United States Patent Office 2,989,449 Patented June 20, 1961

2,989,449

ELECTRODEPOSITION OF ZINC

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No Drawing. Filed Apr. 6, 1960, Ser. No. 20,259
7 Claims. (Cl. 204—55)

This invention relates to an improvement in the electrodeposition of zinc and, more particularly, this invention is concerned with depositing bright zinc plates from aqueous alkaline cyanide-zinc solutions containing a novel brightening additive.

Zinc electroplated onto base metals from a cyanide-zinc electrolyte is usually dull and dark in appearance. The use of brightening additives is necessary to obtain desirable zinc plates that have high luster and a blue-white color.

The problem of finding a combination of ingredients that will function correctly as brightening agents in aqueous alkaline plating solutions is complicated because of solubility, discoloration, stability and other factors, and to date these difficulties have only been partially overcome. Accordingly, past efforts have developed brightening agents that are unsatisfactory because of their inferior performance over a wide current density range due principally to the difficulties encountered in maintaining an effective combination of ingredients in the bath. The plating bath cannot be controlled because of these difficulties and the continuous use of the bath will not deposit bright zinc plates.

Many of the additives now being employed in cyanide-zinc plating baths contain several brighteners. In addition to the principal brighteners, an additive may contain one or more extender or booster brighteners to prolong the life of the bath and to impart superior brightening effects to the plates. Most of these high quality additives are available in the form of solids or slurries. Measuring and handling such additives is undesirable because they must be initially dissolved and otherwise manipulated before being added to the bath.

Many of the desirable ingredients used in cyanide-zinc plating baths are organic and immiscible in water, even in small amounts. For example, some of the aromatic aldehydes are excellent brighteners but require solubilizing. The use of additional organic ingredients as extender or booster brighteners requires a unique combination of ingredients if zinc plates of superior brightness are to be produced.

A single-phase liquid additive containing water and the necessary organic ingredients that are normally immiscible in water offers distinct and obvious advantages. Such an additive can be added directly to aqueous cyanide-zinc plating baths without any of the ingredients separating. It has been found that when certain amounts of water and an alkali metal thiocyanate are added to a combination of conventional brighteners and a protective colloid, a single-phase liquid can be prepared.

It is an object of the present invention to provide a single-phase liquid additive that will demonstrate high brightening activity in cyanide-zinc plating processes.

It is another object of the present invention to provide a single-phase liquid additive that may be readily added to an aqueous alkaline cyanide-zinc plating bath and remain in solution.

It is a further object of the present invention to provide a single-phase liquid additive that may be effectively used in an aqueous alkaline cyanide-zinc plating bath over a relatively broad current density range.

These and other objects are accomplished by employing 10–20% of an alkali metal thiocyanate and 20–70% water in combination with several organic brighteners, solvents and a protective colloid.

Typical single-phase liquid additives can be prepared from the below-listed ingredients or their equivalents which additives include 20–70% water and 10–20% of an alkali metal thiocyanate.

5–25% of an alicyclic alcohol or ketone
2–10% of a protective colloid
6–20% of a water miscible lower (1–6 carbon atoms) aliphatic alcohol
0.05–1.0% polyvinyl alcohol
5–25% of a substituted aromatic aldehyde

Percentages in the above typical formulations and throughout the specification are by weight.

As noted above, most superior brighteners contain a substituted aromatic aldehyde. Anisaldehyde is a suitable brightener, but other and related brighteners are equivalents thereof in the present invention. Among the equivalents are: veratraldehyde, piperonal, hydroxybenzaldehyde and the like. Hydroxybenzaldehyde is not quite as effective as anisaldehyde, but it and the above-listed equivalents can be used either alone or in combination wtih one another. Anisaldehyde is preferred and it produces high luster deposits, but the use of extender or booster brighteners is necessary for optimum results. An alicyclic alcohol or ketone and a small amount of polyvinyl alcohol function as extender or booster brighteners in combination with substituted aromatic aldehydes. The alicyclic compounds also assist to broaden the bright plating current density range.

The alicyclic compounds particularly useful as booster and extender brighteners in the presently described additive include those alicyclic alcohols and ketones having five to seven, preferably six, ring members. The best alicyclic alcohols are cyclohexanol, 2-methyl cyclohexanol and trimethyl cyclohexanol; cyclohexanol is preferred. The alicyclic ketones include cyclohexanone, 2-methyl cyclohexanone, 4-methyl cyclohexanone and trimethyl cyclohexanone. Of these alicyclic ketones, cyclohexanone is preferred. Additional alicyclic compounds include cyclopentanol, cycloheptanol, alicyclic glycols or alicyclic diols, alicyclic mono and di ethers such as tetrahydrofuran and 2,4-dioxane; other equivalents include the ketones disclosed in U.S. Patent No. 2,600,352, and the cyanhydrins of these ketones.

