United States Patent Office 3,734,839 Patented May 22, 1973

3,734,839

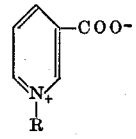
ALKALINE CYANIDE ZINC ELECTROPLATING

Paul Jean Hoyer and John Derek Rushmere, Wilmington, Del., assignors to E. I. du Pont de Nemours and Company, Wilmington, Del.

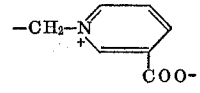
No Drawing. Filed Sept. 30, 1971, Ser. No. 185,348
Int. Cl. C23b 5/10
U.S. Cl. 204—55 Y 18 Claims

ABSTRACT OF THE DISCLOSURE

Aqueous, alkaline cyanide zinc electroplating baths and processes are provided which electrodeposit bright zinc at low cyanide concentrations by using as an addition agent a combination of polyethylenimine having a molecular weight between about 600 and 60,000 and a quaternary pyridine compound of the formula:



wherein R is alkyl, alkenyl or alkynyl of 1 to 4 carbon atoms, benzyl and substituted benzyl wherein the substituent is at least one of alkyl of 1 to 4 carbon atoms, halogen, cyanide, alkoxy of 1 to 4 carbon atoms, phenyl and



or a hydrohalide salt thereof,

the weight ratio of polyethylenimine to quaternary pyridine compound being within the range of 10:1 to 1:100. The electroplating bath has a weight ratio of cyanide to zinc within the range of 0.1–3.5:1, preferably about 1:1.

BACKGROUND OF THE INVENTION

Field of invention

This invention relates to zinc electroplating baths and processes and more particularly to alkaline, cyanide zinc electroplating baths and processes.

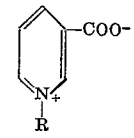
Prior art

Most of the zinc electroplating today is carried out from alkaline cyanide baths having high cyanide concentrations, i.e., greater than about 35 grams per liter. Many materials have been disclosed in the art for use as brighteners in these baths, including aldehydes, polyvinyl alcohols, polyethylenimines (U.S. Pat. 3,393,135) and quaternary nitrogen compounds (U.S. Pats. 3,318,787 and 3,411,996).

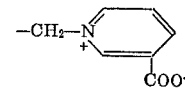
There are occasions when it is desired to electroplate zinc at lower cyanide concentrations. While the aldehyde brighteners are effective at these lower concentrations, they are unstable and necessitate frequent replenishment. On the other hand, the known permanent-type brighteners, i.e., the above polyvinyl alcohols, polyethylenimine and quaternary nitrogen compounds, do not give a fully bright zinc plate at the lower concentrations. Thus, there is a need in the art for a brightening system which will give a fully bright zinc plate at low cyanide levels and which can be used to make a running conversion from high cyanide levels to low cyanide levels without sacrificing zinc brightness.

SUMMARY OF THE INVENTION

According to the present invention there is provided an aqueous, alkaline cyanide zinc electroplating bath which has the improvement comprising: having added to said bath, in an amount effective to yield a zinc deposit of improved brightness, a combination of polyethylenimine having a molecular weight between about 600 and 60,000 and a quaternary pyridine compound of the formula:



wherein R is alkyl, alkenyl or alkynyl of 1 to 4 carbon atoms, benzyl and substituted benzyl wherein the substituent is at least one of alkyl of 1 to 4 carbon atoms, halogen, cyanide, alkoxy of 1 to 4 carbon atoms, phenyl and

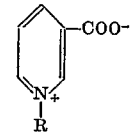


or a hydrohalide salt thereof,

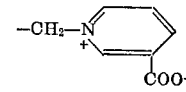
the weight ratio of polyethylenimine to quaternary pyridine compound being within the range of 10:1 to 1:100 and said bath having a weight ratio of cyanide to zinc within the range of 0.1–3.5:1.

There is also provided an improved zinc electroplating process which comprises electroplating zinc from the above-described bath.

