The Theory of Alloy Deposition and The Effect of a Rotating Cathode Upon Such Deposition, with Special Attention to the Possibility of Depositing Sterling Silver

Kenneth J. Stodden

Follow this and additional works at: http://digitalcommons.mtech.edu/bach_theses

Part of the Ceramic Materials Commons, Environmental Engineering Commons, Geology Commons, Geophysics and Seismology Commons, Metallurgy Commons, Other Engineering Commons, and the Other Materials Science and Engineering Commons

Recommended Citation

http://digitalcommons.mtech.edu/bach_theses/142

This Bachelors Thesis is brought to you for free and open access by the Student Scholarship at Digital Commons @ Montana Tech. It has been accepted for inclusion in Bachelors Theses and Reports, 1928 - 1970 by an authorized administrator of Digital Commons @ Montana Tech. For more information, please contact sjuskiewicz@mtech.edu.
THE THEORY OF ALLOY DEPOSITION
AND
THE EFFECT OF A ROTATING CATHODE
UPON SUCH DEPOSITION,
WITH SPECIAL ATTENTION TO THE POSSIBILITY
OF DEPOSITING STERLING SILVER

by
Kenneth J. Stodden

A Thesis
Submitted to the Department of Metallurgy
in Partial Fulfillment of the
Requirements for the Degree of
Bachelor of Science in Metallurgical Engineering

MONTANA SCHOOL OF MINES
BUTTE, MONTANA
MAY 16, 1941
THE THEORY OF ALLOY DEPOSITION

AND

THE EFFECT OF A ROTATING CATHODE

UPON SUCH DEPOSITION,

WITH SPECIAL ATTENTION TO THE POSSIBILITY

OF DEPOSITING STERLING SILVER

by

Kenneth J. Stodden

A Thesis

Submitted to the Department of Metallurgy

in Partial Fulfillment of the

Requirements for the Degree of

Bachelor of Science in Metallurgical Engineering

MONTANA SCHOOL OF MINES

BUTTE, MONTANA

MAY 16, 1941

MONTANA SCHOOL OF MINES LIBRARY.
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Introduction</td>
<td>1</td>
</tr>
<tr>
<td>Theoretical</td>
<td>3</td>
</tr>
<tr>
<td>Experimental Facts</td>
<td>30</td>
</tr>
<tr>
<td>Conclusions</td>
<td>33</td>
</tr>
<tr>
<td>Acknowledgment</td>
<td>34</td>
</tr>
</tbody>
</table>
The Theory of Alloy Deposition

and

The Effect of a Rotating Cathode

Upon Such Deposition,

With Special Attention to the Possibility

of Depositing Sterling Silver

In the past few years a great deal of attention has been given to the electrodeposition of alloys. For the main part, this investigation has been of scientific interest only; but in a few instances, such work has attained commercial importance. Alloys which are deposited commercially at the present time are:

1. lead - tin alloys from fluoborate solutions (1)
2. brasses from cyanide solutions.

The complication of the process depends to a large extent upon the properties which are desired in the final product. As color is the most outstanding property of brass, the product is regulated by this property almost entirely and the process is therefore fairly simple.

There are many articles in use today which are plated with silver. This metal is fairly soft and does not readily lend itself to improvement in its physical properties. If an alloy having the composition of sterling silver could be deposited, such articles could be greatly improved in their resistance to abrasion. This may be seen from the following:

Sterling silver may be defined as an age hardenable alloy of copper and silver containing ninety-two and five-tenths per cent silver and seven and five-tenths per cent copper. That it is age hardenable is easily seen from the silver-copper equilibrium diagram. (2)

Sterling silver has a fairly good corrosion resistance but tarnishes easily in sulphur-bearing atmospheres. Attempts have already been made to improve the resistance of silver to sulphur tarnishing by the simultaneous deposition of another metal along with it. Cadmium has been used commercially for this purpose, and superior tarnish resistance has been claimed for the silver-cadmium alloy deposit. However, a cadmium content of three per cent or more imparts a yellowish tinge to the alloy and therefore cadmium is undesirable. (3)

This work was undertaken to study the effect of a rotating cathode upon the electrodeposition of a silver-base alloy having the composition of sterling silver.

