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UMI®
THE ELECTRODEPOSITION OF ALUMINUM

by

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The Rice Institute

A Thesis
Presented to the Faculty of The
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In Partial Fulfillment of the
Requirements for the
Degree
of
Doctor of Philosophy

The Rice Institute
1943
OUTLINE

The Electrodeposition of Aluminum

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   B. Addition of Benzene
   C. Addition of Toluene
   D. Addition of Xylene
   E. Addition of Petroleum Ether, Kerosene or Gasoline
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   H. Addition of Some Alkyl Halides
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PART I.

THE ELECTRODEPOSITION OF ALUMINUM

FROM SEVERAL MIXED SOLVENTS
THE ELECTRODEPOSITION OF ALUMINUM

PART I: THE ELECTRODEPOSITION OF ALUMINUM FROM SEVERAL MIXED SOLVENTS

I. Introduction

Aluminum coatings have been used for some years as a protection for iron and steel and for aluminum alloys which are susceptible to corrosion in ordinary environments. Although nearly all of the metals used commercially as protective coatings can be deposited in a firmly adhering form electrolytically from aqueous solutions, aluminum is an outstanding exception. At present coatings of aluminum are usually applied by any one of four methods, namely, hot-dipping, cementation, spraying, or mechanical methods.

A variety of uses for aluminum platings has been suggested. The most important use is the prevention of oxidation of ferrous metals at elevated temperatures. Aluminum coatings, applied at present by methods other than electrodeposition, are used extensively in the brewing and canning industries to prevent corrosion (4, 5). Since very pure aluminum is not attacked by certain concentrated acids, especially nitric and acetic, aluminum plated objects presenting a surface of pure aluminum would be useful in the handling of these chemicals. The use of
aluminum plated surfaces for steel economizer tubes has been suggested in patents by Keyes and coworkers (3). These tubes contain water inside and hot flue gases frequently containing corrosive sulfur compounds on the outside. Protection would be afforded by plating the outside of these tubes with aluminum. Other containers for petroleum products could be protected against corrosion by H₂S and other sulfur compounds present in petroleum.

Aluminum coatings are used in valves and seats to prevent "freezing" of the valve (4). There also exists the possibility of aluminum plating the inside of steel cylinders used to store compressed gases (3). This results from the fact that gas stored in iron cylinders reacts with the iron to produce volatile products which prevent the gas from remaining in a state of purity.

Pure aluminum is somewhat unsatisfactory as a structural material for many purposes in spite of its corrosion resistance because it has a rather low tensile strength and low elastic limit. Aluminum plated steel would provide a strong material which would be resistant to corrosion.*

*Hoff (4) demonstrated the relative corrosion resistance of aluminum coatings with atmospheric corrosion data for a five year period using 0.5mm iron sheets coated with various materials. On the basis of the original weight as 100%, after five years exposure to the atmosphere the weights of the various samples were: aluminum 103%, zinc 85%, lead 60%, and tin 50%. An uncoated sample lost 15% of its original weight. The small change in weight of the sample covered with aluminum should be noted.
Methods for the electrodeposition on aluminum on various metals have recently been developed (1,2,3). These methods involve the use of non-aqueous mixtures of various sorts. In the earlier part of this research (1), it was shown that aluminum can be deposited electrolytically on other metals from solutions of anhydrous aluminum chloride in any one of several fused pyridinium compounds, namely ethyl pyridinium bromide or chloride, and ethylene di-pyridinium dibromide or dichloride. Smooth plates may be produced on iron, steel, copper, bronze, brass, platinum, lead and tin using aluminum anodes in the fused bath. However, for satisfactory operation of these baths a plating temperature of about 125° is required. Since it would be very advantageous to be able to perform the plating operation at room temperature, the present research has been directed at the development of an electrolyte from which this can be accomplished. Such lowering of the plating temperature was found possible by the addition of any one of several organic solvent reagents to the mixture of aluminum chloride and one of the pyridinium compounds previously mentioned. The work of earlier investigators in the field of electrodeposition of aluminum has already been discussed (1). An excellent, critical review of the methods of electroplating aluminum has been made by Wadell (6).
II. The Effect of Addition of Organic Solvent Reagents to Ethyl Pyridinium Bromide-Aluminum Chloride Solutions

In order to make a survey of the effect of various types of solvent reagents on the aluminum chloride-pyridinium salt fused baths, the system ethyl pyridinium bromide-aluminum chloride was chosen as representative, the choice being based on the observed similarity of the several pyridinium salt baths to the one chosen. The most important and representative solution in that system was the eutectic mixture with a concentration of 66.7 mol percent aluminum chloride and this solution was used throughout the following preliminary tests. It remains liquid down to a temperature of -40°, but is somewhat viscous even at room temperature. The miscibility of this eutectic mixture with a number of organic solvents was determined. Some of the resulting solutions were electrolyzed to determine whether aluminum could be deposited electrolytically from them at room temperature.

A. Addition of Pyridine: The addition of dry pyridine to the eutectic in amounts from 20% to 50% by volume resulted in the evolution of considerable heat and an increase in melting point. The resulting solutions were not electrolyzed because of this increase in melting point.
B. Addition of Benzene: The addition of dried benzene to the eutectic in amounts from 20% to 50% by volume produced clear, light brown, sometimes somewhat greenish, solutions with no evolution of heat. The viscosity of the resulting solution of about 50% benzene by volume was very low. Further additions of benzene resulted in the formation of a less dense clear layer which seemed to be almost entirely benzene.

Electrolysis of the solution saturated with benzene as well as those of slightly lower concentration showed that aluminum could be deposited from these solutions at room temperature. Furthermore, the plates were smoother and shinier than those obtained from a fused bath containing no benzene.

C. Addition of Toluene: The addition of toluene gave results which were practically identical with those produced by benzene. The viscosity of the solution was very low and the appearance of the second layer occurred at about 50% toluene by volume.

D. Addition of Xylene: The addition of xylene to the eutectic mixture produced the same results as the additions of benzene and toluene did. Shiny plates were also obtained from this solution.
E. Addition of Petroleum Ether, Kerosene or Gasoline: There was no reaction or miscibility between equal volumes of petroleum ether, kerosene or gasoline and the eutectic mixture. Other aliphatic hydrocarbons could be expected to behave similarly.

F. Addition of Ethyl Ether: A vigorous reaction took place when equal volumes of ethyl ether and eutectic were mixed, forming a brownish-purple liquid which solidified between $40^\circ$ and $50^\circ$. When ether was added the same vigorous reaction continued. Electrolysis of the solution produced considerable gas at the cathode but no deposit.

G. Addition of Carbon Disulfide and of Chloroform: Neither of these reagents showed any reaction or miscibility when mixed with the eutectic.

H. Addition of Some Alkyl Halides: The related compounds ethyl bromide, ethyl chloride, ethylene dibromide, and ethylene dichloride were tested as solvents for the eutectic. The amount of solvent which could be added without producing a phase change of some sort varied with the compound used.

The addition of 5 volumes of ethylene dibromide to the eutectic produced a second, more dense layer consisting principally of ethylene dibromide. This was the only one of the solvents in this group which produced a second layer.
The other solvents caused a white, flocculent solid to form after the addition of a certain amount of solvent and the solutions became colorless considerably before the formation of the precipitate.

With ethyl bromide, less than 10 volumes was required to produce the precipitate, whereas with ethylene chloride the precipitate formed after the addition of about 35 to 40 volumes. With ethyl chloride, however, it was possible to add about 500 to 1000 volumes before the precipitate formed.