There is further provided an aqueous addition agent for an alkaline electroplating bath consisting essentially of an aqueous solution at a pH between 4.5 and 8 of a combination of polyethylenimine having a molecular weight between about 600 and 60,000 and a quaternary pyridine compound of the formula:



wherein R is alkyl, alkenyl or alkynyl of 1 to 4 carbon atoms, benzyl and substituted benzyl wherein the substituent is at least one of alkyl of 1 to 4 carbon atoms, halogen, cyanide, alkoxy of 1 to 4 carbon atoms, phenyl and



or a hydrohalide salt thereof,

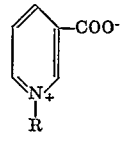
the weight ratio of polyethylenimine to quaternary pyridine compound being within the range of 10:1 to 1:100, said combination being at a concentration in solution of between 1 and 50 percent by weight.

DETAILED DESCRIPTION OF THE INVENTION

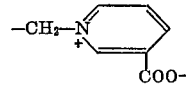
It has now been found that the addition of a combination of polyethylenimine and certain quaternary pyridine compounds to alkaline cyanide zinc electroplating baths results in an improvement in the brightness of the zinc deposit over a wide current density range at low cyanide levels, about 7.5 grams per liter) in the bath without adversely affecting the brightness at high cyanide levels (over 35 grams per liter). Thus, the combination will allow the electroplater to change from the one type bath to another as he desires.

The polyethylenimine useful in the plating bath has a molecular weight range of about 600 to 60,000. Molecular weights below 600 and about 60,000 may also be employed, although those below 600 are not generally available commercially while those much over 60,000 are not sufficiently soluble to be generally useful. Molecular weights between about 600 and 1800 are preferred. Polyethylenimine is added to the bath to give a concentration of 0.005 to 2 grams per liter, preferably 0.02 to 0.2 gram per liter for barrel plating and 0.05 to 0.5 gram per liter for rack plating.

The quaternary pyridine compounds useful in the plating bath have the general formula:



wherein R is alkyl, alkenyl, or alkynyl of 1 to 4 carbon atoms, benzyl and substituted benzyl wherein the substituent is at least one of alkyl of 1 to 4 carbon atoms, halogen, cyanide, alkoxy of 1 to 4 carbon atoms, phenyl and



or a hydrohalide salt thereof.

While particularly preferred compounds are 1-methyl pyridinium 3-carboxylate and 1-benzyl pyridinium 3-carboxylate, other compounds which may be used are 1-(4-methylbenzyl) pyridinium 3-carboxylate, 1-(4-chlorobenzyl) pyridinium 3-carboxylate, 1-allyl pyridinium 3-carboxylate, and 1-propargyl pyridinium 3-carboxylate. These compounds can also be used as the hydrohalide salts such as hydrochloride or hydrobromide. The quaternary pyridine compound is added to the bath to give a concentration of 0.005 to 10 grams per liter, preferably 0.02 to 0.5 gram per liter.

When adding the polyethylenimine and quaternary pyridine compound to the plating bath, the weight ratio of the former to the latter should be within the range of 10:1 to 1:100, preferably about 1:1 to 1:20. The exact ratio used will depend upon the type of plating operation employed, the temperature of operation and the concentration of the bath. Generally, when the concentration of the bath increases, the weight ratio will shift to higher concentrations of the quaternary pyridine compound.

The combination of brightening ingredients used are preferably used in the form of aqueous addition agents for zinc electroplating baths. Additives for the plating baths can be prepared by dissolving the polyethylenimine and quaternary pyridine compound at the desired ratio at a solids content of about 1 to 50 percent by weight, preferably at about 1 to 30 percent by weight. In order to have an addition agent of prolonged shelf stabiilty, the pH of the aqueous solution should be between about 4.5 and 8. At a pH outside this range the quaternary pyridine compound will tend to precipitate or the solution will be unduly unstable. A preferred pH range is 5.5 to 7.