Theoretical

The electrodeposition of alloys is confined to the cases where the current density for each depositing cation is below the limiting current density for that cation. If, in order to deposit these cations simultaneously, their limiting current densities must

(3) Protective Metallic Coatings by Rawdon, Page 195 (1928).
be exceeded, the resulting deposit is spongy and therefore has no value. (4)

The limiting current density of a cation may be defined as that current density at which the concentration of the cation under consideration next to the electrode has become constant and nearly zero. Above this limiting current density the concentration of the cations next the electrode remains the same and the current density may be increased until another cation, commonly hydrogen, is evolved. This example illustrates the case where codeposition of two cations takes place, but with a current density above the limiting current density of one of the cations. Such evolution of hydrogen from the bath would result in stirring the bath and thus increasing the concentration of metal ions next to the electrode. Hydrogen would cease to be given off until that concentration had again been reached when hydrogen would again be evolved. There have been many similar examples of periodic changes between two processes. (5)

In order that two cations can deposit simul-

(4) Theoretical and Applied Electrochemistry, Thompson, Page 153.
(5) Theoretical and Applied Electrochemistry, Thompson, Page 140.
taneously, it is necessary that their electrode potentials be equal through a certain range of current densities as shown in the following illustration:

The curves $M_1$ and $M_2$ are the current density-cathode potential curves of two cations, and are determined in the absence of each other. When in solution together, these may be slightly different due to polarization or depolarization of one by the other. If the cathode potential is equivalent to $A$ and codeposition of both cations is taking place, the current density which is depositing $M_1$ is equivalent to the distance $AC$ while that depositing $M_2$ is measured by $AB$. The total cathode current density which is therefore necessary for codeposi-
tion to take place is $AB + AC$. The current efficiency for the deposition of either cation may be calculated by dividing the current density which is depositing that cation by the total cathode current density.

If the current density-cathode potential curves for the cations under consideration are so far apart that no vertical line representing constant cathode potential intersects them both, only the more electropositive ion will be deposited until the current density is raised above the limiting current density for that ion. The next most electropositive ion present will then carry the current which cannot be carried by the most electropositive ion. As previously mentioned, however, such deposits are not satisfactory due to their spongy character. (6)

It is very important to note that a fairly large rate of change of cathode potential with respect to increasing current density is desirable for the simultaneous deposition of two cations. This statement is obviously true because the greater is the change in potential with respect to current density, the greater is the chance that the two curves may be crossed by a

(6) Theoretical and Applied Electrochemistry, Thompson Page 152.
constant potential line. This is, in my opinion, the most important factor to be considered in the attempt to deposit any alloy.

The Nernst Equation:

\[
E = E_0 + \frac{RT}{nF} \ln C, \quad \text{or}
\]

evaluated at \(18^\circ\) C,

\[
E = E_0 + 0.058 \frac{nF}{n} \ln C
\]

where \(E\) is equal to the difference in potential between a metal and the solution of one of its salts, \(E_0\) is the potential difference between that metal and the solution containing one gram ion of the metal per liter, \(C\) is the concentration of the metal ions in gram ions per liter, \(R\) is the gas constant, \(T\) is the temperature in degrees Kelvin, \(n\) is the valence of the metal ions and \(F\) is one faraday of electricity, reveals the fact that if other factors such as polarization of one ion by the presence of another have little effect upon the process, two cations may have the same cathode potentials due to their respective concentrations in the bath out of which they
are to be deposited. (7)

By means of the following calculation for the ratio of copper ions to silver ions which is required to permit the codeposition of these ions, the above point will be illustrated.

The standard electrode potentials in volts for copper against cuprous ion and silver against silver ion as measured on the hydrogen scale are as follows:

<table>
<thead>
<tr>
<th>Combinations</th>
<th>E in volts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu / Cu⁺</td>
<td>0.528</td>
</tr>
<tr>
<td>Ag / Ag⁺</td>
<td>0.7995</td>
</tr>
</tbody>
</table>

Substituting in the Nernst equation, we have:
for copper against cuprous ion at 18°C,

\[ E = 0.528 + \frac{0.058}{1} \ln C_{Cu^+} \]

and for silver against silver ion at 18°C,

\[ E = 0.7995 + \frac{0.058}{1} \ln C_{Ag^+} \]

Now as these two ions are to be deposited at equal cathode potentials, we equate the above two equations and by this means the required ratio of copper ions to silver ions in the solution may be found.

