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TREATMENT OF AQUEOUS ALKALI CYANIDE ELECTROLYTES

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The present invention relates to the treatment of electrolytes and has particular reference to the treatment of aqueous alkali cyanide electrolytes to purify them and to adjust the components thereof to achieve improved electroplating.

One of the major problems arising in the operation of aqueous alkali cyanide electrolytes in electroplating is the tendency of the electrolyte to become unbalanced whereby it no longer produces satisfactory electroplating and the speed of metal deposition is materially reduced. In particular, the carbonates tend to build up rapidly to a great excess which may amount to from 20 to 25 ounces of alkali meal carbonate per gallon of electrolyte. This is far above the desired carbonate content which usually varies from 4 to 8 ounces per gallon, and preferably not greater than 10 ounces per gallon.

Increase of the carbonate content in alkali cyanide electrolytes has been particularly severe in plating installations wherein the rinse water applied to the plated members to wash off the dragout cyanide solution is returned to the plating tank. Previously, it was a common practice to discard the rinse water containing the electrolyte dragout to a drain. Thus, in the operation of a conveyorized plating line, as previously practiced, the dragout losses were sufficient to equal a complete turnover of the electroplating electrolyte every 3 to 6 months on the average. Such dragout tended to keep the carbonate content of a cyanide electrolyte at a low level. Consequently there was no problem of excessive carbonate build-up as there is today when the rinse water is returned to the plating tank.

Also, due to present day high production demands the operating conditions and components of the electrolyte baths have been changed to meet desired increased plating rates. Shorter plating times are used today than formerly and this necessitates operating the electrolyte at a higher plating current density. Higher plating current densities usually are obtained by increasing the electrolyte temperature, agitating the electrolyte by air bubbling or by mechanical agitation, and increasing the concentration of the components of the electrolyte. These changes in operating conditions and compositions have been important features in the increased rate at which the carbonate concentration is built up in cyanide electroplating baths. In a cyanide bath operated with air or mechanical agitation the oxygen and carbon dioxide in the air have an appreciable effect on the rate at which the carbonates build up in the bath. Higher operating temperatures and higher concentrations of the components of the bath, especially the alkali metal cyanide and alkali metal hydroxide, increase the rates at which these components are converted to carbonates in the cyanide plating bath.

Thus, the present-day practice of returning the rinse water to the electroplating tank and the changes in operating conditions to meet higher production demands has resulted in a great increase in the rate of carbonate build up in cyanide electroplating baths.

It is well known to those in the electroplating industry that organic impurities tend to accumulate in plating tanks. Such organic impurities have been found in many

cases to affect detrimentally the quality of the electrodeposited metal. Such organic contaminants may comprise material leached out of the tank lining and rack coatings.

Air, contaminated with oil and organic dust particles, also contributes a substantial amount of organic impurities to the electrolyte, particularly where air agitation of the electrolyte is employed. In some cases organic matter may be added inadvertently or in some cases it may be the result of the decomposition of organic addition agents present in the electrolyte.

In many cases, the work being plated in the electrolyte drags in some amounts of organic and other impurities such as chromates and sulfates. The chromates and sulfates are generally undesirable components and should be kept at a very low concentration in the alkali cyanide plating bath.

The following reactions have been found to occur in the electrolyte and result in depletion of certain constituents of the plating bath while simultaneously increasing the carbonate content.

(1) $2NaCN+CO_2+H_2O \rightarrow Na_2CO_3+2HCN$

(2) $2NaOH+CO_2 \rightarrow Na_2CO_3+H_2O$

(3)
$NaCN+2H_2O \rightarrow NaHCOO+NH_3$
$4NaHCOO+2NaOH \rightarrow (NaCOO)_2+2Na_2CO_3+3H_2$
$(NaCOO)_2+2NaOH \rightarrow 2Na_2CO_3+H_2$

(4) $2NaCN+2H_2O+2NaOH+O_2 \rightarrow 2Na_2CO_3+2NH_3$

The above equations relate to the reactions of sodium compounds but similar reactions apply to the potassium compounds. It will be observed that in Equation 1 sodium cyanide is depleted, while in Equation 2 sodium hydroxide is depleted. In Equations 3 and 4, sodium cyanide and sodium hydroxide are destroyed by the carbonate forming reaction.