Both the aldehyde and alicyclic compound require solubilizing in aqueous cyanide-zinc plating baths, and these compounds should be solubilized before adding them to the plating bath.

Both of the above compounds are known to be soluble in alcohols, and 6–18% of a lower aliphatic alcohol that is miscible with water will satisfactorily solubilize both the aromatic aldehyde and the alicyclic alcohol or ketone. Those alcohols having 1–6 carbon atoms, such as methanol, ethanol, propanol, tertiary butanol and the like, are satisfactory, with isopropanol being preferred. Other equivalents, such as tetramethlethylenediamine, can be used as a solubilizer for the aromatic aldehyde and the alicyclic compound.

Polyvinyl alcohol is described in the prior art as being useful in cyanide-zinc baths and functions as a booster or extender brightener in combination with cyclohexanone. Polyvinyl alcohols in general are suitable for use in the present invention and they may vary widely in characteristics. Where 90% or more of the acetate groups are hydrolyzed to hydroxyl groups, the resulting polyvinyl alcohol is generally referred to as a "completely hydrolyzed" grade. Where fewer than 90% of the acetate groups are so hydrolyzed (or alcoholized), such an alcohol is usually denoted as "partially hydrolyzed". In addition, the molecular weight of the polyvinyl alco-

hol is likewise not critical, since most commercial polyvinyl alcohols are water soluble. The average molecular weight may vary from about 10,000 to 200,000 or more.

The examples herein refer to completely hydrolyzed polyvinyl alcohols having average molecular weights of about 100,000 to 150,000, and such alcohols comprise about 10% by weight of an aqueous solution. On a dry weight basis, the amount of the polyvinyl alcohol should be 0.05 to 1.0% by weight of the single-phase liquid additive. Carboxymethylcellulose can be used as an equivalent of polyvinyl alcohol, although the latter is preferred.

The combination of ingredients that form a single-phase liquid additive includes a protective colloid that serves to improve coverage under barrel plating conditions at low current densities and facilitates the initial formation of zinc deposit. Protective colloids are often used in cyanide-zinc plating baths and gelatin is preferred, although gum arabic, gum tragacanth, agaragar, peptone soluble starch and other colloids well known in the art are suitable.

In the past, it has been particularly difficult to solubilize the protective colloid in the presence of the brighteners and other constituents. The combination of an alkali metal thiocyanate and water has a unique action in this respect and a single-phase liquid additive containing the above-listed combination of ingredients can be prepared only if water and the thiocyanate compound are used. In particular, the protective colloid will precipitate in the presence of water and alicyclic alcohol or ketone when the alcohol is added to solubilize the alicyclic compound. When additional water is added, together with polyvinyl alcohol, the mixture separates into three layers with the middle layer being an emulsion of the upper organic layer and the lower aqueous layer. The precipitate will slowly redissolve in the aqueous layer.

If the aliphatic alcohol is omitted from the above typical brightening solutions, two layers are formed, with the upper layer being largely organic and the lower layer being predominantly water with dissolved thiocyanate and polyvinyl alcohol.

An appreciable amount of water (20–70% by weight) must be present with the alkali metal thiocyanate in additives that contain conventional organic brighteners and a protective colloid. As noted above, there are numerous equivalents for the brighteners and protective colloid. The essential feature of the present invention is the formation of a single-phase liquid additive through the use of 10–20% of an alkali metal thiocyanate together with 20–70% water. The remainder of the additive can be the combination of organic brightening agents and protective colloids suggested by the above formulations. These formulations give excellent results, but other formulations that include organic brighteners and protective colloids will be benefited through the use of water and alkali metal thiocyanate.

Example 1

An incomplete brightener formulation was prepared containing:

	Percent
Anisaldehyde	10
Cyclohexanone	13
Gelatin	3
Polyvinyl alcohol (10% solution)	3
Sodium thiocyanate	15
Water	56

This resulted in a turbid mixture which separated into two liquid phases. Approximately 40% of the total volume was occupied by the red upper layer, or organic layer, and the remainder by an amber layer. The above illustrates effect of omitting the isopropyl alcohol.

In a similar experiment, the gelatin was omitted and about 12.5% isopropyl alcohol was added to the other ingredients of Example 1 present in approximately the same amounts as indicated in that example. A pale yellow liquid was produced which separated into oily droplets when added to an aqueous solution, indicating that a protective colloid is necessary to retain the substituted aromatic aldehyde in solution.

As indicated above, an aliphatic alcohol and protective colloid must be present in the particular combination of ingredients disclosed herein that form superior additives.