\[
0.528 + 0.058 \ln C_{\text{Cu}^+} = 0.7995 + 0.058 \ln C_{\text{Ag}^+}
\]
\[
0.058 \ln C_{\text{Cu}^+} - 0.058 \ln C_{\text{Ag}^+} = 0.7995 - 0.528
\]
\[
0.058 \left( \ln C_{\text{Cu}^+} - \ln C_{\text{Ag}^+} \right) = 0.2715
\]
\[
\ln C_{\text{Cu}^+} - \ln C_{\text{Ag}^+} = \frac{0.2715}{0.058} = 4.681
\]
\[
\log \frac{C_{\text{Cu}^+}}{C_{\text{Ag}^+}} = 4.681
\]
\[
\frac{C_{\text{Cu}^+}}{C_{\text{Ag}^+}} = 10^{4.681}
\]

Obviously, such a ratio of metal ions in the bath would be very difficult to maintain by using the common salts of the metals in acid solutions. However, this ratio is not a criterion of the ease or difficulty with which codeposition may be carried out. It is worthy of note that a silver base, silver-zinc alloy requiring a ratio of zinc ion to silver ion squared, of approximately ten raised to the fifty-third power, has been deposited while, to date, no one has been able to plate out sterling silver which has a much lower required ratio of concentration of the ions. (8)

Brass represents an important case in the electrolytic deposition of alloys. This alloy cannot be deposited from simple salt solutions of the metals due to the fact that current density - cathode potential curves for such solutions do not enter a common cathode potential field until after the limiting current density for copper is reached, in which case the deposit is spongy and of little value. In cyanide solutions, however, these potentials were brought fairly close together so that with the help of other factors such as interdependent polarization, temperature control and addition agents a smooth deposit of brass was obtained, the composition of which depended upon the composition of the bath and upon other variable factors in the process such as those mentioned above. (9)
Thus we see that the use of a cyanide solution facilitates the codeposition of two cations which could not be effectively deposited together out of simple salt solutions. Evidently, ionic concentrations may be greatly varied by the use of solutions in which the ions to be deposited are present as complexes and accordingly solutions of this type are chosen for this kind of work.

(9) Theoretical and Applied Electrochemistry, Thompson, Page 153.
Much of the following material has been extracted from Preprint 79-7 of The Electrochemical Society. The subject of this paper is "The Constitution and Properties of Cyanide Plating Baths." I am using this material for reasons which are:

1. I feel that in this paper is the answer to the difficulty encountered by Mr. J. U. MacEwan in his attempt to deposit silver and copper simultaneously.

2. This paper indicates another possible way of attacking the problem.

During the past forty years there have been over one hundred papers written on the subject of cyanide plating baths. This interest has been warranted by their commercial importance. Such baths facilitate good anode corrosion; yield smooth, fine-grained deposits; exhibit high throwing power; and, as has already been seen, are useful for the deposition of alloys.

In cyanide solutions the heavy metal is usually considered to be present as a complex metallocyanide anion or possibly as several such ions. The question of the constitution of these baths involves the identification
of these anions. It is important to note that these anions either directly or indirectly control deposition, and determine the properties and operation of the baths. The principle methods for determining the formulas of complex ions in solution are based upon:

1. solubility
2. chemical analyses
3. lowering of the freezing point
4. electrode potentials
5. resistivity
6. transference number
7. viscosity
8. distribution (partition coefficient)
9. hydrolysis
10. spectrophotometry

It is rather difficult to find methods sufficiently sensitive and free from assumptions which will furnish conclusive evidence pertaining to bath constitution. Much of the information which is now available on cyanide complexes has been obtained from solubilities, analytical data, or potentials of concentration cells. This latter method employs dilute solutions in which the cyanide ion activity can be measured only indirectly. Spectrophotometric methods will probably be relied on to a fairly large extent for the study of cyanide complexes in the future.
One very important point regarding the cyanide complexes is that they form a group of coordination compounds.

In any work involving the use of cyanide baths there are certain terms for which definitions are desirable. Therefore, I shall include the definitions of these terms in this paper.

**Total cyanide** or total effective cyanide content is equivalent to the total content of the cyanide radical as it appears in all active forms. This quantity may be determined within a few per cent by titrating with a standard silver nitrate solution using a few drops of potassium iodide as an indicator.