The plating bath is operated according to normal procedures using a sodium cyanide concentration within the range of about 5 to 45 grams per liter, preferably 5 to 20 grams per liter, and most preferably about 7 grams per liter and a zinc concentration of about 5 to 20 grams per liter, and most preferably about 7 grams per liter. As mentioned previously, the higher cyanide concentrations are employed in high cyanide plating baths and the present brightening system is effective at these concentrations to enable the electroplater to convert his bath to lower cyanide levels, i.e., in the range of about 5 to 20 grams per liter. It has been found that the weight ratio of cyanide to zinc should be in the range of about 0.1–3.5:1, preferably about 1:1 to 2:1 at the low cyanide levels. Plating bath temperatures will usually be between 20 and 40° C., however, the brightening system can provide bright deposits over a wide current density range at temperatures up to 55° C.

Other bath-soluble polymers may be added to the plating bath in particular situations to give further improvements in operation. In particular, polyvinyl alcohol or an oxidized polyvinyl alcohol can be used to replace a portion of the polyethylenimine in rack plating to give improved brightness to the zinc deposit.

The brightening system of the present invention has the advantages of good shelf life, good chemical stability in the plating bath and a wide operating range so that the electroplater can make a running conversion from a high cyanide bath to a low cyanide bath without affecting the quality of the plating work.

The invention can be further understood by referring to the following examples in which parts and percentages are by weight unless otherwise indicated.

EXAMPLES 1 TO 8

An aqueous, stock electroplating solution was made having the following composition:

	G./l.
Zn metal(from ZnO)	7.5
Sodium cyanide	7.5
Sodium hydroxide	75
Sodium carbonate	52

Hull Cell panels were plated at 25° C. for 5 minutes at 2 amps. using combinations of polyethylenimine and a quaternary pyridine compound as brighteners in the stock solution. Each panel was bright-dipped in dilute nitric acid before examination. The brightener added and results are shown in Table I.

TABLE I

Example No.	Brightener added	Panel appearance
Control	None	Dull overall.
Do	.2 g./l. PEI, M.W. 1,200	Dull above 2.2 A./dm.²; semibright below 2.2 A./dm.².
Do	.2 g./l. PEI, M.W. 1,800	Do.
Do	.26 g./l. BPC	Semi-bright from high current end to .2 A./dm.²; haze below .2 A./dm.².
1	.2 g./l. PEI, M.W. 1,800; .26 g./l. BPC	Semi-bright from high current end to 4.3 A./dm.²; bright from 4.3 to .2 A./dm.²; light haze below .2 A./dm.².
2	.20 g./l. PEI, M.W. 600; .26 g./l. BPC	Semi-bright high current end to 5.4 A./dm.²; bright from 5.4 A./dm.² to .2 A./dm.²; haze below .2 A./dm.².
3	.20 g./l. PEI, M.W. 1,200; .26 g./l. BPC	Semi-bright from high current end to 4.9 A./dm.²; bright from 4.9 A./dm.² to .3 A./dm.²; haze below .3 A./dm.².
4	.20 g./l. PEI, M.W. 1,200, .26 g./l. trigonelline hydrochloride	Semi-bright above 3.8 A./dm.²; bright from 3.8 A./dm.² to 1.3 A./dm.²; heavy haze below 1.3 A./dm.².
5	.20 g./l. PEI, M.W. 1,200, .26 g./l. 4'-methyl BPC hydrobromide.	Semi-bright above 3.8 A./dm.²; bright 3.8 A./dm.² to .2 A./dm.²; haze below .2 A./dm.².
6	.20 g./l. PEI, M.W. 1,800; 4.0 g./l. BPC	Semi-bright above 6.5 A./dm.²; bright below 6.5 A./dm.²; slight haze below .4 A./dm.².
7	1.1 g./l. PEI, M.W. 1,800; .26 g./l. BPC	Semi-bright above 11 A./dm.²; bright below 11 A./dm.²; slight haze below .3 A./dm.².
8	26.0 g./l. NaCN (total); .2 g./l. PEI, M.W. 600, .26 g./l. BCP.	Whole panel bright, very light light haze above 1.7 A./dm.².

NOTE.—BPC=1-benzyl pyridinium 3-carboxylate; PEI=Polyethylenimine; 4'-methyl BPC=1-(4-methylbenzyl) pyridinium 3-carboxylate hydrobromide.