There seemed to be no simple relationship between this behavior and the dielectric constant of the solvent.

The usefulness of these solvents is somewhat limited for several reasons. The compounds ethyl bromide, ethylene bromide and ethylene dichloride react with aluminum metal, thus reducing the efficiency of the process and changing the composition of the bath. Furthermore, ethyl bromide and especially ethyl chloride are too volatile to be very practical. However, these solvents might find practical application under special conditions.

I. Addition of Chlorobenzene and Benzene-Chlorobenzene Mixtures.

With a freshly prepared sample of eutectic, the addition of chlorobenzene produces a uniform, apparently homogeneous mixture of light color. There seemed to be infinite miscibility of the two materials, but there were two factors which
seemed to act to decrease the miscibility. These were moisture and the age of the eutectic before addition, which may be partly moisture.

The moisture effect was noticed particularly with dilute solutions, which separated into two layers on exposure to the air for a short while with formation of cloudiness in the upper (chlorobenzene) layer. Other, more concentrated solutions, which were corked were found to attack the cork (although not in contact with it) and thus allow moisture to get in. These solutions formed a small amount of solid crust at the surface and a clear second layer which increased in volume with time at the expense of the lower, colored layer.

The following experiment on the effect of water was performed. Ten cc. of chlorobenzene were added to 2 cc. of eutectic to produce 12 cc. of solution. Three drops of water were added, and within two minutes the solution had separated into two layers. After 2 minutes, the volume of the upper layer was 6.0 cc and that of the lower layer was 6.0 cc. The amount of the more dense layer continued to decrease with time and the upper layer increased. After 2½ hours, the volume of the upper layer was 8.3 cc. and that of the lower layer was 3.7 cc. The color increased in the lower layer as the volume decreased. The upper layer remained colorless, but clear.

A similar mixture of the same composition was prepared under similar conditions except that no water was added. The
volume and color remained constant during this period (and for several days thereafter) and no second layer appeared.

With a sample of old electrolyte, a second layer was observed to form at 2.8 cc, when 2 cc of chlorobenzene were added to 1 cc of eutectic.

In order to get some idea of the miscibility of benzene with eutectic-chlorobenzene solutions, benzene was added to a fairly dilute solution of eutectic in chlorobenzene. The following results were obtained:

<table>
<thead>
<tr>
<th>Added</th>
<th>Produced</th>
</tr>
</thead>
<tbody>
<tr>
<td>cc. eutectic</td>
<td>cc. chlorobenzene</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
</tr>
</tbody>
</table>

The addition of a small amount of benzene produced a second layer. The amount of the second layer increased and the amount of the electrolyte layer decreased as the benzene concentration increased.
III. The Systems: Aluminum Chloride-Ethyl Pyridinium Bromide-Toluene or Benzene

The preceding experiments on the effect of addition of various solvent reagents to the 66.7 mol percent aluminum chloride eutectic with ethyl pyridinium bromide showed that aluminum could be deposited at room temperature from the solution obtained by saturation of this eutectic with toluene or benzene. As part of the further investigation of these three component systems, a study of the phase equilibria was made. The experimental method and the results of the study are described below.

A. Phase Equilibria of the Toluene System:

1. Experimental Method: The method used to determine the phase equilibria of the three component system consisted of making up two-component mixtures of aluminum chloride and ethyl pyridinium bromide of various concentrations and adding the third component, toluene, until a change occurred in the number or kinds of phases in equilibrium. Weighed samples of the various aluminum chloride-ethyl pyridinium bromide mixtures were placed in stoppered Erlenmeyer flasks and measured amounts of dry toluene added in small portions from a buret. The stoppered flasks were shaken mechanically until equilibrium in reactions involving solids was usually several hours, but only a few
minutes were required for liquid-liquid systems to attain equilibrium.

Only an approximate phase diagram was desired. Therefore, elaborate time-consuming precautions to eliminate slight errors which might occur from variations in the temperature or atmospheric pressure, evaporation of small amounts of toluene during addition, presence of very small amounts of water vapor, or the like were omitted. The temperature of the measurements was that of the room which varied between 28° and 32°.

2. Data: The data obtained are presented in Table I, which shows the weight percent aluminum chloride, weight percent ethyl pyridinium bromide and weight percent toluene at points where changes occur in the number or kinds of phases in equilibrium. These phase changes are also indicated in the table. The table is divided into a number of sections. Each section contains the phase changes which were observed during the addition of toluene to one starting mixture of aluminum chloride and ethyl pyridinium bromide. Each line of the table represents a point which is plotted on the triangular three-component diagram in Figure 1. It should also be noted that all of the points represented by one section of the table lie on a straight line extending from the point representing the composition of the starting two-component mixture to the corner of the diagram representing 100 percent toluene.
<table>
<thead>
<tr>
<th>Wt.% AlCl₃</th>
<th>Wt.% EtPyBr</th>
<th>Wt.% Toluene</th>
<th>Phases Produced</th>
</tr>
</thead>
<tbody>
<tr>
<td>28.5</td>
<td>71.5</td>
<td>0.0</td>
<td>Orange crystalline solid and orange liquid.</td>
</tr>
<tr>
<td>23.8</td>
<td>59.6</td>
<td>16.6</td>
<td>A turbid orange liquid (probably containing solid) and a clear, less dense liquid.</td>
</tr>
<tr>
<td>30.0</td>
<td>70.0</td>
<td>0.0</td>
<td>Orange crystalline solid and orange liquid.</td>
</tr>
<tr>
<td>27.2</td>
<td>63.5</td>
<td>9.3</td>
<td>Slightly turbid orange liquid, no crystals.</td>
</tr>
<tr>
<td>25.7</td>
<td>59.7</td>
<td>14.6</td>
<td>Turbid orange liquid and clear, less dense liquid.</td>
</tr>
<tr>
<td>32.0</td>
<td>68.0</td>
<td>0.0</td>
<td>Orange crystalline solid and orange liquid.</td>
</tr>
<tr>
<td>28.2</td>
<td>59.8</td>
<td>12.0</td>
<td>Turbid orange liquid; no crystals.</td>
</tr>
<tr>
<td>25.8</td>
<td>54.8</td>
<td>19.4</td>
<td>Turbid orange liquid and clear, less dense liquid.</td>
</tr>
<tr>
<td>35.0</td>
<td>65.0</td>
<td>0.0</td>
<td>Orange crystalline solid and orange liquid.</td>
</tr>
<tr>
<td>28.2</td>
<td>52.4</td>
<td>19.4</td>
<td>One turbid liquid; no crystals.</td>
</tr>
<tr>
<td>36.8</td>
<td>63.2</td>
<td>0.0</td>
<td>Orange crystalline solid and orange liquid.</td>
</tr>
<tr>
<td>28.4</td>
<td>48.7</td>
<td>22.9</td>
<td>Turbid liquid (liquid plus suspended solid). Suspended solid is not crystalline like solid originally present</td>
</tr>
<tr>
<td>25.4</td>
<td>43.6</td>
<td>31.0</td>
<td>Orange liquid, suspended solid and clear, less dense liquid.</td>
</tr>
</tbody>
</table>