It is well known that there is a specified range of proportions within which the components of an electrolyte must be maintained in order to produce the best plating results. If any of the components of an alkaline cyanide electrolyte, such as the alkali metal hydroxide, alkali metal cyanide or alkali metal carbonate, depart from specification, then the plating operation will be less satisfactory and the quality and speed of plating will invariably suffer in proportion to such departure from the desired proportions. Inasmuch as most of the carbonate forming reactions deplete the alkali metal cyanide and alkali metal hydroxide, there not only results an undesirable excess of carbonate but also a reduction of the free alkali metal cyanide present in the electrolyte and an undesirable change in the alkalinity of the electrolyte.

While it has been proposed in the art to add some one ingredient, such as gypsum (calcium sulfate), magnesium carbonate, barium hydroxide, or calcium hydroxide to an electrolyte in order to precipitate magnesium, barium or calcium carbonates therefrom, the treated electrolyte is not in proper balance or adjustment with respect to free cyanide or the hydroxide content. In some cases the addition of such carbonate removing agents has required a plurality of succeeding adjusting treatments of the electrolyte in order to bring it into reasonable operating balance.

The addition of calcium hydroxide alone, for example, to a plating electrolyte has been found to result in a number of unsatisfactory features. In many cases, the calcium carbonate formed thereby is in the form of a colloidal or slimy precipitate that settles out of the electrolyte extremely slowly and is difficult to remove therefrom by filtration.

The object of this invention is to provide a process for treating aqueous alkali cyanide electrolytes with a single composition in order to remove excessive car-

bonates and to return the electrolyte to within the desired operating specification.

Another object of the present invention is to provide a process for treating aqueous alkali cyanide electrolytes with a composition comprising calcium cuprous cyanide to remove excessive carbonates and organic impurities therefrom.

A still further object of the invention is to provide a process for treating an aqueous alkali cyanide electrolyte to remove therefrom an excess of carbonates, organic impurities, chromates, and sulfates by treating said electrolyte with a composition comprising calcium cuprous cyanide, calcium cyanide, calcium oxide, and barium cyanide and/or barium cuprous cyanide.

Other and further objects of the invention will in part be obvious and will in part appear hereinafter.

In the attainment of the foregoing objects and in accordance with the present invention, there is provided a process for purifying an aqueous alkali cyanide electrolyte to remove therefrom an axcess of alkali metal carbonate and organic impurities. Broadly, the process comprises admixing the aqueous electrolyte with a composition comprising calcium cuprous cyanide in an amount sufficient to react with the excess alkali metal carbonate and form a precipitate of calcium carbonate. The electrolyte and the added calcium cuprous cyanide are agitated until the calcium carbonate precipitate-forming reaction is substantially complete. The precipitate which settles out, occluding organic impurities, then is separated from the treated electrolyte.

Certain aqueous alkali cyanide electrolyte electroplating solutions, in addition to having an excess of carbonates and containing organic impurities, also contain relatively small amounts of chromates and sulfates. Such chromates and sulfates may be removed from the electrolyte by treating it with a calcium cuprous cyanide composition containing from 0.01% to 5% by weight of barium cuprous cyanide and/or barium cyanide.

If the electrolyte also is deficient in free alkali metal cyanide and in alkali metal hydroxide, the electrolyte may be returned to specification by treating it with a composition comprising from 84.99% to 5% by weight of calcium cuprous cyanide, from 5% to 45% by weight of calcium cyanide, from 10% to 45% by weight of calcium oxide, and from 0.01% to 5% by weight of barium cyanide and/or barium cuprous cyanide. It will be understood that calcium hydroxide may be used in place of all or a portion of the calcium oxide.

Thus an aqueous alkali cyanide electroplating electrolyte, which is out of desired operating specification by reason of having an excess of alkali metal carbonate, a deficiency of free alkali metal cyanide and alkali metal hydroxide, and containing organic impurities, chromates, and sulfates, may be treated rapidly and effectively to return such electrolyte to within operating specification by adding thereto a composition comprising calcium cuprous cyanide, calcium cyanide, calcium oxide, and barium cyanide and/or barium cuprous cyanide.