Example 2

A second incomplete brightener formulation was prepared by mixing the ingredients in the order shown below:

	Percent
Gelatin	3.0
Water	30.0
Cyclohexanone	13.0
Anisaldehyde	10.0
Isopropyl alcohol	12.5
Polyvinyl alcohol (10% solution)	3.0
Water	38.5

On addition of the isopropyl alcohol, part of the gelatin precipitated. After adding the remaining ingredients, the mixture separated into three layers with the middle layer being an emulsion of the other two liquid layers. After standing several days, the gelatin appeared to slowly redissolve in the lower (aqueous) layer. This example illustrates the effect of omitting the alkali metal thiocyanate.

The importance of developing a single-phase liquid additive cannot be overemphasized. If an incorrectly balanced combination of brighteners and solubilizing agents is added to an aqueous zinc cyanide bath, a precipitate or separate oily phase will appear and inferior zinc plates will result, since the full activity of the brightening agents has been restricted.

Example 3

A brightener formulation was prepared by mixing ingredients in the proportions shown below:

	Percent
Gelatin	3.0
Cyclohexanone	13.0
Isopropyl alcohol	12.5
Sodium thiocyanate	15.0
Polyvinyl alcohol (10% solution)	3.0
Anisaldehyde	10.0
Water	43.5

This was a clear, amber single-phase liquid having a rather pleasant odor. A clear solution was obtained on mixing up to 1 volume of water in 2.5 volumes of brightener. The white precipitate resulting from further additions of water redissolved when the brightener concentration had been reduced to approximately 75 ml. of brightener per gallon of water. No oily droplets were visible when the brightener was added to water or to zinc plating solution in concentrations up to approximately 100 ml./gal.

Additions of this brightener to cyanide-zinc plating solutions may be readily made. For instance, the above additive was added to a typical cyanide-zinc solution containing:

	Oz./gal.
Zinc cyanide	8.0
Sodium cyanide	6.4
Sodium hydroxide	10.4
Sodium carbonate	4.0

Additions of concentrations of 2 to 5 ml. of brightener per gallon of plating bath resulted in the production of a zinc plate having a high luster and a blue-white color. As low as 1 ml. of brightener per gallon of the above or other conventional cyanide-zinc plating bath will improve the plates obtained; up to 10 ml. per gallon will improve zinc plates, but more than this amount need not be added.

Example 4

Repeated plating tests of the brightener of Example 3 were made continuously in a 2-gallon laboratory barrel

plating unit over a period of several days to determine the rate at which the brightener was consumed. These tests indicated that brightener additions of ca. 6 ml./gal. were required to maintain full brightness of the zinc plate for an 8-hour day, or 0.08 gram of anisaldehyde per hour. In similar tests of an additive containing anisaldehyde and gelatin, but no other brighteners, the anisaldehyde was consumed at the rate of 0.14 gram per hour. This illustrates the effectiveness of the other components in the formulation of Example 3 in reducing the anisaldehyde consumption. Potassium and other alkali metal thiocyanates are substituted for the sodium compound in like amounts with the same results.

Example 5

A brightener formulation was prepared containing the following ingredients:

	Percent
Sodium thiocyanate	15.0
Gelatin	8.0
Isopropyl alcohol	13.0
Cyclohexanone	15.0
Polyvinyl alcohol (dry weight basis)	0.2
Anisaldehyde	10.0
Water	38.8

The resulting solution was a single-phase liquid having a clear amber color. Deposits from a zinc plating bath to which two ml. of this brightener per gallon of plating solution had been added were brilliant and had a blue-white color.

Example 6

A brightener formulation was prepared containing the following ingredients:

	Percent
Sodium thiocyanate	15.0
Gelatin	8.0
Cyclohexanol	5.0
Isopropyl alcohol	17.5
Polyvinyl alcohol (dry weight basis)	0.3
Acetic acid	0.6
Anisaldehyde	15.0
Water	38.6

The resulting solution was a single phase liquid having a clear amber color. When added to the cyanide-zinc plating bath, a high luster zinc plate is produced. A small amount of acetic acid was added to decompose inorganic impurities in the technical grade of gelatin used. It can be omitted if desired.

Example 7

A brightener formulation was prepared containing the following ingredients:

	Percent
Sodium thiocyanate	15.0
Gelatin	8.0
Isopropyl alcohol	12.5
Cyclohexanol	10.0
Polyvinyl alcohol (dry weight basis)	0.3
Acetic acid	0.6
Anisaldehyde	15.0
Water	38.6

The resulting solution was a single phase liquid having a clear amber color. Deposits from a zinc plating bath to which two ml. of the brightener per gallon of plating solution had been added were brilliant and had a blue-white color. Repeated plating tests, similar to those described in Examples 3 and 4 indicated that additions of ca. 3 ml./gal. of this brightener (0.06 g./gal. anisaldehyde per hour) were required to maintain full brightness of the zinc plate for an 8-hour day. The above formulation is the preferred additive in the present invention.

Example 8

A brightener formulation was prepared containing the following ingredients:

	Percent
Sodium thiocyanate	14.2
Gelatin	7.5
Isopropyl alcohol	5.7
Cyclohexanol	21.2
Polyvinyl alcohol (dry weight basis)	0.3
Acetic acid	0.6
Anisaldehyde	14.2
Water	36.3

The resulting product was a clear amber single phase solution which promotes the formation of high luster zinc plates.

The alicyclic alcohol or ketone and the polyvinyl alcohol function as booster or extender brighteners. Less anisaldehyde per ampere hour is thereby required. Of greater significance is the fact that the brightness does not decrease rapidly as the anisaldehyde becomes depleted. For example, the plating bath maintained with the liquid brightener containing these constituents will produce fair quality deposits upon resuming operation even after standing 16 hours or over a week-end. In contrast, other brighteners are largely decomposed under these conditions and plates deposited from solutions containing these additives are relatively dull. Larger additions are then required to restore the bath to full-bright plating performance.

This application is a continuation-in-part of our application Serial No. 771,195, filed November 3, 1958, now abandoned.

We claim:

1. A single-phase liquid additive for an aqueous alkaline cyanide-zinc plating bath comprising by weight, 10–20% of an alkali metal thiocyanate, 5–25% of an alicyclic compound selected from the group consisting of alicyclic alcohols and alicyclic ketones, 2–10% of a protective colloid, 6–20% of a water miscible aliphatic alcohol having 1–6 carbon atoms, 0.50–1.0% polyvinyl alcohol; 5–25% of a substituted aromatic aldehyde selected from the group consisting of anisaldehyde, veratraldehyde, hydroxybenzaldehyde, piperonal and mixtures thereof and 20–70% water.

2. A single-phase liquid additive for an aqueous alkaline cyanide-zinc plating bath comprising by weight, 10–20% of an alkali metal thiocyanate, 5–25% cyclohexanol, 2–10% of a protective colloid, 6–20% of a water miscible aliphatic alcohol having 1–6 carbon atoms, 0.05–1.0% polyvinyl alcohol; 5–25% of a substituted aromatic aldehyde selected from the group consisting of anisaldehyde, veratraldehyde, hydroxybenzaldehyde, piperonal and mixtures thereof and 20–70% water.

3. A single-phase liquid additive for an aqueous alkaline cyanide-zinc plating bath comprising by weight, 10–20% of an alkali metal thiocyanate, 5–25% cyclohexanone, 2–10% of a protective colloid, 6–20% of a water miscible aliphatic alcohol having 1–6 carbon atoms, 0.5–1.0% polyvinyl alcohol; 5–25% of a substituted aromatic aldehyde selected from the group consisting of anisaldehyde, veratraldehyde, hydroxybenzaldehyde, piperonal and mixtures thereof and 20–70% water.

4. A single-phase liquid additive for an aqueous alkaline cyanide-zinc plating bath comprising by weight, 10–20% of an alkali metal thiocyanate, 5–25% of an alicyclic compound selected from the group consisting of alicyclic alcohols and alicyclic ketones, 2–10% of a protective colloid, 6–20% of a water miscible aliphatic alcohol having 1–6 carbon atoms, 0.05–1.0% polyvinyl alcohol; 5–25% anisaldehyde and 20–70% water.

5. A single-phase liquid additive for an aqueous alkaline cyanide-zinc plating bath comprising by weight, 10–20% of an alkali metal thiocyanate, 5–25% cyclohexanol, 2–10% of a protective colloid, 6–20% of a water misci-

ble aliphatic alcohol having 1–6 carbon atoms, 0.05–1.0% polyvinyl alcohol; 5–25% anisaldehyde and 20–70% water.

6. A single-phase liquid additive for an aqueous alkaline cyanide-zinc plating bath comprising by weight, 10–20% of an alkali metal thiocyanate, 5–25% cyclohexanol, 2–10% of a protective colloid, 6–20% isopropanol, 0.05–1.0% polyvinyl alcohol; 5–25% anisaldehyde and 20–70% water.

7. A single-phase liquid additive for an aqueous alkaline cyanide-zinc plating bath comprising by weight, 10–20% sodium thiocyanate, 5–25% cyclohexanol, 2–10% gelatin, 6–20% isopropanol, 0.05–1.0% polyvinyl alcohol, 5–25% anisaldehyde and 20–70% water.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 2,989,449 June 20, 1961

Robert W. Mackey et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 6, line 41, for "0.50-1.0%" read -- 0.05-1.0% --; lines 59 and 60 for "0.5-1.0%" read -- 0.05-1.0% --.

Signed and sealed this 14th day of November 1961.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

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