(Continued)
<table>
<thead>
<tr>
<th>Wt.% AlCl₃</th>
<th>Wt.% EtPyBr</th>
<th>Wt.% Toluene</th>
<th>Phases Produced</th>
</tr>
</thead>
<tbody>
<tr>
<td>38.1</td>
<td>61.9</td>
<td>0.0</td>
<td>Orange crystalline solid and orange liquid.</td>
</tr>
<tr>
<td>28.9</td>
<td>46.9</td>
<td>24.2</td>
<td>Orange liquid and suspended solid; No crystals.</td>
</tr>
<tr>
<td>25.7</td>
<td>41.9</td>
<td>32.4</td>
<td>Orange liquid, suspended solid and clear, less dense liquid. Solid becoming more easily separable.</td>
</tr>
<tr>
<td>38.1</td>
<td>61.9</td>
<td>0.0</td>
<td>Orange crystalline solid, and orange liquid.</td>
</tr>
<tr>
<td>29.1</td>
<td>47.3</td>
<td>23.6</td>
<td>Orange liquid and suspended solid. No crystals.</td>
</tr>
<tr>
<td>25.7</td>
<td>41.7</td>
<td>32.6</td>
<td>Orange liquid, suspended solid and clear, less dense liquid.</td>
</tr>
<tr>
<td>38.3</td>
<td>61.7</td>
<td>0.0</td>
<td>Orange crystalline solid and orange liquid.</td>
</tr>
<tr>
<td>28.3</td>
<td>45.5</td>
<td>26.2</td>
<td>Orange liquid, and suspended solid. No crystals.</td>
</tr>
<tr>
<td>25.7</td>
<td>41.4</td>
<td>32.9</td>
<td>Orange liquid, suspended solid and clear, less dense liquid.</td>
</tr>
<tr>
<td>41.6</td>
<td>58.4</td>
<td>0.0</td>
<td>Light brown crystalline solid and brown liquid.</td>
</tr>
<tr>
<td>28.6</td>
<td>40.2</td>
<td>31.2</td>
<td>One slightly turbid, light brown liquid</td>
</tr>
<tr>
<td>25.9</td>
<td>36.3</td>
<td>37.8</td>
<td>Slightly turbid, light brown liquid and clear, less dense liquid.</td>
</tr>
<tr>
<td>41.6</td>
<td>58.4</td>
<td>0.0</td>
<td>Yellow crystalline solid and light brown liquid.</td>
</tr>
<tr>
<td>29.0</td>
<td>40.6</td>
<td>30.4</td>
<td>One solid and one liquid.</td>
</tr>
<tr>
<td>26.1</td>
<td>38.6</td>
<td>37.3</td>
<td>Solid, light brown liquid and clear, less dense liquid.</td>
</tr>
</tbody>
</table>

(Continued)
<table>
<thead>
<tr>
<th>Wt. %</th>
<th>Wt. %</th>
<th>Wt. %</th>
<th>Phases Produced</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlCl₃</td>
<td>EtPyBr</td>
<td>Toluene</td>
<td></td>
</tr>
<tr>
<td>42.9</td>
<td>57.1</td>
<td>0.0</td>
<td>Dark orange, crystalline solid.</td>
</tr>
<tr>
<td>30.1</td>
<td>40.0</td>
<td>29.9</td>
<td>One slightly turbid liquid.</td>
</tr>
<tr>
<td>26.8</td>
<td>35.7</td>
<td>37.5</td>
<td>Turbid liquid and clear, less dense liquid.</td>
</tr>
<tr>
<td>44.5</td>
<td>55.5</td>
<td>0.0</td>
<td>Dark, orange-brown, crystalline solid.</td>
</tr>
<tr>
<td>33.4</td>
<td>41.7</td>
<td>24.9</td>
<td>Clear, deep orange liquid.</td>
</tr>
<tr>
<td>28.7</td>
<td>35.7</td>
<td>35.6</td>
<td>Clear, deep orange liquid and clear, less dense liquid.</td>
</tr>
<tr>
<td>46.3</td>
<td>53.7</td>
<td>0.0</td>
<td>Orange-brown, crystalline solid.</td>
</tr>
<tr>
<td>36.5</td>
<td>42.3</td>
<td>21.2</td>
<td>One clear, orange liquid.</td>
</tr>
<tr>
<td>30.9</td>
<td>35.9</td>
<td>33.2</td>
<td>Clear, orange liquid and clear, less dense liquid.</td>
</tr>
<tr>
<td>47.8</td>
<td>52.2</td>
<td>0.0</td>
<td>Dark orange, crystalline solid.</td>
</tr>
<tr>
<td>40.4</td>
<td>44.1</td>
<td>15.5</td>
<td>One clear, orange liquid.</td>
</tr>
<tr>
<td>32.3</td>
<td>35.3</td>
<td>32.4</td>
<td>Clear, orange liquid and clear, less dense liquid.</td>
</tr>
<tr>
<td>50.5</td>
<td>49.5</td>
<td>0.0</td>
<td>Dark orange, crystalline solid.</td>
</tr>
<tr>
<td>44.8</td>
<td>43.8</td>
<td>11.4</td>
<td>One clear, dark red-brown liquid.</td>
</tr>
<tr>
<td>30.9</td>
<td>30.3</td>
<td>38.8</td>
<td>Clear, dark red-brown liquid and clear, less dense liquid.</td>
</tr>
<tr>
<td>53.0</td>
<td>47.0</td>
<td>0.0</td>
<td>Dark brown liquid.  This point taken from the two-component phase diagram (1).</td>
</tr>
</tbody>
</table>

(Continued)
<table>
<thead>
<tr>
<th>Wt. % AlCl₃</th>
<th>Wt. % EtPyBr</th>
<th>Wt. % Toluene</th>
<th>Phases Produced</th>
</tr>
</thead>
<tbody>
<tr>
<td>55.0</td>
<td>45.0</td>
<td>0.0</td>
<td>Dark brown liquid.</td>
</tr>
<tr>
<td>31.9</td>
<td>26.1</td>
<td>42.0</td>
<td>Dark, orange-brown, transparent liquid and clear, less dense liquid.</td>
</tr>
<tr>
<td>58.6</td>
<td>41.4</td>
<td>0.0</td>
<td>Dark brown liquid.</td>
</tr>
<tr>
<td>32.5</td>
<td>23.0</td>
<td>44.5</td>
<td>Dark brown liquid and clear, less dense liquid.</td>
</tr>
<tr>
<td>58.6</td>
<td>41.4</td>
<td>0.0</td>
<td>Dark brown liquid.</td>
</tr>
<tr>
<td>30.5</td>
<td>21.5</td>
<td>48.0</td>
<td>Dark brown liquid and clear, less dense liquid.</td>
</tr>
<tr>
<td>?</td>
<td>?</td>
<td>99-</td>
<td>No phase change by further addition of toluene to the above solution. There are still two liquids present.</td>
</tr>
<tr>
<td>61.0</td>
<td>39.0</td>
<td>0.0</td>
<td>Dark brown liquid.</td>
</tr>
<tr>
<td>31.2</td>
<td>19.9</td>
<td>48.9</td>
<td>Dark brown liquid and clear, less dense liquid.</td>
</tr>
<tr>
<td>62.5</td>
<td>37.5</td>
<td>0.0</td>
<td>Dark brown liquid and solid AlCl₃. This point taken from the two-component phase diagram (l).</td>
</tr>
</tbody>
</table>
Figure 1. Phase Diagram of the System:
Aluminum Chloride-Ethyl Pyridinium
Bromide-Toluene at 300°C.