**Total alkali cyanide** is defined as being the total amount of alkali cyanide present whether it is combined in the complexes or is free. This quantity may be computed from the knowledge of the total cyanide and metal contained with the stipulation that there is only one possible state of combination for the metal. If such is not the case, certain assumptions regarding bath constitution must be made in order to assign a value to this quantity.
Total combined cyanide is the total content of the cyanide radical in the active complexes and is equal to either the difference between total cyanide and uncombined or free alkali cyanide or the sum of total combined alkali cyanide and total metal cyanide.

Total combined alkali cyanide is the alkali cyanide that is combined with the heavy metal cyanide in one or more complexes. Here again, unless the composition of the complex cyanide is known, this quantity can only be determined by making certain assumptions concerning these cyanides.

Uncombined or free alkali cyanide may be defined as being the difference between total alkali cyanide and total combined alkali cyanide. In actual practice, this quantity is usually determined directly by some simple titration which yields reproducible results even though it is based upon certain assumptions which probably are not entirely true.

Metal cyanide content is just what the name implies, and may easily be computed from a knowledge of the total metal contained.
Cyanide ratio, an important factor in the consideration of cyanide baths, is the mol ratio of the total alkali cyanide to the metal cyanide. This ratio has the following relations when \( v \) is the valence of the heavy metal:

1. Cyanide ratio: \( \frac{\text{total alkali cyanide}}{\text{metal cyanide}} \)
2. Cyanide ratio: \( \frac{\text{total cyanide} - v(\text{metal cyanide})}{\text{metal cyanide}} \)
3. Cyanide ratio: \( \frac{\text{combined alkali cyanide} + \text{free alkali cyanide}}{\text{metal cyanide}} \)

It is worthwhile to note here that the cyanide ratio within a bath as computed by either equation (1) or (2) is less dependent upon assumptions than is that calculated according to equation (3). Under certain conditions, the cyanide ratio indicates the composition of the complex in the solution. The following example will, I believe, amply illustrate this fact.

A solution containing one mole of \( \text{Na}_2\text{Zn(CN)}_4 \) and one mole of \( \text{NaCN} \) would have the following relation:

- Total cyanide: 5M
- Total alkali cyanide: 3M
- Total combined alkali cyanide: 2M
- Uncombined or free alkali cyanide: 1M
- Metal cyanide: 1M
Therefore, the cyanide ratio is equal to three.

The table below illustrates numerically the relation between cyanide compounds as they have already been defined.

<table>
<thead>
<tr>
<th>Bath Number</th>
<th>No Assumption is Involved</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cyanide M</td>
<td>alkali cyanide M</td>
<td>metal cyanide M</td>
<td>cyanide ratio</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.75</td>
<td>0.50</td>
<td>0.25</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1.00</td>
<td>0.75</td>
<td>0.25</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.50</td>
<td>0.25</td>
<td>0.25</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0.75</td>
<td>0.50</td>
<td>0.25</td>
<td>2</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bath Number</th>
<th>Formula of Complex is Assumed</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>complex combined cyanide</td>
<td>combined cyanide</td>
<td>free alkali cyanide</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Cu(CN)_3^-</td>
<td>0.75</td>
<td>0.50</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Cu(CN)_3^-</td>
<td>0.75</td>
<td>0.50</td>
<td>0.25</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Ag(CN)_2^-</td>
<td>0.50</td>
<td>0.25</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Ag(CN)_2^-</td>
<td>0.50</td>
<td>0.25</td>
<td>0.25</td>
<td></td>
</tr>
</tbody>
</table>
From this example, two things are noticeable. These are:

1. The cyanide ratio defines the formula of a possible single complex only when the free cyanide is equal to zero.

2. Two cyanide solutions may possibly have the same composition but different constitutions.

In order that the relations between bath compositions and their properties may be determined it is necessary to understand the mechanism by means of which metals are deposited out of cyanide solutions. Unfortunately, this has not yet been worked out with any degree of finality and our present knowledge of the process is dependent upon theory rather than upon actual fact. Several theories have been developed with respect to the electroplating of metals out of cyanide solutions, some of which I will enumerate and briefly explain.

