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ELECTROPLATING BATH PURIFICATION

Edwin C. Rinker, Morristown, N. J., assignor to Sel-Rex Precious Metals, Inc., Belleville, N. J., a corporation of New Jersey

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This invention relates to an electroplating bath and to a process for purifying such a bath, more particularly it relates to method of precipitating undesirable anions from cyanide baths and to the resultant bath.

Excessive amounts of carbonates, sulfates, and/or chromates in a cynide type of electroplating bath are detrimental to the plating operation since they cause losses in current efficiency and grainy, spongy or burned deposits.

Methods for removing or decreasing the carbonate concentration in such baths include, freezing out the carbonate, chemical precipitation, acid treatment and dilution of the bath.

Many compounds have been suggested as additions to such a plating bath for the chemical removal (by precipitation) of carbonates, sulfates and chromates therefrom without, as far as possible, adding other harmful impurities which affect the properties of the bath. For this purpose calcium sulfate, calcium hydrate, barium hydroxide, and certain soluble barium salts among which is barium cyanide, have been suggested. Of these compounds calcium hydrate and barium hydroxide add hydroxyl ions to the bath, calcium sulfate adds sulfate ions to the bath, barium cyanide is not commercially available and may increase the cyanide ion concentration to a point where it is undesirable.

Among the objects of this invention is to provide a new process of purifying such cyanide baths which is more effective than previous purifiers and which does not undesirably affect the bath in any other way.

This invention is based on the discovery that a complex metal cyanide comprising the metal ion of the metal in the bath to be plated and the barium ion is an excellent purifier which acts to remove carbonates, etc. without altering the free cyanide content of the bath and without adding any undesired impurity thereto.

When the bath is a copper cyanide bath the purifier is copper barium cyanide complex having the formula $BaCu(CN)_3$ or some multiple thereof. When the bath is for cadmium plating the purifier added is the barium cadmium cyanide complex, etc. The complex cyanides of the invention may be employed for purifying copper, cadmium, silver, gold and zinc, cyanide baths, for example. All of these complexes are soluble in water and provide a convenient way to add the complex to the bath. While the complex added removes carbonate from the bath it also adds plating metal to the bath without changing the free cyanide content thereof.

When barium copper cyanide complex is added to a copper cyanide plating bath to remove carbonate, for example, the following reaction takes place

$$BaCu(CN)_3+K_2CO_3=BaCO_3+K_2CU(CN)_3$$

The barium carbonate is precipitated and the complex potassium copper cyanide is formed. Thus, the free potassium cyanide content of the bath is not altered.

The addition of the barium cyanide on the other hand, does increase the concentration of free potassium cyanide according to the following reaction:

$$Ba(CN)_2+K_2CO_3=BaCO_3+2KCN$$

The barium carbonate precipitates but the potassium cyanide is left in the bath.

Many cyanide plating solutions are operated under a narrow range of free cyanide. In a copper cyanide plating solution the range is from 0.75 to 1.5 ounces of free potassium or sodium cyanide per gallon.

The invention both as to its organization and method of operation together with additional objects and advantages thereof will best be understood from the following description of specific embodiments thereof.

The complex is made in the following way. 32 parts of copper cyanide and 68 parts of barium cyanide are added to distilled water or other essentially pure aqueous body. The exact proportion of water employed is not critical. The complex of barium and copper cyanide having the composition $BaCu(CN)_3$ is formed. The solution may be used as such or the barium copper complex may be separated from the solution and employed as the dry complex salt. The exact structural formula of such complexes is not known but from analogy with other complex copper cyanides the composition is probably $BaCu(CN)_3$. That the two salts form a complex is apparent from the fact that the solution is colored, having a bluish color.

To use the purifier of the invention the bath to be purified may be analyzed for carbonate content in any desired way.

The proportion of carbonate to be removed is then decided upon. This will depend on various factors such as whether the bath is for bright plating or high speed plating, etc. For complete utilization of the purifier, however, it is best not to remove all of the carbonate and it is not often necessary to remove the last possible trace of such compounds. The required amount of purifier is added to the plating bath with stirring, etc. The reaction is speeded by warming the bath. A substantial amount of precipitate forms and is allowed to settle for several hours. The clear solution is removed or pumped directly to the plating tank. The final portion or all of the solution may be filtered, if desired.

The filtered or decanted solution may be tested for excess of the purifier by adding a small amount of the original solution to the filtered solution. If no further precipitation occurs all of the added purifier has been used and no further precipitation will take place when the solution is returned to the original bath.

The reaction of the purifier with the bath liquid adds copper ions to the bath without disturbing the free cyanide concentration of the bath.

The same process is employed for making and employing purifiers for zinc, cadmium, silver, gold and similar baths.

The features and principles underlying the invention described above in connection with specific exemplifications will suggest to those skilled in the art many other modifications thereof. It is accordingly desired that the appended claims shall not be limited to any specific feature or details thereof.

I claim:

1. In the process of purifying an electroplating bath of the cyanide type the steps comprising, providing a complex salt of the cyanides of barium and the metal to be plated, adding the salt to the bath liquid in proportions sufficient to remove a substantial proportion of the undesired anions therefrom whereby to precipitate barium salts of said anions without adding to the free cyanide content of said bath, and separating the precipitate from the remainder of the bath.

2. In the process of purifying an electroplating bath of the cyanide type the steps comprising, providing an aqueous solution of a complex salt of the cyanides of

barium and the metal to be plated, adding the complex salt solution to the bath liquid in proportions sufficient to remove a substantial proportion of the undesired anions therefrom whereby to precipitate barium salts of said anions without adding to the free cyanide content of said bath, and separating the precipitate from the remainder of the bath.

3. In the process of purifying a copper electroplating bath of the cyanide type the steps comprising, providing a complex salt of the cyanides of barium and copper, adding the salt to the bath liquid in proportions sufficient to remove a substantial proportion of the undesired anions therefrom whereby to precipitate barium salts of said anions without adding to the free cyanide content of said bath, and separating the precipitate from the remainder of the bath.

4. In the process of purifying a copper electroplating bath of the cyanide type the steps comprising, providing

an aqueous solution of a complex salt of the cyanides of barium and copper, adding the complex salt solution to the bath liquid in proportions sufficient to remove a substantial proportion of the undesired anions therefrom whereby to precipitate barium salts of said anions without adding to the free cyanide content of said bath, and separating the precipitate from the remainder of the bath.

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