Compositions expressed as weight percent. See Table I.
3. **Discussion of the Phase Diagram**: The phases in equilibrium are indicated for the various areas of the diagram and the areas are lettered to facilitate the discussion of the diagram. If pressure and temperature are assumed to be constant and the vapor phase disregarded, the number of degrees of freedom of the system in the various areas will be those given below.

In area A, the three components exist in a single liquid phase. There are two degrees of freedom in this area.

In area B, two liquid phases are in equilibrium. The composition of the colored, more dense phase is given by the line AB (i.e., the line separating areas A and B) and the composition of the less dense phase was found to be greater than 99 percent toluene by weight. Line AB is probably the most important line on the diagram from a practical standpoint as it determines the composition of the electrolyte layer of the solutions which can be used for electrolysis tests. There is only one degree of freedom in area B.

In area C, the compound AlCl$_3$.1EtPyBr is in equilibrium with a liquid whose (variable) composition is given by the line AC. There is only one degree of freedom in this area.

In area D, aluminum chloride is in equilibrium with a liquid whose variable composition is given by the line AD. Points in this area were not measured quantitatively because of the practical difficulties of working with a mixture.
containing a large amount of aluminum chloride in solid form. The nature of the area and the point giving the boundary of the area were deduced from a consideration of the phase equilibria of the two-component system aluminum chloride-ethyl pyridinium bromide. Area D possesses only one degree of freedom.

In area E, aluminum chloride is in equilibrium with two liquids of fixed composition. These compositions are given by the point $P_1$ and by a point representing greater than 99 percent toluene. This is practically the same point as that determining the composition of the less dense liquid of area B. The system is invariant within this area.

In area F, there is indicated an equilibrium between a liquid whose variable composition is given by line AF and a solid which seems to be $\text{AlCl}_3\cdot2\text{EtPyBr}$. The system has one degree of freedom in this area. Unfortunately, the lines FG and FH which bound this area do not converge to exactly the proper composition but rather extend off the diagram without meeting. It should be pointed out, however, that the composition of the compound $\text{AlCl}_3\cdot2\text{EtPyBr}$ lies almost exactly halfway between the points at which the lines FG and FH leave the diagram.

The compound $\text{AlCl}_3\cdot2\text{EtPyBr}$ is probably meta-stable. This is based on the fact that it does not appear as a maximum on the composition-temperature diagram of its two
components (1). As a matter of fact, a eutectic with melting point 45° is indicated for this composition.

In area G, a second invariant condition is present consisting of the compound AlCl₃•1EtPyBr, the compound AlCl₃•2EtPyBr, and the solution of fixed concentration given by point P₂.

Area H is a third portion of the diagram in which the system is invariant. A liquid whose composition is given by the point P₃ is in equilibrium with the compound AlCl₃•2EtPyBr and a second less dense liquid whose composition is greater than 99 percent toluene.

The behavior of the system in the region I was not investigated.

B. Phase Equilibria of the Benzene System: From the similarity of benzene and toluene it would be expected that the phase diagram of the system aluminum chloride-Ethyl pyridinium bromide-Benzene would be about the same as that for the corresponding system with toluene. Accurate measurements were not made to confirm this, but qualitatively the behavior of various mixtures of aluminum chloride and ethyl pyridinium bromide with benzene were about the same as that described for toluene. A quantitative measurement was made of the amount of benzene which could be added to the important eutectic mixture before a second layer formed. The second
...Several solutions of aluminum chloride with...
an area of 6 cm² on the exposed side. The electrolyses were performed at room temperature and a current density of 0.5 amps/ dm².

1. 38.0 weight percent aluminum chloride-Ethyl pyridinium bromide mixture saturated with toluene: A heavy deposit of blue, water-soluble, organic matter was produced at the cathode and the conductivity was low.

2. 41.4 weight percent aluminum chloride-Ethyl pyridinium bromide mixture saturated with toluene: A heavy deposit of blue, organic material was produced at the cathode. The conductivity was about the same as for the 38.9 weight percent solution.

3. 45.9 weight percent aluminum chloride-ethyl pyridinium bromide mixture saturated with toluene: A heavy deposit of blue, organic material was obtained in this case also. Again the conductivity was low.

4. 50.0 weight percent aluminum chloride-ethyl pyridinium bromide mixture saturated with toluene: A slight amount of an amorphous, green, water-soluble, organic material was found on the cathode. No aluminum or blue organic matter was found.

5. 58.6 weight percent aluminum chloride-ethyl pyridinium bromide mixture saturated with toluene: A smooth, shiny deposit of metallic aluminum was produced at the cathode. The conductivity was about twice that for the lower concentrations of aluminum chloride.
The nature of the blue organic material, although not analyzed, is probably the same as that obtained for a fused mixture of aluminum chloride and ethyl pyridinium bromide of high ethyl pyridinium bromide content, namely diethylidihydro-dipyridyl (1). The production of this material would be the result of the reduction of (Ethyl pyridinium)$^+$ ions at the cathode. The nature of the green material is not known.

The results of these tests show that the range of concentrations from which aluminum can be deposited is limited. The actual value for the minimum lies between 50.0 and 58.6 weight percent aluminum chloride in the starting mixture. This value is higher than the limiting value for fused mixtures of aluminum chloride and ethyl pyridinium bromide containing no toluene (1).

D. Description of the Aluminum Deposits and the Effect of Current Density:

The similarity of the solutions saturated with benzene to those saturated with toluene from the standpoint of phase equilibria was discussed in a previous section. The similarity of the two baths was further borne out by the type of plate obtained on electrolysis, the conductivity, and the current density. For this reason, and in order to avoid repetition, the two baths will be discussed together. Most of the following work was first done with toluene solutions and
later confirmed with benzene solutions. Where there seem to be points of difference, these will be pointed out.

1. Apparatus: In order to obtain a better measure of the current density and type of aluminum plates on iron, the cathodes used for this part of the work were thin sheets of iron 1 or 1½ inches (2.5 - 3.8 cm.) wide and immersed about 3 to 5 cm. in the electrolyte. The electrolytic cell first used to make plates of this size was the aluminum pot cell which had been used for the fused salt electrolysis (1). Later the improved design shown in Figure 2 was used. The improved apparatus consisted of a wide-mouth, glass-stoppered bottle 5.2 cm. in diameter and 12.5 cm. deep. This was fitted with a wooden, painted top with an inlet and outlet for the dry air and a slot for the cathode. A sliding plate covered the cathode slot and was held shut by a spring. This also served to hold the cathode in place. One important feature of the apparatus was the use of a small pool of mercury to make contact with the cathode lead. This enabled the rapid removal of the cathode from the cell with the necessity of loosening a connection. If the connection had to be broken before the removal of the cathode from the electrolyte, some reaction inside the cell might have taken place. On the other hand, if the connection had to be broken after the removal of the cathode while the electrode was covered with a film
Figure 2. Cell for Electrodeposition of Aluminum
of adhering electrolyte, reaction with the moisture of the atmosphere would have taken place.

The anode was a circular sheet of aluminum 1/100 inch thick, 5 cm. high and 15 cm. in circumference. The electrolyte used was a 58.6 weight percent aluminum chloride-ethyl pyridinium bromide eutectic mixture saturated with toluene or benzene. The electrolyte layer was usually about 5 cm. deep with a volume of 100-125 cc. This was covered by a 1cm. layer of toluene or benzene to act as a moisture protection and to prevent evaporation of the electrolyte. In order to prevent evaporation of this layer, the air (dried over calcium chloride and phosphorus pentoxide) was first saturated with toluene or benzene by passing it through a wash bottle containing the dry hydrocarbons.