One of the first theories evolved was that which postulated that alkali metal ions, depending upon the type of alkali cyanide used in preparing the solution, were first deposited and then, due to the fact that this metal is higher in the electrochemical series than is the base metal, it displaces base metal ions from the
solution and thus the base metal is deposited on the cathode. However, this theory is little used today due to the fact that the alkali metals, sodium for example, have a higher decomposition potential than hydrogen, and, as plating cells are generally operated below the voltage required for the evolution of hydrogen, it would seem impossible for the deposition of sodium to take place.

Glasstone proposed a theory which helps to account for the fine-grained deposits obtained from cyanide solutions and this theory has been supported by many others. He claimed that complex cations which had been derived from the secondary ionization of complex anions were first deposited and that this was followed up by the dissociation of that cation and the deposition of heavy metal.

Some claim that the mechanism takes place by means of direct deposition of base metal out of complex anions. To speak of depositing metal at the cathode out of an anion seems foolhardy to many. However, this is no new view, and as all deposited metal is eventually derived from such anions it is not entirely improbable.

The classical explanation states that plating is
due to the direct deposition of metal ions which are derived from the secondary ionization of complex ions. If we consider this to be the case, we arrive at the conclusion that plating out of cyanide as well as simple salt solutions is dependent upon the Nernst equation:

\[ E = E_0 + \frac{nF}{RT} \ln C_{\text{metal ions}} \]

and the next thing to consider is the concentration of metal ions in the electrolyte. Bodlander applied the law of mass action to derive a complex ion stability constant which we now use in a reciprocal sense as a dissociation constant. The dissociation constant for a complex anion of the type \( M_{rA_n}^- \) where \( M \) is equal to the heavy metal, \( r \) is the number of atoms of heavy metal per anion, \( A \) is the complex radical and \( n \) is the number of atoms of that radical per anion may be defined as follows:

\[ K = \frac{(M^{+\cdots})^r \times (A^{-\cdots})^n}{(M_{rA_n}^{-\cdots})} \]

In the above equation, the material within each set of parenthesis represents the concentration of that material in gram atoms per liter. A high ionization constant
indicates that the primary anion being considered dissociates greatly into secondary ions while a very small value indicates exactly the other extreme. Several attempts have been made by independent workers to determine the dissociation constants for many of the complex cyanides, but due to the fact that different methods and different assumptions were used by the various investigators, their results were not entirely in agreement with one another. Below are a few of the results obtained.

<table>
<thead>
<tr>
<th>Complex Anion</th>
<th>Dissociation Constant</th>
<th>Investigator</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag(CN)_2^-</td>
<td>1.5 x 10^-21</td>
<td>Euler</td>
</tr>
<tr>
<td>Ag(CN)_2^-</td>
<td>8.8 x 10^-22</td>
<td>Bodlander &amp; Eberlein</td>
</tr>
<tr>
<td>Ag(CN)_2^-</td>
<td>4.2 x 10^-22</td>
<td>Britton &amp; Dodd</td>
</tr>
<tr>
<td>Ag(CN)_3^-</td>
<td>1.1 x 10^-22</td>
<td>Bodlander &amp; Eberlein</td>
</tr>
<tr>
<td>Cu(CN)_3^-</td>
<td>0.5 x 10^-27</td>
<td>Bodlander</td>
</tr>
</tbody>
</table>

This information obviously delegates these complexes to a group which shows slight secondary ionization and this consideration is the stumbling block in the theory of direct deposition of secondarily ionized base metal. For instance, there has been a great deal of discussion by Haber, Glassstone, and others as to the velocities with which complex anions should ionize in order to maintain deposition of
metal from baths having very low concentrations of metal ions. Also one might think that the dissociation constant would be a measure of the ease of deposition. However, this is evidently not the case as mercury, certain complex anions of which show a very slight dissociation, is more easily deposited than are some metals whose complex anions have larger ionization constants. It is possible that the velocity of ionization for complex mercury anions is greater than are those velocities for the complexes of the other metals and thus deposition of mercury is more easily carried out than is that of the other metals.

