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ELECTRODEPOSITION OF COPPER

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16 Claims. (Cl. 204—52)

This invention relates to the electrodeposition of metals, and in particular relates to the electrodeposition of copper from an aqueous solution.

For a long time past the commercial electrodeposition of copper has been effectuated by employing a Rochelle-cyanide solution of known properties. During the many years that have elapsed since the introduction to the art of Rochelle-cyanide solutions, many modifications and refinements have been made, but the basic principles of the early bath remain substantially as originally presented. Accordingly, the most common type of Rochelle bath now includes copper cyanide, alkali cyanide, alkali hydroxide and Rochelle salts, which operate to produce a free cyanide.

In recent years, copper, electrodeposited from Rochelle-cyanide solutions has found increasing application in the field of electroplating. In certain commercial applications, it has been found that a thin "strike" of copper will impart better overall characteristics to the resultant product that is being produced. For example, in the application of nickel by electrolysis, to steel, it has been found that a copper "strike" on the order of 0.001 inch will give better protection than when the electrodeposited nickel is applied directly to the steel. Recently, it has been necessary to apply a preliminary deposit of copper to conserve the amount of nickel that is used in the production of an electroplated part. A still further factor contributing to the increased usage of copper lies in the fact that the same can be employed as an electrodeposit on certain metals that would not otherwise satisfactorily receive a plated deposit. For example, in the field of electroplating die-castings it has been discovered that the acid present in the nickel electrolyte attacks the surface of the die-casting and accordingly, renders the electroplating thereof unsatisfactory. Such a condition does not exist, however, with regard to the electroplating of die-castings in Rochelle-cyanide solutions.

It has been discovered in the filed of plating, that the brightness or lustre of the electroplated surface is directly affected by the brightness of the undercoat employed. This fact motivated the development of bright nickel plating, and has stimulated the recent efforts to increase the brightness of electrodeposited copper.

These efforts at increasing the lustre of the copper deposit have followed the pattern employed in bright nickel plating and accordingly, have been directed toward the use of addition agents that would operate to brighten the bath. These addition agents have been both organic and inorganic in nature, but have met with limited acceptability due to their inherent insolubility in the Rochelle-cyanide solution. Lead and selenium compounds, for example, while possessing brightening properties in baths other than copper, have heretofore met with limited success in Rochelle-cyanide solutions because of their limited solubility in solution, especially over an extended period of time. This limited solubility, which may be expressed in terms of instability, curtails the usefulness of these compounds.

Accordingly, it is one object of this invention to provide improved types of addition agents that are characterized by substantially indefinite stability, as well as being possessed of brightening properties.

It is a further object of this invention to provide a

method for converting insoluble addition agents into addition agents possessing the property of stability in Rochelle solutions.

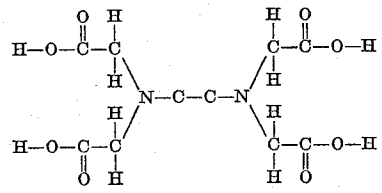
It is a still further object of this invention to provide a Rochelle-cyanide solution that has been modified to permit reception therein of normally unstable addition agents.

These and other objects of the invention will become more apparent upon a reading of the following brief specification.

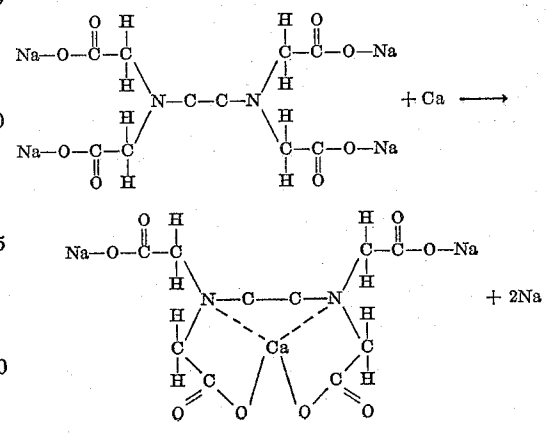
It has been discovered that many organic and inorganic compounds, that possess brightening properties but are normally unstable in Rochelle plating solutions, can be converted into stable compounds by being admixed with certain reaction products of aliphatic amines.

Specifically, it has been discovered that if an aliphatic amine is reacted with an alkaline metal cyanide in the presence of a formaldehyde-yielding substance, the resulting reaction product will further react with normally insoluble compounds to convert the same into soluble compounds having brightening properties in a Rochelle solution. This reaction product may be produced in one of two ways.

First, employing the teachings of Bersworth U. S. Patent 2,407,645, a solution of free unreacted aliphatic amine and alkali metal cyanide is subjected to the addition of formaldehyde. Basically, this patent teaches the reacting of an aliphatic amine having at least one replaceable hydrogen atom attached directly to an amino nitrogen atom, with an alkali metal cyanide formaldehyde-yielding substance under conditions sufficiently alkaline that there is substantially no hydrolysis of said cyanide and in total amounts such that for each replaceable hydrogen atom one molecule of said cyanide and one molecule of said formaldehyde substance are added during the reaction. Following the teachings of Example 2, it is possible to produce a compound known as ethylene diamine tetracetic acid having the below-listed formula.



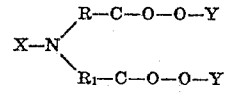
The sodium salt of the above compound, it is believed, operates to chelate or inactivate certain metallic ions by absorbing the same in the ring structure thereof. This reaction prevents the precipitation characteristic of insolubility, and accordingly, these metallic ions are inactivated against precipitation. A typical such reaction is listed below.



The second method of producing this preferred reaction product above described, comprises addition of an aliphatic amine to a Rochelle solution that is characterized by an excess of free cyanide of the alkali metal type. Such cyanide exists in Rochelle plating baths in the form of potassium or sodium cyanide and it is theorized that the secondary reactions occurring in the plating bath upon the addition of the aliphatic amine operate to produce formaldehyde type substance that completes the requisite reaction product. In this regard, it is a well known fact, in the electrodeposition of copper from Rochelle-cyanide solutions, that such solutions possess a certain amount of formic, or methanoic acid

(HCCOOH)

It is entirely possible and within the realm of probability that the subject formic acid is reacted during the complex secondary actions that occur during electroylsis, to form formaldehyde. Thus, it can be seen that the conventional Rochelle-cyanide solution contains the necessary compounds that are capable of reacting with added aliphatic amines to produce the reaction product that is the subject of this invention. As will be observed from the examples that are subsequently set forth, several aliphatic amines have operated with results equivalent to those obtained by using the pre-prepared polycarboxylic amino acids of the Bersworth patent. Accordingly, it is concluded that the reaction product of any aliphatic amine with an alkali metal cyanide will operate to produce a compound having the following representative formula:



where X is an organic radical or hydrogen R and R_1 are the same or different organic radical Y is an alkali metal or hydrogen.

In the below-listed examples, there is illustrated the use of various reaction products of aliphatic amines and alkali metal cyanides that are used in conjunction with certain compounds of selenium and lead. These compounds are believed representative of a wide range of chemical compounds whose use can be improved by combination with any one of several such improved reaction products indicated above.

EXAMPLE 1

Without the aid of heat and by agitation only, .21 gram of selenium dioxide was dissolved in 25 cc. of N-butylamine and 25 cc. distilled H_2O.

EXAMPLE 2

Without the aid of heat and by agitation only, .21 gram of selenium dioxide were dissolved in 25 cc. of ethylene diamine and 25 cc. of distilled H_2O.

EXAMPLE 3

Without the aid of heat and by agitation only, .21 gram of selenium dioxide were dissolved in 25 cc. of Nullapson B. F. acid (ethylene diamine tetracetic acid, powder) and 25 cc. of distilled H_2O.

EXAMPLE 4

Without the aid of heat and by agitation only, .26 gram of lead carbonate were dissolved in 25 cc. of N-butylamine and 25 cc. of distilled H_2O.

EXAMPLE 5

Without the aid of heat and by agitation only, .26 gram of lead carbonate were dissolved in 25 cc. of ethylene diamine and 25 cc. of distilled H_2O.

EXAMPLE 6

Without the aid of heat and by agitation only, .26 gram of lead carbonate were dissolved in 25 cc. of Nullapson B. F. acid (ethylene diamine tetracetic acid, powder) and 25 cc. of distilled H_2O.

EXAMPLE 7

Without the aid of heat and by agitation only, 30 grams of selenium dioxide were dissolved in 800 cc. of Versene T (the sodium salt of ethylene diamine tetracetic acid) and water to make one gallon of solution.

EXAMPLE 8

Without the aid of heat and by agitation only, 10 grams of lead carbonate were dissolved in 1000 cc. of Versene T (the sodium salt of ethylene diamine tetracetic acid) and water to make one gallon of solution.

With the above liquids prepared as indicated, Hull cell panels were made using the solutions of Examples 9, 10, 11 and 12. A current of 3 amps was employed in the Hull cell resulting in a theoretical current density of 0–125 amps per sq. ft.

EXAMPLE 9

	Cc.
Rochelle solution [1]	400
Addition agent per Example 1	4
Addition agent per Example 4	1

EXAMPLE 10

Rochelle solution [1]	400
Addition agent per Example 2	4
Addition agent per Example 5	1

EXAMPLE 11

Rochelle solution [1]	400
Addition agent per Example 3	4
Addition agent per Example 6	1

EXAMPLE 12

Rochelle solution [1]	400
Addition agent per Example 9	4
Addition agent per Example 10	1

[1] The chemical composition of the Rochelle solution employed in Examples 9, 10, 11 and 12 was as follows: Copper cyanide 6.73 oz. per gal. (4.77 oz. per 1 gal. of pure copper by analysis); free potassium cyanide 1.25 oz. per gal; caustic potassium 3.0 oz. per gal; Rochelle salts 6.66 oz. per gal.

The panels obtained from the use of the solutions described were all characterized by extreme brightness of a wide current density range. The solutions of Examples 9, 10, 11 and 12 were then allowed to stand for approximately two weeks and at that time a second set of panels were made from these respective solutions. All of the panels possessed equivalent lustre to the panels originally plated from the respective solutions, thus indicating that the selenium and lead were still stabilized in the addition agent to the extent that the same could function to impart brightness upon being subsequently introduced into a Rochelle solution.

While the above examples have illustrated the invention in connection with the use of certain selected selenium and lead compounds, it is to be understood that these compounds are merely representative, and accordingly, similar selenium and lead compounds could be substituted in the foregoing examples, provided the same were soluble with respect to the reacted aliphatic amine and did not produce a detrimental effect on the plating bath. Accordingly, in Table A listed below, certain additional compounds, submitted to meet the aforementioned requirements are set forth.

Table A

Name	Formula
Selenic acid	H_2SeO_4
Selenious acid	H_2SeO_3
Selenium dioxide	SeO_2
Selenium trioxide	SeO_3
Lead acetate—Lead sub-acetate	$Pb(C_2H_3O_2)_2$
Lead carbonate	$PbCO_3$
Lead formate	$Pb(CHO_2)_2$
Lead oxide	Pb_2O
Lead sub-oxide	Pb_2O
Lead dioxide	PbO_2

By like token, it is manifest that the improved reaction products of an aliphatic amine do not have to be reacted with the selenium or lead compounds prior to introduction to the Rochelle solution. In this regard it has been found that if the Rochelle solution is treated with an excess of these reaction products, addition agents, such as selenium dioxide and lead carbonate, will remain stable in the addition agents employed, and thus can effectively operate in a Rochelle solution to produce a bright copper deposit.

Similarly, while a specific Rochelle solution has been set forth in connection with Examples 9–12 inclusive, it is to be understood that the range of the respective constituents thereof can be varied within known limits of commercial practice, and accordingly, the disclosure is not limited to the Rochelle solution set forth. Additionally, while Examples 9 to 12 inclusive, recite the use of two addition agents, it is to be specifically understood that the stability of any one addition agent in the Rochelle solution is not predicated upon the use of a second addition and accordingly, any one addition agent of Examples 1 to 8 could be employed alone with a Rochelle solution with the equivalent result that the selenium or lead compound is stabilized in the Rochelle solution.

It is also to be noted that the operation of the aforementioned reaction product with lead and selenium compounds is no way predicated upon the use of Rochelle salts in the plating bath. Accordingly, the use of Rochelle salts may be eliminated and citrates or tartrates substituted therefore in known manner. By like token, a sodium cyanide electrolyte could be utilized in place of the potassium solution illustrated in conjunction with Examples 9 to 12 inclusive.

It will be seen from the foregoing that there has been provided a new and novel method of increasing the stability and useability of certain heretofore unstable brightening compounds for plating baths by reacting the same with certain novel reaction products. It has been shown how the use of these novel reaction products operates to increase the lustre and ductility of an electrodeposit from a Rochelle-cyanide solution, and accordingly, effectuates a savings in time and money as well as resulting in the improvement of the end product. It has also been shown how these improved reaction products can be added to the bath, either separately or with other addition agents, thus increasing the overall utility of the same.

Accordingly, modifications of the invention may be resorted to without departing from the spirit thereof or the scope of the appended claims.

What is claimed is:

1. A bath for the electrodeposition of copper, comprising copper cyanide in concentrations ranging from 2.5 to 16.0 oz. per gallon of solution; potassium cyanide in concentrations ranging from 3.5 to 25.0 oz. per gallon of solution; potassium hydroxide in concentrations ranging from 2.0 to 8.0 oz. per gallon of solution; Rochelle salts in concentrations ranging from 3.0 to 12.0 oz. per gallon of solution; and a selenium chelate; said selenium chelate being the product resulting from the reaction of a soluble selenium compound with the reaction product obtained by reacting an aliphatic amine having at least one replaceable hydrogen atom attached directly to an amino nitrogen atom with an alkali metal cyanide and a formaldehyde-yielding substance under conditions sufficiently alkaline that there is substantially no hydrolysis of said cyanide and in total amounts such that for each replaceable hydrogen atom one molecule of said cyanide and one molecule of said formaldehyde substance are added during the reaction; said selenium chelate being present in solution in excess of .1 gram per gallon of solution and being without valence.

2. A bath for the electrodeposition of copper, comprising copper cyanide in concentrations ranging from 2.5 to 16.0 oz. per gallon of solution; potassium cyanide in concentrations ranging from 3.5 to 25.0 oz. per gallon of solution; potassium hydroxide in concentrations ranging from 2.0 to 8.0 oz. per gallon of solution; Rochelle salts in concentrations ranging from 3.0 to 12.0 oz. per gallon of solution; and a lead chelate; said lead chelate being the product resulting from the reaction of a soluble lead compound with the reaction product obtained by reacting an aliphatic amine having at least one replaceable hydrogen atom attached directly to an amino nitrogen atom with an alkali metal cyanide and a formaldehyde-yielding substance under conditions sufficiently alkaline that there is substantially no hydrolysis of said cyanide and in total amounts such that for each replaceable hydrogen atom one molecule of said cyanide and one molecule of said formaldehyde substance are added during the reaction; said lead chelate being present in solution in excess of .01 gram per gallon of solution and being without valence.

3. A bath for the electrodeposition of copper, comprising copper cyanide in concentrations ranging from 2.5 to 16.0 oz. per gallon of solution; potassium cyanide in concentrations ranging from 3.5 to 25.0 oz. per gallon of solution; potassium hydroxide in concentrations ranging from 2.0 to 8.0 oz. per gallon of solution; Rochelle salts in concentrations ranging from 3.0 to 12.0 oz. per gallon of solution; a selenium chelate; said selenium chelate being the product resulting from the reaction of a soluble selenium compound with the reaction product obtained by reacting an aliphatic amine having at least one replaceable hydrogen atom attached directly to an amino nitrogen atom with an alkali metal cyanide and a formaldehyde-yielding substance under conditions sufficiently alkaline that there is substantially no hydrolysis of said cyanide and in total amounts such that for each replaceable hydrogen atom one molecule of said cyanide and one molecule of said formaldehyde substance are added during the reaction; and a lead chelate; said lead chelate being the product resulting from the reaction of a soluble lead compound with the reaction product obtained by reacting an aliphatic amine having at least one replaceable hydrogen atom attached directly to an amino nitrogen atom with an alkali metal cyanide and a formaldehyde-yielding substance under conditions sufficiently alkaline that there is substantially no hydrolysis of said cyanide and in total amounts such that for each replaceable hydrogen atom one molecule of said cyanide and one molecule of said formaldehyde substance are added during the reaction; said selenium chelate being present in solution in excess of .1 gram per gallon of solution and being without valence; said lead chelate being present in solution in excess of .01 gram per gallon of solution and being without valence.

4. A bath for the electrodeposition of copper, comprising; copper cyanide in concentrations ranging from 2.5 to 16.0 oz. per gallon of solution; potassium cyanide in concentrations ranging from 3.5 to 25.0 oz. per gallon of solution; potassium hydroxide in concentrations ranging from 2.0 to 8.0 oz. per gallon of solution; Rochelle salts in concentrations ranging from 3.0 to 12.0 oz. per gallon of solution; and a selenium chelate; said selenium chelate being the product resulting from the reaction of a soluble selenium compound with ethylene diamine tetracetic acid; said selenium chelate being present in solution in excess of

.1 gram per gallon of solution and being without valence.

5. A bath for the electrodeposition of copper, comprising; copper cyanide in concentrations ranging from 2.5 to 16.0 oz. per gallon of solution; potassium cyanide in concentrations ranging from 3.5 to 25.0 oz. per gallon of solution; potassium hydroxide in concentrations ranging from 2.0 to 8.0 oz. per gallon of solution; Rochelle salts in concentrations ranging from 3.0 to 12.0 oz. per gallon of solution; and a selenium chelate; said selenium chelate being the product resulting from the reaction of selenium dioxide with ethylene diamine tetracetic acid; said selenium chelate being present in solution in excess of .1 gram per gallon of solution and being without valence.

6. A bath for the electrodeposition of copper, comprising copper cyanide in concentrations ranging from 2.5 to 16.0 oz. per gallon of solution; potassium cyanide in concentrations ranging from 3.5 to 25.0 oz. per gallon of solution; potassium hydroxide in concentrations ranging from 2.0 to 8.0 oz. per gallon of solution; Rochelle salts in concentrations ranging from 3.0 to 12.0 oz. per gallon of solution; and a lead chelate; said lead chelate being the product resulting from the reaction of a soluble lead compound with ethylene diamine tetracetic acid; said lead chelate being present in solution in excess of .01 gram per gallon of solution and being without valence.

7. A bath for the electrodeposition of copper, comprising copper cyanide in concentrations ranging from 2.5 to 16.0 oz. per gallon of solution; potassium cyanide in concentrations ranging from 3.5 to 25.0 oz. per gallon of solution; potassium hydroxide in concentrations ranging from 2.0 to 8.0 oz. per gallon of solution; Rochelle salts in concentrations ranging from 3.0 to 12.0 oz. per gallon of solution; and a lead chelate; said lead chelate being the product resulting from the reaction of lead carbonate with ethylene diamine tetracetic acid; said lead chelate being present in solution in excess of .01 gram per gallon of solution and being without valence.

8. A bath for the electrodeposition of copper, comprising copper cyanide in concentrations ranging from 2.5 to 16.0 oz. per gallon of solution; potassium cyanide in concentrations ranging from 3.5 to 25.0 oz. per gallon of solution; potassium hydroxide in concentrations ranging from 2.0 to 8.0 oz. per gallon of solution; Rochelle salts in concentrations ranging from 3.0 to 12.0 oz. per gallon of solution; a selenium chelate; said selenium chelate being the product resulting from the reaction of a soluble selenium compound with ethylene diamine tetracetic acid; and a lead chelate; said lead chelate being the product resulting from the reaction of a soluble lead compound with ethylene diamine tetracetic acid; said selenium chelate being present in solution in excess of .1 gram per gallon of solution and being without valence; said lead chelate being present in solution in excess of .01 gram per gallon of solution and being without valence.

9. A bath for the electrodeposition of copper, comprising copper cyanide in concentrations ranging from 2.5 to 16.0 oz. per gallon of solution; potassium cyanide in concentrations ranging from 3.5 to 25.0 oz. per gallon of solution; potassium hydroxide in concentrations ranging from 2.0 to 8.0 oz. per gallon of solution; Rochelle salts in concentrations ranging from 3.0 to 12.0 oz. per gallon of solution; a selenium chelate; said selenium chelate being the product resulting from the reaction of selenium dioxide with ethylene diamine tetracetic acid; and a lead chelate; said lead chelate being the product resulting from the reaction of lead carbonate with ethylene diamine tetracetic acid; said selenium chelate being present in solution in excess of .1 gram per gallon of solution and being without valence; said lead chelate being present in solution in excess of .01 gram per gallon of solution and being without valence.

10. A bath for the electrodeposition of copper, comprising copper cyanide in concentrations ranging from 2.5 to 16.0 oz. per gallon of solution; sodium cyanide in concentrations ranging from 3.5 to 25.0 oz. per gallon of solution; sodium hydroxide in concentrations ranging from 2.0 to 8.0 oz. per gallon of solution; Rochelle salts in concentrations ranging from 3.0 to 12.0 oz. per gallon of solution; a selenium chelate; said selenium chelate being the product resulting from the reaction of selenium dioxide with ethylene diamine tetracetic acid; and a lead chelate; said lead chelate being the product resulting from the reaction of lead carbonate with ethylene diamine tetracetic acid; said selenium chelate being present in solution in excess of .1 gram per gallon of solution and being without valence; said lead chelate being present in solution in excess of .01 gram per gallon of solution and being without valence.

11. A method of electrodepositing copper, comprising the step of electrolyzing a Rochelle copper cyanide solution containing a selenium chelate; said selenium chelate being the product resulting from the reaction of a soluble selenium compound and ethylene diamine tetracetic acid; said selenium chelate being present in solution in concentrations exceeding .1 gram per gallon of solution.

12. A method of electrodepositing copper, comprising the step of electrolyzing a Rochelle copper cyanide solution containing a lead chelate; said lead chelate being the product resulting from the reaction of a soluble lead compound and ethylene diamine tetracetic acid; said lead chelate being present in solution in concentrations exceeding .01 gram per gallon of solution.

13. A method of electrodepositing copper, comprising the step of electrolyzing a Rochelle copper cyanide solution containing a selenium chelate and a lead chelate; said selenium chelate being the product resulting from the reaction of a soluble selenium compound and ethylene diamine tetracetic acid; said selenium chelate being present in solution in concentrations exceeding .1 gram per gallon of solution; said lead chelate being the product resulting from the reaction of a soluble lead compound and ethylene diamine tetracetic acid; said lead chelate being present in solution in concentration exceeding .01 gram per gallon of solution.

14. A method of electrodepositing copper, comprising the step of electrolyzing a Rochelle copper cyanide solution containing a selenium chelate; said selenium chelate being the product resulting from the reaction of a soluble selenium compound and the reaction product obtained by reacting an aliphatic amine having at least one replaceable hydrogen atom attached directly to an amino nitrogen atom with an alkali metal cyanide and a formaldehyde-yielding substance under conditions sufficiently alkaline that there is substantially no hydrolysis of said cyanide and in total amounts such that for each replaceable hydrogen atom one molecule of said cyanide and one molecule of said formaldehyde substance are added during the reaction; said selenium chelate being present in solution in concentrations exceeding .1 gram per gallon of solution.

15. A method of electrodepositing copper, comprising the step of electrolyzing a Rochelle copper cyanide solution containing a lead chelate; said lead chelate being the product resulting from the reaction of a soluble lead compound and the reaction product obtained by reacting an aliphatic amine having at least one replaceable hydrogen atom attached directly to an amino nitrogen atom with an alkali metal cyanide and a formaldehyde-yielding substance under conditions sufficiently alkaline that there is substantially no hydrolysis of said cyanide and in total amounts such that for each replaceable hydrogen atom one molecule of said cyanide and one molecule of said formaldehyde substance are added during the reaction; said lead chelate being present in solution in concentrations exceeding .01 gram per gallon of solution.

16. A method of electrodepositing copper, comprising the step of electrolyzing a Rochelle copper cyanide solution containing a selenium chelate and a lead chelate; said selenium chelate being the product resulting from the reaction of a soluble selenium compound and the reac-

tion product obtained by reacting an aliphatic amine having at least one replaceable hydrogen atom attached directly to an amino nitrogen atom with an alkali metal cyanide and a formaldehyde-yielding substance under conditions sufficiently alkaline that there is substantially no hydrolysis of said cyanide and in total amounts such that for each replaceable hydrogen atom one molecule of said cyanide and one molecule of said formaldehyde substance are added during the reaction; said selenium chelate being present in solution in concentrations exceeding .1 gram per gallon of solution; said lead chelate being the product resulting from the reaction of a soluble lead compound and ethylene diamine tetracetic acid; said lead chelate being present in solution in concentrations exceeding .01 gram per gallon of solution.

References Cited in the file of this patent

UNITED STATES PATENTS

2,694,677 Ostrow ---------- Nov. 16, 1954

2,732,336 Ostrow ---------- Jan. 24, 1956
2,737,485 Overcash et al. ---------- Mar. 6, 1956

OTHER REFERENCES

Versenes: Bersworth Chemical Co., Framingham, Mass., February 1952, pp. 2–5 (Sec. 1).

Senderoff Metal Finishing, vol. 48 (July 1950), pp. 59–64; vol. 48 (September 1950), pp. 71–78.

Graham et al.: Transactions Electrochemical Society, vol. 80 (1941), pp. 341–354.

Versenes: Bersworth Chemical Co., Framingham, Mass., February 1952, pp. 46–48 (Sec. 2).

Ser. No. 351,241, Weiner (A. P. C.), published May 18, 1943.