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REMOVING ORGANIC IMPURITIES FROM
COPPER-CYANIDE ELECTROPLATING
BATHS

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This invention relates to the purification of electroplating baths and more particularly to the removal of organic impurities from alkaline plating baths.

When electroplating metals from alkaline plating baths, for example, cyanide plating baths, the baths commonly become contaminated with organic materials from various sources. Common sources of contamination are lacquers and varnishes used to insulate plating racks or other equipment or parts of the work plated, organic buffing compounds, oils, greases and the like which have not been completely removed from the work prior to plating, and various accidental contaminations. Also in some plating baths organic materials are added as brightening or anti-pitting agents and these addition agents tend to gradually decompose to form organic residues in the baths. The presence of such organic contaminants has various adverse effects on the plating operation, depending upon the nature of the organic compounds present and other factors. In many cases it causes the formation of unsightly stains on the electrodeposit, particularly in bright electroplating processes. If the organic compounds are present as suspended solids, they tend to cause pits and roughness in the electrodeposited metal.

An object of the present invention is an improved method for the purification of electroplating baths. A further object is a method for removing organic contaminants from alkaline electroplating baths. Another object is to electrodeposit bright metal, bright copper, for example, from alkaline plating baths. Other objects will be apparent from the ensuing description of the invention.

We have discovered that organic compounds can be efficiently and completely removed from an alkaline electroplating bath or rendered innocuous by adding to the bath a soluble salt of an alkaline earth metal so as to cause precipitation of an alkaline earth metal hydroxide. For the purpose of this invention, the term "alkaline earth metal" in the specification and in the appended claims includes magnesium, as well as calcium, barium and strontium.

Any soluble salt of an alkaline earth metal may be utilized in practicing the invention. While effective results sometimes can be obtained by using soluble alkaline earth metal salts of organic acids, e. g. formates, acetates, propionates or butyrates, we generally prefer to utilize the soluble inorganic salts. Examples of these are the soluble alkaline earth metal chlorides, bromides,

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iodides, nitrates, cyanides, thiocyanates, and nitrites, and magnesium sulfate. Ordinarily, because of their cheapness and availability we prefer to use alkaline earth metal chlorides or magnesium sulfate.

The amount of alkaline earth metal salt required to be added will depend upon the nature of the electroplating bath and the alkaline earth metal salt employed and upon the amount and kind of organic impurities to be removed. We have found however that a very slight precipitate of an alkaline earth metal hydroxide ordinarily is sufficient to completely purify a bath which is badly contaminated with organic impurities. In determining the amount of alkaline earth metal salt to be added, account must also be taken of the amount of carbonate ions in the bath, if any, and also the nature of the alkaline earth metal salt utilized. For example, calcium carbonate is more insoluble than calcium hydroxide; and hence, in order to precipitate the desired calcium hydroxide in the electroplating bath, we have found it necessary first to add sufficient calcium salt or other carbonate precipitant to complete the precipitation of any carbonate ions as calcium carbonate and then to add a further amount of the calcium salt to cause subsequent precipitation of the desired amount of calcium hydroxide. Alternatively, the carbonate ions first may be wholly or partially removed by any other suitable means before precipitating the calcium hydroxide. If the carbonate ions are removed by precipitation with the calcium salt, it is not essential that the carbonate precipitate be removed before adding the remainder of the precipitate of the calcium to calcium hydroxide. The same considerations apply to the use of salts of barium and strontium to precipitate the corresponding hydroxides.

On the other hand, magnesium hydroxide is more insoluble than magnesium carbonate and hence magnesium hydroxide may be precipitated in a bath containing carbonate ions without precipitating any substantial amount of carbonate and without first removing the carbonate ions. For this reason, unless it is desired simultaneously to remove carbonate from the bath, we generally prefer to use a magnesium salt for the bath purification, if carbonate is present. Hence we prefer to use a soluble magnesium salt to treat cyanide baths, which usually contain appreciable amounts of carbonate.

The amount of alkaline earth metal hydroxide ordinarily required for complete bath purification is small. In most cases a precipitate of the

hydroxide equal to 0.1 to 0.3 per cent by weight of the electroplating bath will be sufficient although in some cases it may be necessary to precipitate a larger amount of the hydroxide.

The means by which the hydroxide precipitate removes the organic impurities has not been determined. This phenomenon apparently cannot be explained simply as the result of precipitating an inorganic material because we have found that the precipitation of aluminum hydroxide, which sometimes is used to purify water, is not suitable for purification of an alkaline plating bath. Also, as indicated above, we have found that the precipitation of carbonate without precipitation of the hydroxide does not give the desired results.

The precipitate of alkaline earth hydroxide may or may not be removed from the bath before resumption of electroplating, as desired. When the amount of precipitate is large it is sometimes desirable to remove it from the bath, as the particles of precipitate may tend to cause rough deposits by coming in contact with the cathode. In many cases however, where the amount of precipitation required is slight, the bath may be satisfactorily operated without removal of the precipitate.

In practicing our invention, we may stop operation of a contaminated electroplating bath and precipitate therein the alkaline earth metal hydroxide as above described. This may be done in the electroplating tank, or the bath may be transferred to another vessel, as desired. The bath then may be again placed in operation, with or without first removing the hydroxide precipitate. If the amount of precipitate is sufficiently small, or where solid particles in the bath are not objectionable, the bath purification may be carried out without interrupting the electroplating operations. However, we prefer to purify the bath without electrolysis, either by stopping the flow of current or by transferring all or part of the bath to a separate vessel for the purifying treatment.

In one preferred modification, for example, we may continuously or intermittently circulate the bath through a purifying vessel where the alkaline earth metal salt is added and the resulting hydroxide precipitate is removed by filtration or settling and the purified electrolyte led back to the plating tank. Various other modes of operating our invention will be apparent to those skilled in electroplating.

The following examples illustrate specific modes of practicing our invention:

Example I

A copper cyanide plating bath was made up containing approximately:

	Oz. per gal.
Copper cyanide	8
Free cyanide (NaCN)	0.5
Sodium hydroxide	4
Sodium carbonate	3.8

With the addition of suitable brightening agents, this bath operated at about 30 amps. per sq. ft. to produce excellent, clean, bright copper plate on steel cathodes.

This bath then was contaminated by adding 0.25 oz. per gal. of a greasy buffing compound. Deposits were then made at 30 amps. per sq. ft. and showed the typical blotched irregular effect resulting from organic contaminants. After treatment with 1 oz. per gal. of magnesium chloride and filtration to remove magnesium hy-

droxide, deposits were again bright at a current density of 30 amps. per sq. ft.

Example II

A bright copper cyanide plating bath in satisfactory operation to produce bright plate contained:

	Oz. per gal.
Copper cyanide	17.73
Free cyanide (NaCN)	0.5
Sodium hydroxide	3.7
Sodium carbonate	6.26

This bath was contaminated by adding small amounts of buffing compound, oil and grease, boiled for four hours and filtered. The bath then was placed in operation and the resulting copper plate was stained and mottled, exhibiting the typical effects of organic contaminants.

The bath then was treated by adding 8 oz. per gal. of calcium chloride (CaCl_2), which was an excess of approximately 1.73 oz. per gal. over that required to precipitate all carbonate in the bath. The resulting precipitate of calcium carbonate and hydroxide was filtered off and the bath replaced in operation. Good bright plate was obtained from the purified bath in a current density range of 10 to 100 amps. per sq. ft.

Example III

An operating conventional bright zinc bath, which produced satisfactory bright zinc plate contained:

	Oz. per gal.
Zinc cyanide	10
Sodium cyanide	5
Sodium hydroxide	10

This bath was contaminated by the addition of a greasy buffing compound and thereafter the resulting plate was dull at current densities of 10 amps. per sq. ft. and 70 amps. per sq. ft. After the addition of 2 oz. per gal. of magnesium sulfate and filtering off the precipitated magnesium hydroxide, the bath produced good bright plate at the aforesaid current densities.

Our method is applicable to all alkaline electroplating baths, wherein the degree of alkalinity is sufficient to cause the desired precipitation of alkaline earth metal hydroxide. Thus, for example, our process is adapted for the purification of the various cyanide baths for plating metals such as zinc, copper, brass, cadmium, silver, gold and bronzes (tin-copper alloys), and also for other alkaline plating baths, e. g., for plating zinc and tin (stannate and stannite baths). If the alkalinity is not sufficiently great to precipitate the required amount of alkaline earth metal hydroxide, we may add sufficient alkaline reagent such as an alkali metal hydroxide or an alkali metal salt, e. g., sodium or potassium cyanide, tetraborate, carbonate or the like, which will impart the required degree of alkalinity to the bath. In most alkaline plating solutions, such addition of alkali is unnecessary.

We claim:

1. The process for removing deleterious organic compounds from a used electroplating bath containing hydroxyl ions and carbonate ions which comprises precipitating magnesium hydroxide in said bath by adding a soluble magnesium salt to said bath and replacing the acid radicles of said magnesium salt with hydroxyl radicles substantially without precipitating magnesium carbonate therein.

2. The process for removing deleterious organic compounds from a used copper cyanide electro-

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plating bath containing hydroxyl ions and carbonate ions which comprises precipitating magnesium hydroxide in said bath by adding a soluble magnesium salt to said bath and replacing the acid radicles of said magnesium salt with hydroxyl radicles substantially without precipitating magnesium carbonate therein.

3. The process for removing organic impurities from an alkaline electroplating bath containing carbonate ions and sufficient hydroxyl ions to replace the acid radicles of a magnesium salt which comprises adding thereto a soluble magnesium salt in amount sufficient to precipitate magnesium hydroxide but substantially insufficient to precipitate magnesium carbonate therein.

4. The process for purifying a cyanide electroplating bath containing carbonate ions and sufficient hydroxyl ions to replace the acid radicles of a magnesium salt which comprises adding thereto a soluble magnesium salt in amount sufficient to precipitate magnesium hydroxide but substantially insufficient to precipitate magnesium carbonate.

5. The process for removing organic impurities from a copper cyanide electroplating bath containing carbonate ions and sufficient hydroxyl ions to replace the acid radicles of a magnesium salt which comprises adding thereto a soluble magnesium salt in amount sufficient to precipitate magnesium hydroxide in an amount equal to about 0.1 to 0.3% of the weight of said bath, substantially without precipitating magnesium carbonate therein.

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6. In a process for electroplating bright copper from a metal cyanide bath normally containing carbonate ions and sufficient hydroxyl ions to replace the acid radicles of a magnesium salt and subject to contamination with organic impurities which cause imperfections in the electrodeposit, the step comprising adding to said bath a soluble magnesium salt in the amount required to precipitate therein an amount of magnesium hydroxide equal to about 0.1 to 0.3% of the weight of the bath, substantially without precipitating magnesium carbonate therein.

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