As has already been pointed out, the constitution of cyanide baths may be estimated when the solution is saturated with heavy metal cyanide or, in other words, the free alkali cyanide content is equal to zero. Also, under these conditions a minimum cyanide ratio is attained. From data of this type, Bassett and Corbet found that for a solution which contained one and one-tenth moles of potassium cyanide and was saturated with one and one-tenth moles of silver cyanide a cyanide ratio of one and three-
hundredths existed, and from this information they calculated that the complex ion which was predominantly present was $\text{Ag(CN)}_2^-$. As for the potassium compound containing this type of anion, one mole of potassium cyanide ties up one mole of silver cyanide or

$$\text{KCN} + \text{AgCN} \xrightarrow{\text{K}^+ + \text{Ag(CN)}_2^-}$$

Similar work has been done on alkali cyanide solutions saturated with cuprous cyanide and the results point toward one generalization regarding complex cyanides, and this is that the higher the cyanide ratio is, the greater is the valence of the complex anion. This statement points toward the control of the properties of solutions by controlling the cyanide ratios existing in them.

This, then, is where the Werner theory of coordination compounds may be applied. Progress in the study of composition and properties of the complex cyanides may be expected from the systematic application of the coordination theory. The theory, as developed to the present time describes a complex cyanide ion as consisting of a central positive heavy metal ion about which are grouped negatively charged cyanide ions. The coordina-
tion number is equal to the number of pairs of shared electrons with which the complex ion is built up and upon this value depends the net negative charge exhibited by the complex anion. There are indications that coordination numbers of two, three, four, five, six, seven or eight may exist. However, values of five and seven are unlikely to exist due to the fact that they do not permit an orderly arrangement of the atoms, while coordination numbers of four and six are most likely to occur due to ease of orientation.

The possible space configurations for various coordination numbers have been worked out as follows:

<table>
<thead>
<tr>
<th>Coordination Numbers</th>
<th>Space Configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>linear</td>
</tr>
<tr>
<td>3</td>
<td>plane triangular</td>
</tr>
<tr>
<td>4</td>
<td>square planar or tetrahedral</td>
</tr>
<tr>
<td>6</td>
<td>octahedral</td>
</tr>
<tr>
<td>8</td>
<td>cubic</td>
</tr>
</tbody>
</table>

The coordination theory also subdivides true complex ions into two groups. These are:

(1) Those which show a small but significant dissociation to produce metal ion.

(2) Those which show no significant dissociation.

These two groups have been referred to by Biltz as normal
and penetration complexes respectively.

It has been found that the properties of cyanide plating baths are greatly affected by what has been defined as being the coordination number of the complexes existing in the solutions. To illustrate this point, it has been found that a low coordination number is, in general, indicative of easy deposition and higher cathode efficiency. Thus, it has been stated that dicyanides within the bath are favorable, tetracyanides are fairly satisfactory, and hexacyanides and octacyanides are unfavorable for electrolytic work. Increasing the metal content of the solution has a tendency to increase the concentration of metal-bearing anions and of metal cations within the electrolyte, thus lowering the coordination number and thereby rendering the plating process easier. It is very important to note that the addition of more alkali cyanide has a tendency to decrease the metal-bearing anion and metal cation concentrations, and to increase the coordination number yielding a lower cathode efficiency. Also, generally, as the alkali cyanide in the bath is increased, there is a faster rate of change of cathode polarization with respect to increasing current
density. It has sometimes been found that cathode efficiency increases as the concentration of alkali cyanide is increased and this may be ascribed to the theory that the addition of alkali cyanide increases the pH of the solution due to hydrolysis with water and increasing the pH has the effect of increasing the potential necessary for hydrogen discharge.

Either stirring, such as that resulting from rotation of the cathode, or heating has the effect of maintaining a higher metal concentration within the diffusion layer immediately adjoining the cathode surface; and this, in turn, makes for a higher cathode efficiency possibly due to a decrease in coordination number for the complexes existing within the diffusion layer.

Literature indicates that there is a definite relation between cyanide ratio and cathode polarization and this relation may be shown by the subsequent cathode potential - cathode current density curves in which curve one represents solutions in which the cyanide ratio is low or metal concentration is relatively high, curve two is that obtained with an intermediate cyanide ratio, and curve three is the result found when the cyanide ratio
was high. These curves are also arranged in the order of increasing coordination numbers. (10)

It is readily seen that for the codeposition of two cations, curves of type two are desirable as they yield a wide range through which the cathode polarizes, and for that reason it is far more likely that the two metals being considered would have the same cathode potential at some particular current density. Curves of this type have been readily obtained for copper which apparently shows an ability to form complexes revealing an intermediate coordination number. However, this type of curve

has never been obtained for silver complexes. Apparently, as the cyanide ratio within silver baths is increased, the type of curve obtained changes suddenly from type one to type three without showing the intermediate phase. As a result of these considerations, I would recommend that the cathode potential - current density curves for silver cyanide solutions be investigated with a view toward increasing the slope of the curve or toward increasing cathodic polarization with respect to increasing current density. It is well to note here that in order to commercially deposit silver and copper together out of cyanide baths, this is the goal which must be attained. The curves on pages 28 and 29 have been extracted from Mr. MacEwan's thesis, and it is worthwhile to note that his curves for the complex silver salts show little polarization while those for copper indicate a widely variant cathode potential. Also it is noticeable that the silver potential changes very little with change of metal concentration but the copper potential changes rather rapidly with changing concentrations of copper. It is probable that under some conditions which have not yet been attained, silver and copper would have the same potential for dis-
Current Density - Cathode Potential Curves

- AgCN
  - 60° 18°
- CuCN
  - 75°
- CuCN
  - 18°
- Zn(CN)₂
  - 18°
Change of Potential with Metal Conc.
We have now considered the fundamental principles underlying the codeposition of two cations and we may now study the effect of the rotating cathode upon such work. There are four reasons for the use of a rotating cathode, only one of which is really fundamental. Of minor consideration are the facts that the deposit is burnished as a result of the friction between the solution and the cathode surface, air bubbles are brushed away thus preventing nodule formation, and the thickness of the deposit is uniform. Crystal size decreases with increasing rotation of the cathode and increasing current density. Therefore, as tensile strength varies inversely as crystal size, that physical property increases with increased stirring and also with increased current density.

The primary reason for the use of a rotating cathode lies in the fact that such a cathode produces an agitation of the electrolyte which tends to prevent impoverishment of the diffusion layer lying between the body of the electrolyte and the cathode surface. Thus the con-

(11) The Electrodeposition of Silver Base Binary Alloys from Cyanide Solutions by J. U. MacEwan, Pages 7 and 17.
centration of metal-bearing anions and of metal cations in this layer is higher at a certain current density than would that concentration be if a stationary cathode were being used. Therefore, the limiting current density would not be as low when using a rotating cathode as it would be when using a stationary cathode. As a result, metals may be deposited at a much faster rate when using a stirring cathode than when a stationary electrode is employed. This has been illustrated by C. W. Bennett and C. O. Brown (12) who found that the electrolytic refining of copper may be illustrated in one hour by using a revolving cathode.

It is known that cathode polarization is a function of impoverishment of metal ions within the diffusion layer, and that as such impoverishment decreases, cathodic polarization or the slope of current density - cathode potential curves decreases also. This is exactly opposite to the desired effect as, by decreasing the rate of change of cathode potential with respect to current density, the chance of having an electrode potential equal to that of another cation to be deposited is made smaller than when using a stationary cathode. This fact has been shown by C. W. Bennett and A. W. Davison (13) who found


that, as rotation of the cathode increased, the cathodic polarization for either cation changed less rapidly with respect to current density than it did when using a stationary electrode. As would be expected, with increasing speed of rotation, a point was finally reached at which neither cation had the same electrode potential and only the more positive metal, zinc, was deposited.

This then is the answer to the problem at hand. While the use of a rotating cathode decreases the chances of codepositing zinc and copper, it absolutely prohibits the idea of codepositing silver and copper together as their electrode potentials have never been found to be equal even when using a stationary electrode.
Conclusions

1. The use of a rotating cathode decreases the possibilities of codepositing two cations due to the fact that cathodic polarization decreases as impoverishment of metal cations within the diffusion layer decreases.

2. I would recommend that, with the idea of the deposition of sterling silver in view, the effect of various addition agents on the single electrode potential of silver in cyanide solutions be studied, the object being to form a compound within the bath having an intermediate coordination number, and therefore yielding a cathode potential - cathode current density curve having a fairly large slope.
Acknowledgment

I should here like to express my most sincere gratitude to Dr. C. L. Wilson for his aid and counsel in the writing of this thesis. Also I desire to thank Dr. A. E. Koenig, Professor B. D. Cullity, and Miss Guinevere E. Crouch for their assistance in obtaining material pertaining to this subject.