

United States Patent
Sloan

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[54] CARBONATE REMOVAL
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[58] Field of Search204/52 Y, 55 Y, 45, 46;
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[57] ABSTRACT
Removal of carbonate ions from cyanide-containing elec-
troplating baths, or bath rinse solutions by contacting with an
acid ion exchange resin, and liberating the carbon dioxide
formed as off gas.

4 Claims, No Drawings

CARBONATE REMOVAL

BRIEF SUMMARY OF THE INVENTION

Generally, this invention comprises the removal of carbonate ions from cyanide-containing electroplating bath, or bath rinse solutions comprising, in sequence, (1) contacting said solutions with the hydrogen form of a cation exchanger selected from the group consisting of carboxylic, phosphonic and sulfonic ion exchange resins to convert said carbonate ions to carbonic acid; (2) reducing the pressure on said solutions to promote decomposition of said carbonic acid to water and carbon dioxide; and (3) recycling said solutions, reduced in carbonate ion content, to said electroplating bath.

Electroplating of nickel, copper, and other metals frequently utilizes a cyanide ion-containing bath which is usually operated at temperatures in the range of 120° to 160° F., maintained by steam coils or other indirect heating means. Under these conditions, substantial cyanide is oxidized to the carbonate, which is associated with sodium or potassium ions, which are also normal ingredients of the baths.

The presence of a limited amount of carbonate salts in plating baths is not objectionable and, in fact, is desirable, in that the electrical conductivity of the baths is thereby improved. However, excessive amounts adversely affect the quality of the electroplating obtained and, therefore, carbonate concentration is normally controlled by crystallization of carbonates from the plating bath, as by refrigeration or evaporation, or by discarding the plating bath. Discarding can be effected by running the entire bath to the sewer, or by replacing with fresh water the normal "drag-out" of plating solution occurring as a result of plating solution being carried off as surface wetness by articles which have been plated.

Both loss by either blow-down or by drag-out is objectionable, since cyanides constitute a toxicity hazard, as do metal ions which are also a bath ingredient. Moreover, the lost chemicals constitute an appreciable economic loss. The chemical treatments for cyanide wastes, such as electrooxidation, or oxidation with hypochlorite, or chlorine plus caustic, are relatively expensive. Also, the sludges which result from the complex metal cyanides must be disposed of in a suitable manner.

The principal object of this invention is to remove excess carbonates from plating bath solutions followed by return of valuable constituents of the bath, such as cyanide and complex metal cyanides, back to the plating bath system.

This I accomplish by contacting the bath solution with a weak acid ion exchange resin, such as CC-3, a polymer of cross-linked acrylic acid, for example. The hydrogen form of such a resin converts carbonate to carbonic acid, which readily decomposes to water and carbon dioxide, which can then be vented to the atmosphere as off gas. The resin also converts sodium cyanide to hydrogen cyanide, which may remain substantially in solution because of the presence of complex metal cyanides, and the pH of the processed solution. Only a minor conversion of the complex metal cyanides to their corresponding acids occurs, because the hydrogen form of a weak acid ion exchange resin cannot generate an acid greater than its own strength.

The hydrogen cyanide will be neutralized by the normally present and excess basicity in the plating bath, supplemented, if necessary, by the addition of more caustic. Also, the very small amounts of acids corresponding to complex metal cyanides will be neutralized by the basicity of the bath. Since the hydrogen cyanide produced by the resin is poorly ionized, it may be held, to some extent, by the water which is occluded in the ion exchange resin particles. A rinse with an alkali, e.g., sodium or potassium hydroxide, will remove any hydrogen or alkali cyanide in the bed, and preclude hydrogen cyanide release when the exchanger is eventually regenerated with acid.

Weak and intermediate acid ion exchange resins are particularly preferred over strong acid resins in the practice of my invention. If a strong acid resin is utilized, there could be a loss

in useful capacity of the system, because of the complete conversion of complex cyanides to their corresponding acids. Also, the strong acid resins generate more waste, because they require at least two times theoretical acid for proper regeneration, and this excess acid must be neutralized later in a subsequent waste stream. In contrast, the weak acid and intermediate acid resins do not require a large excess of regenerant acid, and what excess there is can be utilized. Thus, if one accumulates the second half of the effluent from a given regeneration, it, of course, contains, substantially, the excess acid. Then, if the recovered acid solution is used as the first solution through a later exchanger requiring regeneration, substantially all of the excess acid is converted to salt. The usual acid addition can then be made, and it displaces the recovered solution from the bed. The second half of this second acid addition is again collected, and the sequence is repeated during the next-occurring regeneration of an exhausted exchanger.

If a strong acid resin is utilized to reduce carbonates, all of the salts in the plating bath or bath rinse will be converted to their corresponding acids. By proper control, the acid solution can be mixed under pressure with untreated bath or rinse in such a manner that the alkali carbonate is neutralized. On exposure to the atmosphere, the carbonic acid will be decomposed to form water and carbon dioxide, which escapes. If the acid stream is not neutralized, or neutralization is incomplete, a low pH results, and considerable HCN will escape, because its solubility decreases markedly with decrease in pH.

The lower the pK_a of the hydrogen form of a resin, the lower the pH of ion exchange-treated plating bath or bath rinse solution. If HCN release is to be retarded, the carbonate removal should be accomplished with the resin having the highest pK_a . Table II, infra, shows that IRC -50, a copolymer of methacrylic acid and divinylbenzene, and having a pK_a 5.9, reduced the pH of a solution from about 12 to the range of 5.7-6.0, and that IRC -84, a polymer of cross-linked acrylic acid, and having a pK_a of 5.3, reduced the pH of the same solution to the range of 4.5-4.9. A phosphonic resin has a pK_a in the 3.0-3.5 range. Strong acids such as sulfonics are not defined in terms of a pK_a value.

When the pH of a cyanide-containing electroplating bath, or bath rinse solution is reduced, by carbonate and alkali removal by ion exchange or direct acid addition, the solubility of the metal cyanide is decreased. For example, if all the alkalinity due to carbonate and hydroxide is removed from a copper plating bath by ion exchange, cuprous cyanide (CuCN) will become visible as a very fine white precipitate. As noted in Table II, infra, the lower pH caused the heaviest CuCN precipitate. The amount of precipitate can be minimized by maintaining a relatively high pH, e.g., using a resin with a high pK_a and operating upflow such that some bypassing occurs in the exchanger bed. This type of operation has the disadvantage of limiting carbonate removal. The CuCN precipitate is not necessarily objectionable. It forms slowly, and does not plug the exchanger bed or pipelines. It dissolves in the plating bath to which the treated solution is returned, and absence of the turbidity, in normal operation, is an index of exhaustion of the exchanger bed.

The lowering of the pH of a cyanide-containing electroplating bath processed with a carboxylic resin can be minimized, and to some degree controlled, by partially neutralizing the hydrogen form of the resin. This can be done batchwise with hydroxides, carbonates or bicarbonates. Another method is to add a neutral salt, e.g., NaCl or KCl, too a bed of the hydrogen form of the resin. The degree of neutralization effected is determined by such variables as amount of chemical added, concentration, time of contact and the type of chemical employed. The partial neutralization limits the conversion of complex metal cyanides to their corresponding acids, and the resulting relatively higher pH minimizes the precipitation of cuprous cyanides. The loss of hydrogen cyanide is, at the same time, decreased because of its greater solubilities at the relatively higher pH levels.

Usually, bath rinse solution can be turned directly to the plating bath after the ion exchange resin contacting, thereby making up for normal evaporation from the bath. However, if the drag-out or rinse is excessive in volume, evaporation can be resorted to before ion exchanger treatment of the waste.

It is preferred to effect carbonate removal by contacting the ion exchange resin by upflowing the solution. The carbon dioxide will rise with the solution, as do the metal cyanide precipitates. The carbon dioxide can generally be held in solution by operation at moderate pressures, and downflow operation can then be used. However, bubbles of carbon dioxide would then be released in localized regions, and their presence interferes with the normal and even flow through the bed. Also, with downflow, the metal cyanide precipitate can cause plugging of the exchanger bed unless precautions are taken to minimize its formation, e.g., with a fast flow rate, the treated solution discharges before the precipitate formed. Such a fast rate is sometimes feasible, as previously discussed, where the effluent is mixed with untreated solution. The slow reaction rates of the weak acid resins can be improved if they are mixed with strong, sulfonic type, cation resins.

In tests conducted with my invention, I was able to reduce readily the carbonate content of a copper plating bath from about 68 gm/liter to 7.4 gm/liter by using a fluidized bed. In a static bed test it was practicable to reduce carbonate to zero value for the first hundred milliliters of solution passed through a 30 cm bed in a 25 mm inside diameter column. A cross-linked acrylic polymer, IRC-84, was used for the tests.

A larger scale test was made with CC-3, a weak acid ion exchange resin consisting of a cross-linked acrylic polymer in the hydrogen form. Drag-out from a commercial copper plating bath was run upflow at 0.35 gpm through a column 173/8 inch inside diameter, containing about 6 cu ft. of resin. Substantial CuCN precipitate was formed and most of it rose through the equipment with upflowing effluent. As shown by Table I, all of the alkalinity of the solution was removed, and a trace of acidity was formed. Samples of 100 ml were titrated, and methyl orange indicator was used.

TABLE I

4/6/70 Time	Titration of 100 ml. Samples of Influent with 1 normal HCl, ml.	Titration of 100 ml. Samples of Effluent with 0.1 normal NaOH, ml.
11:10 a.m.	27.5	0.0
11:35 a.m.	27.8	0.2
12:15 p.m.	27.3	0.3
1:00 p.m.	26.3	0.4
2:15 p.m.	24.4	2.4
3:55 p.m.	24.3	5.3

The weak acid resins (carboxylic type) vary in acidity. The following data show how the acidity, indicated by the pK_a value, affects the removal of alkalinity NaOH, Na_2CO_3 , and basicity due to NaCN) from a diluted copper plating bath. The flow was upward through a 30 cm bed in a 25 mm ID tube at 10 ml/min.

TABLE II

Resin	pK_a of Hydrogen Form of Resin	Titration of column effluent with 0.1 normal HCl, ml.	pH of column effluent	Remarks, 10 ml. samples for titration
IRC-50	5.9	11.8-14.2	5.7-6.0	Least CuCN
IRC-84	5.3	4.3-4.5	4.5-4.9	Intermediate CuCN
CC-3 Influent	5.3 -	3.1-4.8 41.6	4.7-5.0 ca. 12	Most CuCN Column Feed

What is claimed is:

1. A process for removal of carbonate ions from cyanide-containing electroplating bath, or bath rinse solutions, comprising, in sequence, (1) contacting said solutions with the hydrogen form of a cation exchanger selected from the group consisting of carboxylic, phosphonic, and sulfonic ion exchange resins to convert said carbonate ions to carbonic acid; (2) reducing the pressure on said solutions to promote decomposition of said carbonic acid to water and carbon dioxide; and (3) recycling said solutions, reduced in carbonate ion content, to said electroplating bath.

2. A process for removal of carbonate ions from cyanide-containing electroplating bath or bath rinse solutions according to claim 1 in which said solutions are flowed upwardly through said cation exchanger.

3. A process for removal of carbonate ions from cyanide-containing electroplating bath or bath rinse solutions according to claim 1 in which the said solution which has been contacted with said hydrogen form of a cation resin is mixed with said solution which has not been ion-exchange pH treated, to obtain a recycle solution of preselected pH.

4. A process for removal of carbonate ions from cyanide-containing electroplating bath or bath rinse solutions according to claim 1 wherein said hydrogen form of said cation exchanger is partially neutralized prior to said contacting with said solutions as provided in step (1).

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,661,734 Dated May 9, 1972

Inventor(s) WALTER JOHN SLOAN

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

Page 1, right-hand column, second line

Cancel "2,164,927" and substitute

-- 2,164,924 -- .

Signed and sealed this 5th day of September 1972.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents