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ELECTROPLATING

Richard O. Hull, Lakewood, Ohio, assignor to
E. I. du Pont de Nemours & Company, Wil-
mington, Del., a corporation of Delaware

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This invention relates to electroplating processes employing cyanide baths, and is more particularly directed to processes employing calcium sulfate or the removal of undesired carbonate from such baths.

One of the major problems arising in the operation of cyanide plating solutions is their tendency to build up an undesired sodium carbonate content. This deterioration of cyanide baths results from the absorption of carbon dioxide from the air and from the decomposition and oxidation of sodium cyanide during operation of the solution.

The accumulation of carbonate in a cyanide plating solution has a number of deleterious effects. The bright current density range is varied, and in cadmium solutions, for instance, the bright current density range is markedly lowered when there is present more than about five ounces per gallon of carbonate.

The cathode efficiencies of cyanide plating baths such as those of copper and brass are markedly decreased by the presence of more than about twelve ounces per gallon of carbonate.

The formation of carbonate in cyanide plating baths requires that many hundreds of gallons of solution be discarded annually.

Various methods have been proposed for the removal of carbonates from cyanide plating baths. It has been suggested that carbonate could be removed by the addition of barium cyanide or barium chloride, thus precipitating barium carbonate. This type of operation has not proved successful however because of the high cost of the barium compounds and because of the production by metathesis of sodium cyanide which upsets the bath composition or of sodium chloride which acts deleteriously in the bath.

It has also been proposed to remove sodium carbonate by cooling cyanide plating baths, but this method is expensive. Cooling may be used with moderate success in very cold weather but even then the cost is excessive.

A greater disadvantage of this procedure of removal of carbonate by cooling is the fact that it is successful only in reducing the sodium carbonate content to about eight and one-half to ten ounces per gallon. The extent of removal is not adequate for most baths.

I have found that substantially complete removal of sodium carbonate from cyanide plating baths may be effected by the use of calcium sulfate. Calcium sulfate is only slightly soluble in a plating bath and does not itself exercise any deleterious action. Calcium carbonate is much less soluble than the sulfate, and therefore substan-

tially all of the sodium carbonate may be precipitated as calcium carbonate.

The calcium sulfate besides precipitating the very insoluble calcium carbonate also produces by metathetical reaction, sodium sulfate. The sodium sulfate thus produced is not deleterious in cyanide plating solutions but, rather, is of value as it increases the conductivity of the solution. In fact, it has frequently been found desirable to add sodium sulfate because of its beneficial influence upon the bath conductivity. If removal is desired the sodium sulfate can readily be crystallized out by cooling.

The practice of my invention may be better understood by reference to the following illustrative examples.

Example I

A cyanide plating bath was made up with the following:

	Grams per liter
Cadmium oxide (CdO)	43
Sodium cyanide (NaCN)	130
Sodium sulfate (Na ₂ SO ₄)	58

To the plating bath thus prepared there was added seventy-five grams per liter of anhydrous sodium carbonate. To the solution there was then added one hundred and twenty grams per liter of calcium sulfate (CaSO₄·2H₂O) and the solution was agitated. Analyses were taken after various intervals of time of stirring with the following results:

Time of stirring	Sodium carbonate content
	Grams per liter
0 minutes	72.5
15 minutes	6.4
90 minutes	5.4
28 hours	3.0

Example II

A commercial cyanide-cadmium plating solution which had become unsatisfactory by reason of the high content of carbonate was analyzed and found to have the following composition:

	Grams per liter
Cadmium (Cd)	3.75
Sodium cyanide (NaCN)	41.2
Sodium carbonate (Na ₂ CO ₃)	61.5

Calcium sulfate in the form of a commercial

grade of ground gypsum was added in the amount of seventy-five pounds to seventy-five gallons of the solution. This quantity of calcium sulfate amounts to an excess of about eleven pounds over that stoichiometrically required to precipitate all of the carbonate. After the addition of gypsum, the bath was agitated for one hour with a garden hoe and the solution again analyzed. The sodium carbonate was found to amount to only 12.5 grams per liter. A longer time of treatment reduced the sodium content still further.

Example III

Following a procedure such as that shown above in Example II a cyanide-zinc plating bath was treated with commercial ground gypsum. The amount of gypsum used was 129 grams per liter. The carbonate content of the bath before the addition of gypsum was 77.6 grams per liter and after fifteen minutes of agitation with the gypsum, the carbonate content was 9.7 grams per liter.

Example IV

A cyanide-copper plating bath containing 69.5 grams per liter of sodium carbonate was treated with 113 grams per liter of gypsum. After fifteen minutes of agitation with the gypsum the bath was analyzed and it was found that the sodium carbonate content had dropped to 1.6 grams per liter.

Example V

A cyanide-silver plating bath containing 79.2 grams per liter of sodium carbonate was treated with 129 grams per liter of ground gypsum. After fifteen minutes of agitation the carbonate content had dropped to 1.6 grams per liter. Before the carbonate addition the silver content of the bath was 22.7 grams per liter and after the addition was 23.3 grams per liter. It is to be noted that while silver sulfate is only slightly soluble in water, it is nevertheless easily soluble in cyanide solutions and there is no danger that the gypsum will cause precipitation of the silver from the plating bath.

While I have shown above the treatment of certain specific plating baths, it will be understood that my invention is applicable to the treatment of any cyanide plating solution which contains an undesirably high content of carbonate.

The calcium sulfate employed in the foregoing examples is the calcium sulfate dihydrate commercially available as gypsum. It is generally preferable to use gypsum because it is readily obtained at very low cost and in very pure form. It desired, other forms of calcium sulfate which are more soluble than calcium carbonate can be used.

The amount of calcium sulfate to use is determined by the amount of carbonate it is desired to remove. In general it is preferred to

determine the carbonate content of a cyanide bath by analysis and then to add about the amount of gypsum required to precipitate the amount of carbonate present. If less of the calcium sulfate is used, the reduction in carbonate content will naturally be proportionately smaller.

The addition of an excess of calcium sulfate to a bath is not particularly objectionable, and under some circumstances it may even be desired to maintain a considerable excess of calcium sulfate in the bath. When so operating the calcium sulfate will simply go into solution as required to remove the carbonate as it forms.

After calcium sulfate has been added in an amount required to remove undesired carbonate it is generally desirable to stir the bath well for about an hour, tho an even longer time may be required under some circumstances to effect a desired extent of removal of carbonate.

After calcium carbonate has been precipitated and allowed to settle, the supernatant liquid can be transferred, or the calcium carbonate can simply be shoveled out of the tank. If the carbonate is shoveled out of the plating tank some of the plating solution will be carried with it. This plating solution can readily be recovered either by filtering or by transferring the calcium carbonate into a separate crock of water and stirring. The weak solution resulting may then be used as make-up for the plating bath without appreciable loss of plating salts.

While I have shown certain specific procedures, it will be understood that those skilled in the art may readily employ calcium sulfate for the removal of undesired carbonate content from various cyanide plating baths without departing from the spirit of my invention.

I claim:

1. In a process for the removal from an aqueous cyanide plating bath of excess carbonate which has deleterious effects upon the bath, the step comprising adding calcium sulfate thereto.

2. In a process for the removal from an aqueous cyanide plating solution of excess carbonate which has deleterious effects upon the solution, the step comprising adding gypsum thereto.

3. In a process for the removal from an aqueous cyanide-cadmium plating solution of excess carbonate which has deleterious effects upon the solution, the step comprising adding gypsum thereto.

4. In a process for the removal from an aqueous cyanide-zinc plating solution of excess carbonate which has deleterious effects upon the solution, the step comprising adding gypsum thereto.

5. In a process for the removal from an aqueous cyanide-copper plating solution of excess carbonate which has deleterious effects upon the solution, the step comprising adding gypsum thereto.

RICHARD O. HULL.