EXAMPLE 9

Hull Cell panels were plated for 5 minutes at 2 amps. at 25° C., 35° C. and 45° C. from a plating bath of the following composition:

	G./l.
Zinc metal (from ZnO)	7.5
Sodium cyanide	15.0
Sodium bicarbonate	20
Sodium carbonate	132
1-benzyl pyridinium 3-carboxylate	1
Polyethylenimine M.W. 1200	1

The panel plated at 25° C. was bright overall with light haze above 2.6 a./dm.^{2} and dark haze below 2.6 a./dm.^{2}, the panel plated at 35° C. was bright overall with the top 4 mm. of the panel dull and the panel plated at 45° C. was bright overall with light haze below .1 a./dm.^{2}

EXAMPLE 10

Screws barrel plated for 20 minutes at 1.5 amps. at both 25° C. and 35° C. were full bright when plated from a bath of the following composition:

	G./l.
Zinc metal (from ZnO)	7.4
Sodium cyanide	7.6
Sodium hydroxide	77
Sodium carbonate	62
Polyethylenimine—M.W. 1200	.43
1-benzyl pyridinium 3-carboxylate	.43

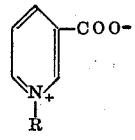
EXAMPLE 11

Screws barrel plated at 25° C. for 20 minutes at 1.5 amps. were liquid bright when plated from a bath of the following composition:

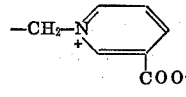
	G./l.
Zinc metal (from ZnO)	7.5
Sodium cyanide	7.5
Sodium hydroxide	75
Sodium carbonate	52
Polyethylenimine—M.W. 1200	.047
1-benzyl pyridinium 3-carboxylate	.047

What is claimed is:

1. In an aqueous alkaline cyanide zinc electroplating bath the improvement comprising: having added to said bath, in an amount effective to yield a zinc deposit of improved brightness, a combination of polyethylenimine having a molecular weight between about 600 and 60,000 and a quaternary pyridine compound of the formula:



wherein R is alkyl, alkenyl or alkynyl of 1 to 4 carbon atoms, benzyl and substituted benzyl wherein the substituent is at least one of alkyl of 1 to 4 carbon atoms, halogen, cyanide, alkoxy of 1 to 4 carbon atoms, phenyl and



or a hydrohalide salt thereof, the weight ratio of polyethylenimine to quaternary pyridine compound being within the range of 10:1 to 1:100, said bath having a weight ratio of cyanide to zinc within the range of 0.1–3.5:1, and said polyethylenimine being at a concentration within the range of 0.005 to 2 grams per liter.

2. The zinc electroplating bath of claim 1 wherein the polyethylenimine molecular weight is within the range of about 600 and 1800 which is at a concentration within the range of 0.005 to 2 grams per liter.

3. The zinc electroplating bath of claim 1 wherein the quaternary pyridine compound is at a concentration within the range of 0.005 to 10 grams per liter.

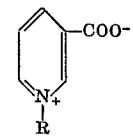
4. The zinc electroplating bath of claim 1 wherein the quaternary pyridine compound is 1-benzyl pyridinium 3-carboxylate.

5. The zinc electroplating bath of claim 1 wherein the ratio of polyethylenimine to quaternary pyridine compound is about 1:1 to about 1:10.

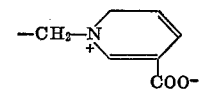
6. The zinc electroplating bath of claim 1 wherein the ratio of cyanide to zinc is about 1:1 to about 2:1.

7. In an aqueous alkaline cyanide zinc electroplating bath the improvement comprising: having added to said bath a combination of polyethylenimine having a molecular weight within the range of about 600 and 1800 and 1-benzyl pyridinium 3-carboxylate, at a weight ratio within the range of about 1:1 to 1:20 and each at a concentration within the range of about 0.02 to 0.5 gram per liter, said bath having a weight ratio of cyanide to zinc of 1:1 at a cyanide concentration as sodium cyanide of about 5 to 20 grams per liter.

8. In a process for electrodepositing zinc from an aqueous, alkaline cyanide electroplating bath, the improvement comprising: adding to said bath in an amount effective to yield a zinc deposit of improved brightness a combination of polyethylenimine having a molecular weight between about 600 and 60,000 and a quaternary pyridine compound of the formula:



wherein R is alkyl, alkenyl or alkynyl of 1 to 4 carbon atoms, benzyl and substituted benzyl wherein the substituent is at least one of alkyl of 1 to 4 carbon atoms, halogen, cyanide, alkoxy of 1 to 4 carbon atoms, phenyl and



or a hydrohalide salt thereof,
the weight ratio of polyethylenimine to quaternary pyridine compound being within the range of 10:1 to 1:100, maintaining said bath at a weight ratio of cyanide to zinc within the range of 0.1–3.5:1, and said polyethylenimine being at a concentration within the range of 0.005 to 2 grams per liter.

9. The process of claim 8 wherein the polyethylenimine molecular weight is within the range of of about 600 to 1800 and wherein the polyethylenimine is added to give a concentration within the range of 0.005 to 2 grams per liter.

10. The process of claim 8 wherein the quaternary pyridine compound is added to give a concentration within the range of 0.005 to 10 grams per liter.

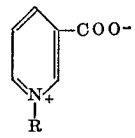
11. The process of claim 8 wherein the ratio of polyethylenimine to quaternary nitrogen compound is about 1:1 to about 1:10.

12. The process of claim 8 wherein the ratio of cyanide to zinc is about 1:1 to about 2:1.

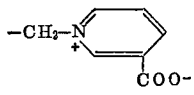
13. In a process for electrodepositing zinc from an aqueous, alkaline, cyanide electroplating bath, the improvement comprising: electroplating zinc from the electroplating bath of claim 7.

14. An aqueous addition agent for an alkaline electroplating bath consisting essentially of an aqueous solution at a pH between 4.5 and 8 of a combination of polyethylenimine having a molecular weight between about 600

and 60,000 and a quaternary pyridine compound of the formula:



wherein R is alkyl, alkenyl or alkynyl of 1 to 4 carbon atoms, benzyl and substituted benzyl wherein the substituent is at least one of alkyl of 1 to 4 carbon atoms, halogen, cyanide, alkoxy of 1 to 4 carbon atoms, phenyl and



or a hydrohalide salt thereof,

the weight ratio of polyethylenimine to quaternary pyridine compound being within the range of 10:1 to 1:100, said combination being at a concentration in solution of between 1 and 50 percent by weight.

15. The aqueous addition agent of claim **14** wherein the solution is at a pH between 5.5 and 7.

16. The aqueous addition agent of claim **15** wherein the polyethylenimine molecular weight is within the range of about 600 and 1800.

17. The aqueous addition agent of claim **16** wherein the quaternary pyridine compound is 1-benzyl pyridinium 3-carboxylate.

18. The aqueous addition agent of claim **17** wherein the ratio of polyethylenimine to 1-benzyl pyridinium 3-carboxylate is within the range of about 1: to 1:20.

References Cited

UNITED STATES PATENTS

3,318,787	5/1967	Rindt et al.	204—55 Y
3,411,996	11/1968	Rushmere	204—55 Y X
3,472,743	10/1969	Rushmere	204—55 Y

FREDERICK C. EDMUNDSON, Primary Examiner

U.S. Cl. X.R.

204—Dig 2

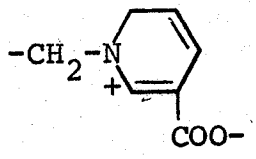
PO-1050
(5/69)

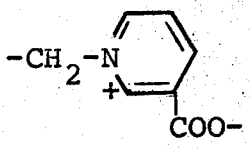
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,734,839 Dated May 22, 1973

Inventor(s) Paul Jean Hoyer and John Derek Rushmere

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 6, line 45, "  " should read

--  --.

Column 8, line 11, "1:" should read --1:1--.

Signed and sealed this 5th day of March 1974.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents