethines as brightening agents for cyanide zinc plating for both barrel and still operations. All parts and percentages are by weight unless otherwise specified.

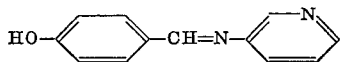
#### Example I

The zinc plating bath used in tests 1-5 was prepared in 4 liter batches having the following composition:

	Grams per liter
Sodium cyanide .....	40
Sodium hydroxide .....	90
Zinc cyanide .....	60
Sodium carbonate .....	80
Sodium sulfide .....	1

Plating operations were conducted at room temperature, i.e., 25-30° C.

The brightening agent used was 3-(4-hydroxybenzylidene)3-aminopyridine



3-(4-hydroxybenzylidene)3-aminopyridine

which was prepared by the condensation of 3-aminopyridine and p-hydroxybenzaldehyde.

*Test 1.*—This test demonstrates that an improvement in brightness can be obtained over a wide range of current densities. A steel Hull cell panel was plated at 2 amps for 5 minutes in a bath as prepared above containing 0.8 g./l. of 3-(4-hydroxybenzylidene)3-aminopyridine. After washing in water and dipping in 0.5 wt. percent HNO<sub>3</sub> to remove stains, the panel had the following appearance:

	Amp/sq. ft.
Bright plate with slight haze .....	1-10
Bright plate .....	10-50
Semi-bright plate .....	50-120

In a control experiment conducted in the absence of any brightening agent, a uniformly dull plate was obtained over the entire face of the panel where densities varied from 1-120 amp/sq. ft. This dull plate was considerably inferior to even the semibright plate obtained in the presence of the brightening agent.

*Test 2.*—This test demonstrates the utility of 3-(4-hydroxybenzylidene)3-aminopyridine as a brightening agent in practical still plating. A steel automobile crank hole cover (the crank hole cover which was used in the electroplating tests has an outer surface comprises of a series of convex surfaces and an inner surface comprised of a series of concave surfaces) was plated at 3.5 amps for 15 minutes in a cyanide plating bath, as prepared above, containing 1.5 g./l. of 3-(4-hydroxybenzylidene)3-aminopyridine. After washing and dipping in 0.5 wt. percent HNO<sub>3</sub>, a very bright and shining plate was obtained on all surfaces except those of very low current density, which were somewhat duller. However, the plate on all surfaces was considerably improved over that obtained in the absence of any brightening agent.

*Test 3.*—This test demonstrates the co-use of polyvinyl alcohol with 3-(4-hydroxybenzylidene)3-aminopyridine in practical still plating. A steel crank hole cover was plated for 3.5 amps for 15 minutes in a cyanide plating bath, as prepared above, to which has been added 3.0 g./l. of 3-(4-hydroxybenzylidene)3-aminopyridine and 0.09 g./l. of "Elvanol" polyvinyl alcohol 51-03 (trademark

for Du Pont's water-soluble polyvinyl alcohol having an average molecular weight of about 16,800). After washing and dipping in 0.5 wt. percent HNO<sub>3</sub>, a very bright plate was obtained on all surfaces, including those of low current density. The product was judged to be equal or superior to that obtained with the best commercial cyanide zinc brighteners.

*Test 4.*—This test demonstrates the co-use of polyvinyl alcohol with 3-(4-hydroxybenzylidene)3-aminopyridine in practical barrel plating. One hundred gms. of steel screws were barrel plated at 5 amps for 18 minutes in the bath from test 3. The screws produced were bright, but were somewhat stained. The stains were readily removed by dipping the screws in 0.5 wt. percent HNO<sub>3</sub>. The resulting product had an overall quality equivalent to similar products available commercially.

*Test 5.*—This test demonstrates the excellent stability of the 3-(4-hydroxybenzylidene)3-aminopyridine "Elvanol" 51-03 system in the cyanide plating bath. The bath from test 4 was stored for two weeks and then used to plate an automobile crank hole cover at 3.5 amps for 15 minutes. The cover was then washed and dipped in 0.5 wt. percent HNO<sub>3</sub>. The result was a uniformly bright plate only slightly inferior to that produced from test 3. The stability of the system used here is even more striking when compared with those using aromatic aldehydes, which lose their activity in a twenty-four hour idle period.

#### Example II

The plating bath used in tests 1 and 2 was the same as that in Example I, i.e., it was prepared in 4 liter batches and had the following composition:

	Grams per liter
Sodium cyanide .....	40
Sodium hydroxide .....	90
Zinc cyanide .....	60
Sodium carbonate .....	80
Sodium sulfide .....	1

Plating operations were conducted at room temperature, 25-30° C. The brightening agent used was 1-(4-hydroxybenzylidene)aniline prepared by the condensation of p-hydroxybenzaldehyde with aniline.

*Test 1.*—This test demonstrates the utility of using 1-(4-hydroxybenzylidene)aniline as a brightening agent in practical still plating. A series of crank hole covers were plated in a bath to which successive additions of 1-(4-hydroxybenzylidene)aniline had been added. Plating was conducted at 3.5 amps for 15 minutes and the covers were then washed and dipped in 0.5 wt. percent HNO<sub>3</sub>. The following observations were made:

- 1.5 g./l. of brightener added—The coating was somewhat brighter than that on a blank.
- 3.0 g./l. brightener added—Significant improvement in brightness on all surfaces, equal to that obtained using many commercial brighteners.
- 6.0 g./l. brightener added—No further improvement noted.

*Test 2.*—In this test, demonstrating the co-use of 1-(4-hydroxybenzylidene)aniline and polyvinyl alcohol in practical still plating, 0.18 g. of "Elvanol" polyvinyl alcohol 51-03 was added to the plating bath of test 1 after the last addition of 1-(4-hydroxybenzylidene)aniline. A crank hole cover plated in this bath showed a significant improvement on all surfaces over the best sample in test 1, giving a shining bright zinc plated product.

#### Example III

In Examples 1-22 in the table which follows are listed a variety of azomethines which were prepared by the condensation of selected aldehydes and amines and tested for activity as cyanide zinc plating agents. The principal test used was the still plating of automobile

crank hole covers; the various brightening agents being added to the plating bath of Example I in amounts varying between about 0.1 and 10 g./l. All azomethines listed in the Table gave an improved electroplate which was brighter and smoother than that obtained without a brightening agent. The performance of the various azomethine brightening agents was rated as follows:

Fair—A significant improvement over the blank.

Good—Equal to the performance of many commercial brighteners.

Excellent—Equal to the performance of the best commercial products.

Examples 23-42 in the table are other azomethines which are active brighteners for cyanide zinc plating baths.

The primary advantage of the brightening agents of this invention is the excellent quality of bright zinc plate obtained. Also, the compositions of this invention are stable both in storage and in the plating bath during use and periods of non-use. Their rate of consumption is low, thus, making them economically attractive. Of particular importance is the fact that a brightener composition containing an azomethine is usually equally effective both in still plating and in barrel plating operations. Other advantages of the brightener compositions of this invention include their effectiveness over a wide range of current densities and also the fact that bright zinc deposits obtained from their use are responsive to treatment with protective agents such as chromate conversion coating preparations.

Since many different embodiments of this invention

TABLE.—AZOMETHINES AS ZINC BRIGHTENERS

Examples 1-22

Example No.	Source		Resulting Azomethine	Performance
	Aldehyde	Amine		
1	p-Hydroxybenzaldehyde	Aniline	1-(4-hydroxybenzylidene)aniline	Good.
2	do	p-Aminophenol	4-(4-hydroxybenzylidene)4-aminophenol	Fair.
3	p-Hydroxybenzaldehyde (2 mols)	m-Phenylene diamine	1,3-bis-(4-hydroxybenzylidene)-1,3 phenylene diamine.	Fair to good.
4	p-Hydroxybenzaldehyde	o-Aminobenzoic acid	2-(4-hydroxybenzylidene)2-aminobenzoic acid.	Do.
5	do	m-Aminobenzoic acid	3-(4-hydroxybenzylidene)3-aminobenzoic acid.	Fair.
6	do	3-aminopyridine	3-(4-hydroxybenzylidene)3-aminopyridine.	Excellent.
7	do	4-aminopyridine	4-(4-hydroxybenzylidene)4-aminopyridine.	Fair to Good.
8	p-Hydroxybenzaldehyde (2 mols)	Ethylene diamine	1,4-bis-(4-hydroxybenzylidene)-ethylene diamine.	Good.
9	do	Diethylene triamine	1,7-bis-(4-hydroxybenzylidene)-diethylene triamine.	Fair to Good.
10	do	Tetraethylene pentamine	1,13-bis-(4-hydroxybenzylidene)tetraethylene pentamine.	Do.
11	do	1:2 propane diamine	1,2-bis-(4-hydroxybenzylidene)propane diamine-1,2.	Do.
12	do	Hexamethylene diamine	1,8-bis-(4-hydroxybenzylidene)hexamethylene diamine.	Do.
13	p-Hydroxybenzaldehyde	Cyclohexylamine	1-(4-hydroxybenzylidene)cyclohexylamine.	Fair.
14	m-Hydroxybenzaldehyde (2 mols)	Ethylene diamine	1,4-bis-(3-hydroxybenzylidene)ethylene diamine.	Do.
15	m-Hydroxybenzaldehyde	Aniline	1-(3-hydroxybenzylidene)aniline	Fair to Good.
16	Benzaldehyde	m-Aminophenol	3-benzylidene 3-aminophenol	Fair.
17	do	p-Aminophenol	3-benzylidene 3-aminophenol	Do.
18	p-Methoxybenzaldehyde	o-Aminobenzoic acid	2-(4-methoxybenzylidene)2-aminobenzoic acid.	Do.
19	Furfural	m-Aminophenol	3-furfurylidene 3-aminophenol	Do.
20	do	o-Aminobenzoic acid	2-furfurylidene 2-aminobenzoic acid	Do.
21	do	Cyclohexylamine	furfurylidene cyclohexylamine	Do.
22	Pyridine 3-carboxaldehyde	p-Aminobenzoic acid	4-(3-pyridylidene)4-aminobenzoic acid	Do.

Examples 23-42

Example No.	Source		Resulting Azomethine
	Aldehyde	Amine	
23	p-Hydroxybenzaldehyde	Methylamine	1-(4-hydroxybenzylidene)methylamine.
24	do	Ethylamine	1-(4-hydroxybenzylidene)ethylamine.
25	do	Propylamine	1-(4-hydroxybenzylidene)propylamine.
26	do	Butylamine	1-(4-hydroxybenzylidene)butylamine.
27	do	Pentylamine	1-(4-hydroxybenzylidene)pentylamine.
28	do	Hexylamine	1-(4-hydroxybenzylidene)hexylamine.
29	do	4-methoxypentylamine	1-(4-hydroxybenzylidene)4-methoxypentylamine.
30	1-hexaldehyde	o-Aminobenzoic acid	2-(1-hexylidene)2-aminobenzoic acid.
31	Benzaldehyde	5-amino-1-naphthalene sulfonic acid	5-benzylidene 5-amino-1-naphthalene sulfonic acid.
32	2-naphthaldehyde	2-amino benzoic acid	2-(2-naphthylidene)2-aminobenzoic acid.
33	p-Hydroxybenzaldehyde	3-aminoquinoline	3-(4-hydroxybenzylidene)3-amino quinoline.
34	Benzaldehyde 2-sulfonic acid	5-aminoisoquinoline	5-(benzylidene 2-sulfonic acid)5-aminoisoquinoline.
35	3-formyl benzoic acid	Aniline	1-(3-carboxybenzylidene)aniline.
36	Benzaldehyde	Amino acetic acid	Benzylidene aminoacetic acid.
37	m-Hydroxybenzaldehyde	Ethylene diamine	3-hydroxybenzylidene ethylene diamine.
38	Glycolic acid	m-Phenylene diamine	1-glycolidene 1,3-phenylene diamine.
39	3-formylbenzoic acid	4-amide aniline	4-(3-carboxybenzylidene)4-amidoaniline.
40	4-hydroxybenzaldehyde	p-Toluidine	4-(4-hydroxybenzylidene)4-toluidine.
41	do	p-Aminoethylbenzoate	4-(4-hydroxybenzylidene)4-aminoethylbenzoate.
42	Anisaldehyde	4-ethoxy 2-aminobenzoic acid	2-(4-methoxybenzylidene)2-amino- 4-ethoxybenzoic acid.

In addition to the azomethine compounds previously cited as having utility in the present invention, similar compounds containing additional substituent groups on the R and X groups in the molecule having a general formula  $RCH=NX$ , such as  $-NH_2$ ,  $-COOH$ ,  $-COO$  alkyl, alkyl, alkoxy, OH, and  $-SO_3H$  may be used. The plating baths exemplified may, of course, be modified to substitute for the sodium salts, other salts, e.g., potassium and lithium compounds, which behave similarly in the bath. Also zinc oxide rather than zinc cyanide may be used. Details for preparing and using the baths are, of course, well known to those skilled in the art.

may be made without departing from the spirit and scope thereof, it is to be understood that the invention is not limited to the specific illustrations except to the extent defined in the following claims.

What is claimed is:

1. An aqueous cyanide zinc electroplating bath containing as a brightening agent an aromatic azomethine of the general formula  $RCH=NX$  wherein R and X are selected from the group consisting of phenyl, naphthyl and pyridyl and at least one of the groups R and X has substituted therein at least one substituent selected from the group consisting of  $-NH_2$ ,  $-COOH$ ,  $-OH$ ,  $-SO_3H$

7

and alkoxy, said azomethine being soluble in said bath and being present in said bath in an amount sufficient to yield a zinc electrodeposit of improved brightness.

2. The bath of claim 1 wherein said azomethine is present in said bath in an amount from about 0.1 to 10 grams per liter of bath.

3. The bath of claim 2 wherein a bath-soluble organic polymer selected from the group consisting of polyvinyl alcohol, polyethyleneimine, gelatin and peptone is present in an amount from about 0.01 to 10 grams per liter of bath.

4. The bath of claim 3 wherein said organic polymer is a polyvinyl alcohol having a molecular weight from about 5,000 to 20,000.

5. The bath of claim 1 wherein said brightening agent comprises 3-(4-hydroxybenzylidene)3-aminopyridine.

6. The bath of claim 1 wherein said brightening agent comprises 1-(4-hydroxybenzylidene)aniline.

7. The bath of claim 3 wherein said azomethine comprises 3-(4-hydroxybenzylidene)3-aminopyridine or 1-(4-hydroxybenzylidene)aniline and said organic polymer comprises polyvinyl alcohol having a molecular weight from about 5,000 to 20,000, said polyvinyl alcohol being present in an amount from about 0.05 to 0.5 gram per liter of bath.

8. An additive for an aqueous cyanide zinc electroplating bath consisting essentially of from about 1:1 to 50:1 parts by weight of an aromatic azomethine of the gen-

8

eral formula  $RCH=NX$  wherein R and X are selected from the group consisting of phenyl, naphthyl and pyridyl and at least one of the groups R and X has substituted therein at least one substituent selected from the group consisting of  $-NH_2$ ,  $-COOH$ ,  $-OH$ ,  $-SO_3H$  and alkoxy and a bath-soluble organic polymer selected from the group consisting of polyvinyl alcohol, polyethyleneimine, gelatin, and peptone, said additive being soluble in said bath.

9. The composition of claim 8 wherein said azomethine is 3-(4-hydroxybenzylidene)3-aminopyridine or 1-(4-hydroxybenzylidene)aniline and said organic polymer is polyvinyl alcohol having a molecular weight of about 16,800.

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