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DISPOSAL OF WASTE CYANIDE

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5 Claims. (Cl. 204—106)

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This invention relates to the treating or disposal of waste cyanide.

It is frequently necessary to dispose of the residue in the bottom of the tanks used in electro depositing metals such as copper, zinc, etc., from cyanide electrolytes. In the case of the residue from copper plating tanks the residue is essentially sodium and/or potassium carbonate. The residue is in a sludge form and necessarily entrains a considerable amount of the plating solution which contains sodium and/or potassium cyanide, copper cyanide and sodium hydroxide. In some cases it is necessary to dispose of entire plating solutions containing the above mentioned constituents, which have been evaporated and which because of high carbonate content are not considered suitable for plating use. Zinc baths and sludges therefrom contain zinc cyanide, sodium cyanide, sodium hydroxide and sodium carbonate.

Various methods have been employed or have been proposed heretofore for disposing of waste cyanide from cyanide plating baths. All of the prior methods of which I am aware are subject to one or more objections.

For example, one method of disposing of waste cyanide is by controlled acid treatment under ventilated stacks thereby dissipating the resulting HCN high in the air. This method does not take care of metallic cyanides such as copper, zinc, etc., which are precipitated by the acid treatment. It has been proposed, also, to treat the waste with calcium hypochlorite (bleaching powder). However, this method is expensive and requires large quantities of calcium hypochlorite. Another proposed method is treatment with lime sulphur. This method is unsatisfactory because reaction is not complete. It is also quite expensive and impractical to treat large quantities of waste cyanide material in this way. Other proposed methods are to burn the solid material in out-of-the-way places, or to run it into open pits from which it would be absorbed and diffused into the earth. These procedures are objectionable because of the danger of contaminating underground water supplies.

The primary object of this invention is to provide an improved, simple and practical method of disposing of the residue from cyanide plating tanks as well as to dispose of entire plating baths of the cyanide-type which are no longer to be used. Other cyanides such as those used in heat treating operations (barium cyanide, sodium cyanide, potassium cyanide, etc.) sometimes have to be disposed of and it is also an object of the

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present invention to provide an improved, simple and practical method of disposing of such waste cyanides.

I have found that the waste cyanide material can be treated by electrolyzing a heated aqueous solution of the cyanide-bearing material using insoluble anodes, and continuing the electrolyzing action until the cyanide is reduced to a negligible amount.

The desired high temperature of the solution can be had by means of suitable heating means in the bath such as, for example, steam coils. A bath temperature of 200° F. has proven quite satisfactory and in practice is obtained with simple heating equipment. Higher temperatures accelerate decomposition. Of course, boiling will cause slopping over of solution. The process proceeds more slowly at temperatures lower than 200° F.

The solution composition is not critical and may range from a very low figure to the limit of solubility of the material being destroyed. In disposing of cyanide residues the process can be carried out in simple manner by merely dissolving all the material possible in the tank which is used leaving some excess on the bottom. This residue later goes into solution as metal is plated out and cyanide is destroyed.

The current density employed can vary over a wide range as it is not critical. In certain applications a D. C. generator having a voltage of about 13 volts has been employed. In these cases the initial cathode current density has been about 80 amperes per square foot. Anode polarization and depletion of free cyanide cause this current density to drop off to about 20 amperes per square foot as decomposition progresses. Improved results can be obtained by using somewhat lower initial current density to plate out all metal possible before the free cyanide is decomposed. However, the procedure first described requires a minimum of attention and control.

Speed of decomposition decreases as the process proceeds, being rapid at first and slow for the last traces of cyanide. Analyses for metal (copper, zinc, etc. as the case may be), free cyanide (titration), and total cyanide (by distillation) are made at frequent intervals, and the solution may be discarded whenever the metal and free cyanide are zero and the "total" cyanide reaches such a low figure that its subsequent dilution in the sewer renders it unimportant. This "total" cyanide is probably in the form of ferri-, or ferro-cyanide and is not generally regarded toxic.

Any suitable insoluble anodes are used. In a large installation anodes and cathodes of heavy expanded metal, steel, for example, have been used.

In one specific example involving a large amount of waste material from copper cyanide plating baths, a large tank was installed in the open to eliminate the need for an exhaust system. A steam coil was installed in the tank and waste salts and solutions were dissolved in this tank. The solution temperature was maintained at 200° F. and a generator having a voltage of about 13 volts connected across the tank with anodes and cathodes made of heavy expanded metal. It was found that under the above conditions the cyanide concentration could be reduced to less than four parts per million which represents the limit of sensitivity of the distillation method of determination. The time required ranged from several hours to three or four days depending, of course, upon the original concentration of solution. Air agitation can be employed for the purpose of speeding up the process. By use of a suitable exhaust system the treatment can be carried out inside a building.

By use of the procedure described herein large amounts of waste material from metal cyanide plating baths have been destroyed. The process destroys both the free cyanide and the metal cyanide of the plating bath. The metal that is plated on the cathode in the process of destroying the waste cyanide can be recovered and may be used as anode material in metal plating baths.

I claim:

1. The process of treating waste cyanide material from metal cyanide plating baths which comprises passing an electric current from an insoluble anode to a cathode through an aqueous solution of the waste cyanide material at a temperature of about 200° F. until the metal and free cyanide are substantially zero and the solution is substantially non-toxic.

2. The process of treating waste cyanide material from copper cyanide plating baths which comprises passing an electric current from an insoluble anode to a cathode through an aqueous solution of the waste copper cyanide material at a temperature of about 200° F. until the copper and free cyanide are substantially zero and the solution is substantially non-toxic.

3. The process of treating waste cyanide material from zinc cyanide plating baths which comprises passing an electric current from an insoluble anode to a cathode through an aqueous solution of the waste zinc cyanide material at a temperature of about 200° F. until the zinc and free cyanide are substantially zero and the solution is substantially non-toxic.

4. The process of treating the residue from the bottoms of metal cyanide plating baths which includes dissolving all of the waste material possible in an aqueous solution in a tank and leaving some undissolved waste material on the bottom of said tank, heating said solution in the tank substantially to boiling temperature, and passing an electric current through said heated solution from an insoluble anode to a cathode until the metal and free cyanide are substantially zero, said undissolved waste material dissolving in said solution in the tank during the earlier stages of said current flow.

5. The process of treating waste cyanide material which includes passing an electric current from an insoluble anode to a cathode through an aqueous solution of the waste cyanide material at a temperature of about 200° F. until the solution is substantially non-toxic.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
756,211	Butters	Apr. 5, 1904
1,531,863	Liebknecht	Mar. 31, 1925

OTHER REFERENCES

"Chemical Abstracts," vol. 27 (1933), page 4741.

"Products Finishing," Feb. 1942, page 48.