The treating composition is added to the electrolyte in an amount sufficient (1) to react with the excess alkali metal carbonate to form a precipitate of calcium carbonate, (2) to react with substantially all the chromates and sulfates to form a precipitate of calcium chromate and calcium sulfate, and (3) to provide additional free alkali metal cyanide to remedy the deficiency of said free alkali metal cyanide in the electrolyte. The composition is agitated vigorously with the electrolyte for a period of time sufficient to permit all the reactions to go substantially to completion with the formation of precipitates. The agitation then is terminated and the liquid mixture is permitted to stand to allow the precipitates to settle out in the form of coarse particles which occlude the organic impurities. The alkalinity or the pH of the liquid electrolyte is maintained at a level imparted by not over substantially 16 ounces per gallon of alkali metal hydroxide. The precipitates which settle out may be separated from the electrolyte in any convenient manner. Thus, in a single brief treatment, an electrolyte that is out of specification may be treated or purified and thereby returned to specification.

The calcium cuprous cyanide employed in the treating compositions of this invention may be prepared in any convenient manner. One method comprises passing hydrogen cyanide through a solution of copper sulfate containing a suspension of calcium carbonate. The reactions involved in such a preparation include:

$$2CuSO_4+4HCN\rightarrow 2CuCN+(CN)_2+2H_2SO_4$$
$$CaCO_3+H_2SO_4\rightarrow CaSO_4+CO_2+H_2O$$
$$CaCO_3+2HCN\rightarrow Ca(CN)_2+H_2O+CO_2$$
$$Ca(CN)_2+CuCN+H_2O\rightarrow CaCu(CN)_3\cdot H_2O$$

Calcium cuprous cyanide suitable for use in accordance with this invention also may be prepared by passing hydrogen cyanide through a solution of copper sulfate containing a suspension of calcium hydroxide. A stable product is obtained if a slight excess of calcium hydroxide is used. The reactions involved in this preparation include:

$$2CuSO_4+4HCN\rightarrow 2CuCN+(CN)_2+2H_2SO_4$$
$$Ca(OH)_2+H_2SO_4\rightarrow CaSO_4+2H_2O$$
$$Ca(OH)_2+2HCN\rightarrow Ca(CN)_2+2H_2O$$
$$Ca(CN)_2+CuCN+H_2O\rightarrow CaCu(CN)_3\cdot H_2O$$

The various ingredients forming the electrolyte treating composition of this invention may be introduced into the electrolyte either in the form of solids or after they have been dissolved in water, preferably deionized water. While the use of chemically pure ingredients is preferred, it has been determined that the presence of minute amounts of carbon, metal oxides, halogen salts and the like may be present in the compositions. When the compositions are employed in solid form, it is preferred that they be finely divided, 20 mesh and finer being the most desirable particle size.

In applying the compositions of this invention to aqueous alkali cyanide electrolytes, it is desirable that the electrolyte be at a temperature of not over 160° F., and preferably at or near room temperature, for example, 70° F. to 80° F. If the calcium cuprous cyanide compositions are added to electrolytes while at 165° F. and higher, any calcium cyanide present in the composition tends to form some resinous polymers such as azulmic acid which will not remove alkali metal carbonates from the electrolyte.

In order to indicate even more fully the advantages and capabilities of the present invention, the following examples are set forth. The parts indicated are by weight unless otherwise indicated.

Examples 1 and 2 illustrate ten compositions suitable for adding to electrolytes which are out of specification. The examples are presented for illustrative purposes only, the invention being limited only as defined in the appended claims.

Example 1

	(a), percent	(b), percent	(c), percent	(d), percent
Calcium cuprous cyanide	98	99.9	95	100
Barium cuprous cyanide	2	0.1	5	0

Example 2

	(a), percent	(b), percent	(c), percent	(d), percent	(e), percent	(f), percent
Calcium cuprous cyanide	35	85	5	40	84.99	5
Calcium cyanide	42	5	45	40	5	45
Calcium oxide	20	10	50	19	10	45
Barium cyanide	3	0	0	0	0.01	0
Barium cuprous cyanide	0	0	0	1	0	5

Example 3

A 1000 gallon tank of electrolyte for copper plating has the following composition:

	Oz./gal.
Free KCN	1.7
K_2CO_3	16.7
KOH	5.2
Cu	5.4

The electrolyte is treated by adding to it 600 pounds of calcium cuprous cyanide. The resulting mixture is agitated for an hour and then allowed to stand quiescent to permit the calcium carbonate precipitate to settle out. After removal of the precipitate the electrolyte has the following composition:

	Oz./gal.
Free KCN	1.6
K_2CO_3	9.6
KOH	5.0
Cu	8.7

The electrolyte is in better balance for electroplating and produces improved copper plating by reason of a decrease in carbonate and an increase in copper metal.

Example 4

A tank containing 500 gallons of a cyanide copper electrolyte is found to contain over 14 ounces per gallon of potassium carbonate and less than 5 ounces per gallon of copper metal. The electrolyte also is contaminated by a substantial amount of organic impurities and sulfates and chromates which render the electrolyte unsatisfactory for plating use. To overcome these defects there is added to the electrolyte 250 pounds of a composition comprising 98% by weight of calcium cuprous cyanide and 2% by weight of barium cuprous cyanide. The resulting mixture is agitated for about one hour during which time a coarse precipitate forms. The precipitate is removed to leave an electrolyte in which the potassium carbonate content has been reduced to about 8 ounces per gallon and the copper metal content increased to about 8 ounces per gallon. The barium cuprous cyanide serves to precipitate out the sulfates and chromates. The precipitates occlude organic impurities present in the electrolyte. On completion of this treatment the electrolyte is in better operating specification.

Example 5

A 100 gallon tank containing an aqueous cyanide copper electrolyte has the following composition:

	Oz./gal.
Free KCN	0.1
K_2CO_3	16.2
KOH	3.8
Cu	7.0

The electrolyte is treated by adding to it a composition comprising 40% by weight of calcium cuprous cyanide, 30% by weight of calcium cyanide and 30% by weight calcium oxide. The resulting mixture is stirred vigorously with a propeller-type stirrer for about two hours and then allowed to stand quiescent. The coarse precipitate which settles out is removed to leave an electrolyte having the following composition:

	Oz./gal.
Free KCN	2.0
K_2CO_3	8.7
KOH	6.4
Cu	8.1

The electrolyte is in better balance for electroplating after this treatment.

Example 6

A tank containing an aqueous cyanide copper electroplating solution has the following composition:

	Oz./gal.
Free NaCN	0.4
Na_2CO_3	12.9
NaOH	4.2
Cu	10.6
Chromates	0.03

The electrolyte is treated at room temperature by adding thereto four ounces per gallon of a composition containing 60% by weight calcium cuprous cyanide, 20% by weight of calcium oxide, 17% by weight of calcium cyanide, and 3% by weight of barium cyanide. The resulting mixture is agitated thoroughly and then is allowed to stand quiescent until the precipitate which forms settles out. Upon removal of the precipitate the electrolyte has the following composition:

	Oz./gal.
Free NaCN	1.1
Na_2CO_3	9.4
NaOH	5.1
Cu	11.3
Chromates	Less than 0.0013

The electrolyte is in better balance for satisfactory electroplating operation.

The treating composition employed in Example 6 contains an excess of barium cyanide above that which is required to remove the chromates present in the electrolyte. The excess barium cyanide precipitates excess sodium carbonate from the electrolyte and, therefore, does not appear in the electrolyte after removal of the precipitates.

Example 7

A tank containing 250 galons of a cyanide copper plating electrolyte is found to contain a carbonate content of above 16 ounces per gallon and a deficiency of free alkali metal cyanide and alkali metal hydroxide. The electrolyte also is contaminated with organic impurities as well as chromates and sulfates. To the electrolyte there is added 8 ounces per gallon of a composition comprising 40% by weight of calcium cuprous cyanide, 30% by weight of calcium cyanide, 29% by weight of calcium oxide, and 1% by weight of barium cyanide. The resulting mixture is agitated thoroughly and then allowed to stand quiescent to permit the precipitates which form to settle out. The precipitate, as a whole, comprises coarse particles and includes calcium carbonate, barium chromate, barium sulfate, and barium carbonate. This treatment reduces the alkali metal carbonate to below 8 ounces per gallon, the chromates and sulfates to less than 0.001 ounce per gallon, and increases the alkali metal cyanide and alkali metal hydroxide to within operating specification whereby improved electroplating results.

While the present invention has been described with particular reference to the preferred embodiments thereof, it will be understood that changes, substitutions, modifications and the like may be made therein without departing from its true scope.

We claim as our invention:

1. In the process of treating an aqueous alkali copper cyanide electrolyte having an excess of carbonate, containing organic impurities and having a deficiency of free alkali metal cyanide, the improvement which comprises adding to the aqueous electrolyte a composition comprising from 85% to 5% by weight of calcium cuprous cyanide, from 5% to 45% by weight of calcium cyanide, and from 10% to 50% by weight of calcium oxide, the composition being added in an amount sufficient (1) to react with only the excess of carbonate to form a precipitate of calcium carbonate, there remaining at least about 4 ounces per gallon of carbonate in the electrolyte, and

(2) to provide additional free alkali metal cyanide to remedy the deficiency thereof, said composition maintaining the pH of the aqueous electrolyte at a level of not over substantially 16 ounces per gallon of alkali hydroxide to promote the rapid settling of the calcium carbonate precipitate in the form of a mass of relatively coarse easily filterable particles which precipitate occludes the organic impurities in the electrolyte, agitating the electrolyte and the added composition until the precipitate-forming reaction is substantially complete and separating the treated electrolyte from the precipitate.

2. In the process of treating an aqueous alkali copper cyanide electrolyte having an excess of carbonate, containing organic impurities, chromates and sulfates, and having a deficiency of free alkali metal cyanide, the improvement which comprises adding to the aqueous electrolyte a composition comprising from 84.99% to 5% by weight of calcium cuprous cyanide, from 5% to 45% by weight of calcium cyanide, from 10% to 45% by weight of calcium oxide, and from 0.01% to 5% by weight of barium cyanide, said composition being added in an amount sufficient (1) to react with only the excess of carbonate to form a precipitate of calcium carbonate, there remaining at least about 4 ounces per gallon of carbonate in the electrolyte, (2) to react with substantially all the chromates and sulfates to form a precipitate of barium chromate and barium sulfate, and (3) to provide additional free alkali metal cyanide to remedy the deficiency thereof, said composition maintaining the pH of the aqueous electrolyte at a level of not over substantially 16 ounces per gallon of alkali hydroxide to promote the rapid settling of the precipitates in a mass of relatively coarse particles which precipitates occlude the organic impurities in the electrolyte, agitating the electrolyte and the added composition until the precipitate-forming reactions are substantially complete, and separating the treated electrolyte from the precipitates.

3. In the process of treating an aqueous alkali copper cyanide electrolyte having an excess of carbonate, containing organic impurities, chromates, and sulfates, and having a deficiency of free alkali metal cyanide, the improvement which comprises adding to the aqueous electrolyte a composition comprising from 84.99% to 5% by weight of calcium cuprous cyanide, from 5% to 45% by weight of calcium cyanide, from 10% to 45% by weight of calcium oxide, and from 0.01% to 5% by weight of barium cuprous cyanide, said composition being added in an amount sufficient (1) to react with only the excess of carbonate to form a precipitate of calcium carbonate, there remaining at least about 4 ounces per gallon of carbonate in the electrolyte, (2) to react with substantially all the chromates and sulfates to form a precipitate of barium chromate and barium sulfate, and (3)

to provide additional free alkali metal cyanide to remedy the deficiency thereof, said composition maintaining the pH of the aqueous electrolyte at a level of not over substantially 16 ounces per gallon of alkali hydroxide to promote the rapid settling of the precipitates in a mass of relatively coarse particles which precipitates occlude the organic impurities in the electrolyte, agitating the electrolyte and the added composition until the precipitate-forming reactions are substantially complete, terminating the agitation and maintaining the electrolyte quiescent to allow the precipitates to settle out, and separating the treated electrolyte from the precipitates.

4. In the process of treating an aqueous alkali copper cyanide electroplating electrolyte containing over 8 ounces per gallon of alkali carbonate, less than 0.8 ounce per gallon of free alkali metal cyanide, and having chromates, sulfates and organic impurities present therein, the improvement which comprises admixing the aqueous electrolyte with a composition comprising a mixture of from 84.99% to 5% by weight of calcium cuprous cyanide, 5% to 45% by weight of calcium cyanide, from 10% to 45% by weight of calcium oxide, and from 0.01% to 5% by weight of barium cyanide, said composition being added in an amount sufficient (1) to provide enough calcium to react with the alkali carbonate in excess of 8 ounces per gallon to produce a calcium carbonate precipitate, (2) to provide enough barium to react with the chromates and sulfates to produce a precipitate of barium chromate and barium sulfate, and (3) to provide alkali metal cyanide in a quantity above 0.8 ounce per gallon but not above 6 ounces per gallon, the composition maintaining the alkalinity of the electrolyte at a level not exceeding that produced with 16 ounces per gallon of sodium hydroxide, agitating the electrolyte and added composition for at least five minutes to allow the precipitate-forming reactions to go to completion, terminating the agitation and maintaining the electrolyte quiescent whereby the precipitates occluding organic impurities settle out, and separating the treated electrolyte from the precipitates.

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