2. Procedure:

a) Preliminary treatment of cathodes: Two methods of preparation were used: 1) sanding with emery paper and 2) etching with 6N hydrochloric acid after previous sanding. The effect of these will be discussed later.

In some cases the sanding procedure was followed by polishing on a felt wheel saturated with a rouge suspension in water. However, to prepare very smooth, flat, highly polished surfaces would necessitate a long series of sanding operations graduating in small steps from emery paper to the felt wheel. To do this in a reasonable length of time and
for the number of surfaces needed, mechanical polishing
wheels would be required. These were not available so pre-
paration of the cathodes to this state of polish was not at-
temted.

b) Subsequent treatment of cathodes: When
using fused baths (1) the rate of reaction of the electrolyte
with the water used to wash the plates was reduced by first
washing the plate, with its adhering film of electrolyte, in
benzene, then in water, after removal from the plating bath.
However, this was not necessary with these electrolytes as
the electrolyte is already saturated with benzene or toluene.
Washing directly in water did not affect the plates with these
solutions.

3. Description of Plates: A survey of plates made
at different current densities and with different baths re-
vealed that the best current density for plating varied between
0.5 and 2.0 amps/dm² depending on certain conditions of use.
These conditions will be discussed. It is interesting to
note that this current density is considerably higher than that
found to be the optimum for the electrodeposition of aluminum
from the fused bath of aluminum chloride and ethyl pyridinium
bromide at temperatures of around 125°C. The plates from the
bath saturated with toluene or benzene at these current densities
were remarkably shiny and very uniform. In general, they were
much smoother, more uniform and shinier than the plates from
the fused bath.

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At somewhat lower current densities than that for shiny plates, the plates were white and showed more diffuse reflection. Very low current densities produced plates which were gray, very coarse and not very coherent or adherent.

As the current density was raised above the value at which shiny plates were obtained, brown striations of an unknown nature began to appear on the shiny deposit. These were frequently arranged vertically and the amount seemed to increase slowly on long standing. Microscopic examination of these stains showed that they apparently were in the deposit (or on its surface) and were not minute pinholes. The stains could be removed in concentrated nitric acid, which at the same time produces faint rainbow colors over the whole plate probably due to diffraction of oxide films. The increase in amount of stain on standing in air suggests that the material is oxidizable and possibly organic.

At slightly higher current densities, "burned" areas, bare areas bordered in black, appeared on the edges of the plate. At very high current densities the deposits were heavy, black and non-adherent and seemed to contain occluded aluminum chloride or electrolyte. They reacted vigorously with water.

The plates adhered well under rubbing or polishing if the sheet was not bent. When the shiny aluminum plates on sheets of iron, steel, brass or copper were bent they were found to be brittle and to buckle on the compression side with resultant flaking off. It was also found that the shiny, uniform deposits could be made on cathodes formed in circular and zig-zag shapes.
The plates would then be fairly satisfactory on objects of odd or irregular shape as long as the object was too stiff to be bent. This brittleness was considered a disadvantage. A method will be described in Part II by which this may be overcome.

The thicker the plate the more brittle it was found to be. The usual thickness of the plates was 0.006 mm. Thicker deposits could be obtained readily but this was more than sufficient to give complete coverage (see pictures later.) Plates were made as much as 0.025 mm thick but they were somewhat coarser and less uniform. In Part III a method of obtaining thicker plates will be described.

The adherence was somewhat dependent on the preliminary treatment, as would be expected. Plates made on steel without an acid etch were about the same at first as those plates made on steel with an acid etch. However, those which were not acid-etched frequently tended to peel off in a day or so.

Aluminum was plated from this electrolyte on copper, brass, bronze, lead, zinc, nickel and tin as well as iron. In general, the plates were the same as those on iron. The shiny plates on these metals were also brittle and did not adhere on bending. Zinc was found to be an unsatisfactory base on which to plate because the zinc contaminated the electrolyte very easily when in contact with it.

4. **Pictures of Plates:** A series of photographs and photomicrographs (100 power magnification) were made to show the influence of a number of factors on the aluminum plate. Pictures
of aluminum plated on brass or iron are used to show the effect of current density, length of electrolysis and polishing of the plates.

Before discussing the pictures it is necessary to have clearly in mind certain facts about reflection of light from the plated surface.

The expression "shiny plate" or "bright deposit" denotes plates which have a high proportion of specular reflection and a low proportion of diffuse reflection. It does not refer to the total amount of light reflected or to the amount of various wave lengths reflected. On the other hand, plates at lower current densities which are "white" show a low specular reflection and a high proportion of diffuse reflection.

It might be well to point out here that Egeberg and Promisel (7), R. Springer (8), and G. A. Lux (9) have devised methods for measuring the brightness of plates based on the proportions of specular and diffuse reflection, but apparently it is not possible to express or to measure the brightness of a surface by any simple system. The photographs included here merely attempt to represent the way the plate would look to an observer under the specified conditions of illumination.

The relation between the type of plate and the kind of reflection is of considerable importance in the examination of the accompanying photographs of aluminum plated on iron and brass, for it means that the source of lighting with respect to the
camera and to the plated specimen must be taken into account. The normal photographs were made with the light source at an angle of about 45° to the plated surface in order to obtain better detail. The camera was at right angles to the plated surface. This means that in these photographs, plates with a high diffuse reflection and low specular reflection will reflect more light into the camera and appear whiter than the shiny plates with high specular and low diffuse reflection.

The photomicrographs were necessarily made with the light source at right angles to the plated surface. Thus, shiny plates, with a high specular reflection, would reflect most of the light directly back into the camera and appear bright in these pictures.

a) Effect of Current Density: As previously stated, plates at low current density were white and showed considerable diffuse reflection. Figures 3-a and 3-b show a white plate on brass at this current density. The uniformity of the surface, although course, and the completeness of the coverage, shown in the photomicrograph, should be carefully noted. Figures 4-a and 4-b show a sample of an aluminum plate on iron at this current density. The pictures demonstrate that the aluminum plates on the two base metals are identical in
Figure 3-a. Aluminum plate on brass at low current density.

Figure 3-b. Aluminum plate on brass at low current density. 100 X.

Figure 4-a. Aluminum plate on iron at low current density.

Figure 4-b. Aluminum plate on iron at low current density. 100 X.
appearance. The iron surface, although more difficult to obtain smooth, is seen to be completely covered even in the ruts and pits.

Figures 5-a and 5-b show a sample of a shiny aluminum plate on brass. The surface is seen to be much smoother and with a higher specular reflection than the plates at lower current densities. In the 100 power photomicrograph of Figure 5-b the small black spots are pits but are not actually pinholes. The dark streak is a ridge and its shadow. The striations shown are vertical on the plate and may be related to the surface preparation since the sanding was in this direction.

Occasionally the shiny plates on brass and on iron showed, upon microscopic examination, a peculiar appearance which might be termed "bubbled" or "bumpy". This appearance is shown in Figure 6-a (on brass) and 6-b (on iron). The plates are adherent, except to bending, of course, and can be polished to produce a smooth uniform surface, as will be shown later. Since they can be polished, this constitutes no particular difficulty. Their cause is not known. The macro appearance of the shiny plate on iron is shown in Figure 6-c.

b) Effect of Length of Electrolysis: The effect of the length of electrolysis on the coarseness of the surface can be seen by comparing a plate made on iron at a low current density for 90 minutes, shown in Figure 4-b, with one made on iron at
Figure 5-a. Shiny aluminum plate on brass.

Figure 5-b. Shiny aluminum plate on brass. 100 X.

Figure 6-a. "Bumpy" aluminum plate on brass. 100 X.
Figure 6-b. "Bumpy" aluminum plate on iron. 100 X.

Figure 6-c. Shiny, but "bumpy" aluminum plate on iron.

Figure 7-a. Aluminum plate on iron. Long electrolysis at low current density.

Figure 7-b. Aluminum plate on iron. Long electrolysis at low current density. 100 X.
the same current density for 220 minutes, which is shown in Figure 7-b. The increased thickness has resulted in a coarse surface. According to Blum, Beakman, and Meyer (10), it is not advisable to state definitely on the basis of photomicrographs whether the grain or crystal size is larger or smaller for one plate or another, but only whether the surface is smooth or coarse. A comparison of the normal photographs of these plates, shown in Figures 4-a and 7-a, reveals that the increased length of electrolysis at this current density does not affect the uniformity of the plate and does not produce crystalline "trees." These "trees" have been obtained on some occasions in which exceptionally long electrolysis and very low current density were used, but it is not normal.

c) Effect of Polishing: Polishing of the aluminum plated specimens has been found to improve the brightness of white plates and to smooth out non-uniformities in brilliance which sometimes occur in shiny plates. The polishing in these cases was done by means of a flat felt wheel saturated with a suspension of rouge.

The increase in brilliance of a white plate produced by polishing is shown in Figures 8-a (unpolished) and 8-b (polished). The photomicrographs of Figures 7-b (unpolished) and 8-c (polished) show the smoothing out as well as the increased brightness produced by polishing. The non-uniformity found in Figure 8-b was the result of the sample not being flat. This would
Figure 8. Effect of Polishing. Low current density aluminum plate on iron.
not occur on flat samples or ones polished by some means more suitable to the shape of the object. A more nearly flat sample was obtained by using brass. The effect of polishing this sample is shown in Figures 9-a (unpolished) and 9-b (polished). The effect on the microscopic appearance is shown in Figures 9-c (unpolished) and 9-d (polished).

The advantage of being able to polish white aluminum plates is that if a plate has any white areas on it, or, if it is desired to run the bath at a current density less than that required for shiny plates, the plates may be made shiny by polishing.

The way in which a plate on brass with some shiny areas and some "bumpy" areas can be transformed into a uniform, shiny plate is shown in Figures 10-a (unpolished) and 10-b (polished). The white portion of Figure 10-a, which gives more diffuse reflection, is the bumpy section. Its microscopic appearance is that shown in Figure 6-a. The shiny part of Figure 10-a is similar in appearance to Figure 5-b under the microscope. After polishing, the entire surface of the plate had the uniform appearance shown in Figure 10-c. The smoothing-out effect of polishing a shiny but "bumpy" plate on iron is seen by comparing Figure 6-b (unpolished) and Figure 10-d (polished).

Thus, a number of difficulties which might normally bother the electroplater can be overcome by polishing.
Figure 9. Effect of Polishing low current density plates on brass.
Figure 10. Effect of Polishing. Uniformity produced by polishing "bumpy" or partly "bumpy" plates.
5. **Effect of Stirring:** In an attempt to reduce the polarization and thus increase the current density, the electrolyte was stirred mechanically. The effect of this stirring was to reduce the uniformity of the plates. The eddy currents were plainly marked on the plates. This method obviously did not produce a uniform lowering of the polarization. Another method of accomplishing this will be described in Part II.

6. **Effect of Method of Inserting Cathode:** A short study was made of two procedures for inserting the cathode to determine which was the better. In one procedure, the cathode was completely inserted before the voltage was applied. In the other procedure, the voltage was applied to the cathode and it was inserted at different rates.

The experimental method consisted of fixing the current density for all tests and determining the equilibrium voltage and type of plate for each procedure. The following conclusions were reached.

a) Plates obtained by immersing the cathode before the voltage was applied showed a lower and more reproducible equilibrium voltage than those obtained by applying the voltage and then immersing either slowly or rapidly.

b) In cases where the voltage was applied before the immersion, the equilibrium voltage was found to depend on the rate of immersion; and very slow rates produced black deposits with relatively high voltages required.
There was also the general increase in the number of the pinnules observed to the method of which were not generally shown by plates made of iron showed a few pinnules after exposure to air during which there were occasional rain. In a number of the same pinnules made on the surface of the solution such as a nitric acid bath (17). It may be mentioned in passing that the procedure is contrary to the appearance of the pinnule on the atmospheric resistance of any other objections or phases. However, aluminum vapor to produce an oxide film over the surface metal. For example, aluminum vapor was to exert a considerable amount of energy in the procedure which electrochemical potential of aluminum, L. Corrosion Tests.

* Effect was observed.

* Except the case of very slow rates.

* There seemed to be no apparent reason for the increased rate of the plate obtained by the cathode of the plates operated by the anode.
the brown stains on plates which had them. This usually reached its maximum after a few weeks weathering and did not further increase to any extent over a period of a year or more.

Pictures of some plates were made under special conditions of illumination in an attempt to show the increase in the brown stains on plates. This is somewhat handicapped by the lack of color in the photographs. Figure II-a gives the general appearance of a plate which has brown stains before the corrosion test. These stains were most frequently located at the edges of the plates where the current density was slightly higher. After more than eighteen months, during which the increase in intensity of brown stains took place, the appearance was that shown in Figure II-b or II-c. As stated, most of this took place during the first few weeks. The plate still had a shiny finish. There was no powdering of the deposit due to prolonged exposure. This is shown in the photomicrograph of Figure II-d, which also, incidentally, shows the poor surface preparation used at that time.

The value of the coatings as corrosion protection was demonstrated by inspection of the unplated portion of the cathodes which had been exposed to the same weather conditions. In every case there was a great deal of heavy rust on both iron and steel, whereas the aluminum plated portion retained its shiny appearance and only showed occasional pinholes. Furthermore, these pinholes did not spread and rusting under the aluminum
Figure 11. Aluminum plates on iron. Effect of prolonged exposure (over 18 months).
did not take place.

It is felt that clean, shiny plates could be made which would resist change in appearance by:

a) preparing the surface carefully before plating so as to prevent pinholes, and

b) making the plate at a current density just high enough to be shiny but not high enough to produce brown stains.

The surface preparation should not be difficult to accomplish with the proper equipment.

E. **Effect of Temperature**: Tests were made to determine the effect of temperature on both the type of plate and the life of the bath. The electrolysis cell was a small one about 1 inch in diameter, which was maintained at a temperature of 55°-60°.

The current density at which shiny plates could be obtained was found to be about 1.6 amperes/dm² at 55°-60° at the beginning of the heating. This would be the expected result of an increase in diffusion or ionization with an increase in temperature. The plates at 0.5 amperes/dm² were white and more adherent than those obtained at this current density at room temperature.

However, the current density at which shiny plates could be obtained fell to 0.6 amperes/dm² after 38 hours heating at 55°-60°. The bath became useless even at very low current densities after heating at this temperature for about 70 hours.
F. Contamination of the Electrolyte: Tests were made to determine whether the presence of certain metals, or the excess reagents from the preparation of ethyl pyridinium bromide, namely ethyl bromide and pyridine, would interfere with the plating operations. The purpose was to find how much care need be exercised to exclude these foreign substances from the electrolyte.

1. Contamination by metals: In order to determine the contamination of the electrolyte caused by reaction with various metals, six 10 cc. portions of freshly prepared toluene electrolyte plus a layer of toluene were placed in tubes of about 2.5 cm. diameter. A strip of freshly etched and dried metal was then placed in each solution. The metals tested were copper, brass, tin, nickel, iron, and mercury. The total exposed area of metal in each case was about 4 cm². The tubes were then corked and allowed to stand for one week, at the end of which time the metal strips were removed and the solution electrolyzed to determine the type of plate obtained. Steel cathodes and aluminum anodes were used for this purpose. There was some indication of moisture having gotten into the tubes. This would increase the amount of corrosion of the metal but would more nearly represent a practical situation.

a) Iron: The iron strip was considerably etched. The plates obtained on electrolysis had a metallic luster but there were black marks on them. The amount of iron was not sufficient to cause the deposition of black, non-adherent
deposits but the effect seemed to be setting in. Other tests had indicated that black plates would result if sufficient iron were dissolved, which would occur in time.

b) Copper: The copper strip was visibly attacked. On electrolysis, the cathode was covered with an orange copper deposit with small "trees" along the edges. The anode was similarly covered, probably by galvanic action. The amount of copper is evidently so high that it is beyond the stage of causing black, non-adherent aluminum deposits.

c) Brass: The brass had also been etched. A soft, black, non-adherent deposit was obtained on electrolysis.

d) Nickel: The nickel strip showed the results of etching. A very thin deposit having a brown cast was obtained at low current density. On increasing the current density somewhat to allow for the gas evolution, a black deposit was obtained.

e) Tin: Considerable etching of the metal was observed, especially at the electrolyte-toluene junction. A fairly large amount of a white and brown precipitate was noted on the bottom of the cell. On electrolysis, a clean, gray, crystalline deposit was produced. The deposit did not dissolve in hydrochloric acid at a dilution at which aluminum was observed to. Upon increasing the strength of the acid by increments, the deposit did not begin dissolving with gas evolution until after the beginning of attack on the steel cathode itself. The deposit is evidently tin or a tin-aluminum alloy high in tin.
f) Mercury: A dull, gray plate which seemed about usual for the current density used was produced on electrolysis. The mercury did not seem to interfere particularly.

g) Zinc: Zinc was found in a separate test to contaminate the bath, causing black deposits to be obtained after a shorter time than without it.

However, it should be pointed out that iron, copper, brass, nickel and tin were found not to contaminate the bath when used as cathode objects, whereas zinc definitely does, and mercury has not been tested.

2. Contamination by Excess of Starting Materials:

a) Ethyl Bromide: In the presence of aluminum chloride, ethyl bromide will react slowly with aluminum to produce a gas and dissolve the aluminum. The presence of excess ethyl bromide in small amounts would have the effect of slightly lowering the overall cathode current efficiency and of increasing the apparent anode efficiency. Not much of this material would be expected in a properly prepared electrolyte.

b) Pyridine: The addition of 4 percent pyridine by volume to an electrolyte from which a shiny plate had just been obtained produced a black, non-adherent plate at the same current density. The presence of this much excess pyridine is thus detrimental to the bath. However, this represents about 8 percent free pyridine in the eutectic and a properly prepared eutectic would not be expected to
contain anywhere near this amount. If it is possible for the amount of free pyridine in an electrolyte to increase with use, then deterioration from this source would be expected.

G. Determination of Cathode Efficiency:

1. First Method

   a. Apparatus:

   1) Cell: The cell first used to determine the cathode efficiency of the electrodeposition of aluminum was the aluminum pot cell mentioned in the previous section. The electrolyte was the saturated toluene solution of 58.6 weight per cent AlCl₃-Ethyl pyridinium bromide mixture which had been used for about 25 electrolyses totalling about 10 hours.

   The determination was made by weighing the cathodes before and after plating with aluminum. The cathodes were designed to be completely immersed in order to avoid weighing errors which might result from oxidation of or adherence of a substance to any of the exposed iron surface. The cathodes were steel strips, 2.5 cm. wide and 5.5 cm. long, supported by a fine aluminum wire. The aluminum wire was not included in the weighings because of its corrosion in the bath atmosphere. Therefore, it was carefully removed after plating and before weighing. Upon removal of the cathode from the solution, it was washed in benzene, then water, and dried carefully in acetone.

   2) Coulometer: The current was measured by a gas coulometer consisting of platinum electrodes immersed in 20 percent sodium hydroxide. The containing vessel was leak-proof
and was connected by a short rubber tube to the tip of a 50 cc. buret. The buret was inverted in a long tube of water which could be raised or lowered to keep the water level inside and outside the buret about the same all of the time. The volume of hydrogen and oxygen evolved could be measured easily to the nearest 0.1 cc., which, in these cases, was about 1 part in 400.

The gas coulometer was calibrated against a silver coulometer and was found to give volumes about 4 percent too low. Corrections were applied to the gas volumes measured to correct for this discrepancy. The gas volumes were converted to the dry basis at 0° and 760 mm.

b. Data: Table II gives the apparent cathode current efficiencies for seven runs made at two different current densities. The current density, temperature, type of plate, gain in weight of cathode, gas volume as measured, gas volume corrected to moisture-free basis and standard conditions, gas volume corrected for silver coulometer, theoretical weight of aluminum calculated from gas volume, and the apparent cathode efficiencies are shown in the table.

c. Discussion of Results: In six out of the seven runs, the apparent cathode efficiency was found to be greater than 100 percent, the values varying from 103 percent to 111 percent. The efficiency runs made at the higher current density gave the higher values. It is also seen from Table II that the runs showing the highest apparent efficiencies were the ones which had small "burnt" areas on the plates. Run 6, which had some brown striations on the plate, gave a value
<table>
<thead>
<tr>
<th>Run No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current density</td>
<td>0.50</td>
<td>0.50</td>
<td>0.50</td>
<td>0.27</td>
</tr>
<tr>
<td>Temperature°C</td>
<td>31</td>
<td>30</td>
<td>31</td>
<td>31</td>
</tr>
<tr>
<td>Type of Plate</td>
<td>Shiny except dark upper edge -darkened on standing.</td>
<td>shiny; burnt on bottom of one side.</td>
<td>Burnt on bottom edge; partly cracked.</td>
<td>very clean, smooth, white; shiny edges.</td>
</tr>
<tr>
<td>Wt. gain-g. cathode</td>
<td>0.0246</td>
<td>0.0259</td>
<td>0.0258</td>
<td>0.0221</td>
</tr>
<tr>
<td>Gas vol.-cc. measured</td>
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<td>48.6</td>
<td>48.7</td>
<td>48.5</td>
</tr>
<tr>
<td>Gas vol.-cc. Dry basis (STP)</td>
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<td>41.9</td>
<td>41.8</td>
<td>41.6</td>
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<tr>
<td>Gas vol.-cc. Corr. for Ag coulometer</td>
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<td>43.6</td>
<td>43.5</td>
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<tr>
<td>Theo. wt. Al -g. from gas</td>
<td>0.0230</td>
<td>0.0233</td>
<td>0.0232</td>
<td>0.0231</td>
</tr>
<tr>
<td>Apparent Cathode Efficiencies</td>
<td>107</td>
<td>111</td>
<td>111</td>
<td>96</td>
</tr>
<tr>
<td>Run No.</td>
<td>5</td>
<td>6</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>---------</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td></td>
</tr>
<tr>
<td>Current density, a/dm²</td>
<td>0.27</td>
<td>0.27</td>
<td>0.27</td>
<td></td>
</tr>
<tr>
<td>Temperature, °C</td>
<td>31</td>
<td>28</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>Type of Plate</td>
<td>very clean, shiny plate, very little brown striations</td>
<td>shiny, faint brown striations</td>
<td>Very clean, shiny; only very few brown striations.</td>
<td></td>
</tr>
<tr>
<td>Wt. gain, g. cathode</td>
<td>0.0238</td>
<td>0.0245</td>
<td>0.0240</td>
<td></td>
</tr>
<tr>
<td>Gas vol., cc. measured</td>
<td>48.4</td>
<td>48.2</td>
<td>48.6</td>
<td></td>
</tr>
<tr>
<td>Gas vol., cc. Dry basis (STP)</td>
<td>41.5</td>
<td>42.1</td>
<td>42.0</td>
<td></td>
</tr>
<tr>
<td>Gas vol., cc. Corr. for Ag Coulometer</td>
<td>43.2</td>
<td>43.8</td>
<td>43.7</td>
<td></td>
</tr>
<tr>
<td>Theo. wt. Al, g. from gas</td>
<td>0.0231</td>
<td>0.0234</td>
<td>0.0234</td>
<td></td>
</tr>
<tr>
<td>Apparent effic. Cathode, %</td>
<td>103</td>
<td>105</td>
<td>103</td>
<td></td>
</tr>
</tbody>
</table>
somewhat higher than the other runs made at low current density. Furthermore, run 4, the plate which had the most white area and the least shiny area, gave the lowest value for the apparent efficiency. The magnitude of the apparent efficiency thus seems to be related to the amount of brown or "burnt" area. The nature of these brown stains is not known. However, the true value of the cathode efficiency must be very close to 100 percent. Because of experimental difficulties involved in determining cathode efficiencies in this electrolyte and the fact that the weight gain of the cathode was necessarily small, the efficiency values are probably only accurate to about 2 percent.

2. Second Method

When the efficiency was determined by weighing, the weight gains involved were so small that the procedure did not seem entirely reliable. In order to avoid this, a different method of measuring the efficiency was introduced. This involved the measurement of the volume of hydrogen evolved when the plated aluminum was dissolved in acid.

a. Apparatus: The apparatus used to carry out these determinations is shown in Figure 12. A glass cylinder, A, serves as the reaction chamber. The cathode plated with aluminum is fitted tightly into a rubber stopper which is inserted in the upper end of the cylinder, as shown. The cylinder is connected on its upper end by means of a
Figure 12. Apparatus for Measuring Cathode Efficiency.
slanting side-arm to a capillary which delivers the gas formed in the reaction into the measuring buret. The gas is released at the mouth of the inverted 10 cc buret contained in a hydrometer cylinder. The buret mouth is made wide to avoid "flooding" in the event of a sudden rush of gas.

In the other end of cylinder A, there is fitted a stopper attached to an inlet tube. The tube is connected to a two-way stopcock so that either acid for the reaction or water for flushing the apparatus may be admitted.

b. Procedure: In determining the efficiency, the procedure is as follows: The cathode is first inserted in the cylinder. The apparatus is then flushed with distilled water to remove all gas bubbles. The level in the hydrometer jar may be adjusted during the flushing operation so that the buret may be set on the 10.00 mark at the water level. Overflow is prevented by the siphon arrangement. After the buret is set and read, it is placed over the hook in the capillary tube. The acid is then passed into the reaction chamber until gas is evolved at the aluminum surface. The two-way stopcock is then closed and the apparatus may be left until the reaction is complete, which is evidenced by the end of the gas evolution. This may require 5-15 minutes, seldom more. The gas may then be flushed from the apparatus and collected in the buret by simply turning the two-way stopcock to allow the water to flow. The temperature of the gas
is allowed to come to equilibrium with the water and the tempera-

nure, barometric pressure and volume read after raising

the buret until the water levels inside and outside are the

same.

The acid used was about 4M hydrochloric acid which

became more dilute on mixing with the water in the reaction

chamber. The test cathodes on which the aluminum was plated

were brass. This was found to give no gas evolution in

acid of the strength used. Iron cathodes could not be used

as they gave efficiencies over 100% as a result of their

reaction with the acid.

The total current was determined from the ammeter

reading. The current was held constant by use of a large

series resistance and by carefully watching the meter during the

electrolysis. The total time in seconds (determined by a

stopwatch) was multiplied by the current in amperes to obtain

the number of coulombs and from that the theoretical quantity

of gas.

This method gave results reproducible to less than

1%. The speed and reproducibility possible with this

method were much greater than with the first method.

a. Efficiency Values: In Table III are

given the data for the cathode efficiencies determined by this

method on a benzene bath. Included are the current density,

the volume of gas as read, temperature, barometric pressure,
volume of gas corrected to the dry basis at 0°C and 760 mm of mercury, the theoretical volume of gas under the same conditions and the apparent cathode efficiency in percent. There was a rise in efficiency of about 7-8% during the first few hours of use of the bath, then the values became constant for a given current density. The values given in the table are for the equilibrium condition.

It will be seen from the table that the efficiency increased with current density from 81% at 0.21 amperes/dm² to 92% at 1.0 amperes/dm². It then became constant at very close to 92% for the higher current densities. This is the reverse of the usual variation of efficiency with current density, although such a trend is found in some other processes. One thing to note is that when the current density is high enough to produce a burnt plate, the efficiency shows a decrease. The plate at 2.08 amperes/dm² in the table was burnt on about one-half of its surface. This decrease is more to be expected than the increase indicated by the weighing procedures previously described. However, it should be pointed out that the two methods measure the same thing only when the deposit is pure aluminum.
### TABLE III. Cathode Efficiencies of Aluminum Chloride-Ethyl Pyridinium Bromide-Benzene Baths.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0.21</td>
<td>4.46</td>
<td>25.9</td>
<td>762.0</td>
<td>3.94</td>
<td>4.87</td>
<td>81.0</td>
</tr>
<tr>
<td>0.42</td>
<td>5.50</td>
<td>25.9</td>
<td>761.3</td>
<td>4.86</td>
<td>5.57</td>
<td>87.2</td>
</tr>
<tr>
<td>0.31</td>
<td>3.15</td>
<td>24.5</td>
<td>772.6</td>
<td>7.39</td>
<td>8.35</td>
<td>88.5</td>
</tr>
<tr>
<td>1.00</td>
<td>7.24</td>
<td>26.0</td>
<td>762.0</td>
<td>6.41</td>
<td>6.96</td>
<td>92.0</td>
</tr>
<tr>
<td>1.25</td>
<td>7.86</td>
<td>24.3</td>
<td>772.6</td>
<td>7.14</td>
<td>7.77</td>
<td>91.9</td>
</tr>
<tr>
<td>1.50</td>
<td>8.10</td>
<td>25.5</td>
<td>762.0</td>
<td>7.18</td>
<td>7.84</td>
<td>91.7</td>
</tr>
<tr>
<td>1.51</td>
<td>8.00</td>
<td>24.0</td>
<td>772.6</td>
<td>7.25</td>
<td>7.84</td>
<td>92.6</td>
</tr>
<tr>
<td>1.75</td>
<td>7.99</td>
<td>24.5</td>
<td>772.6</td>
<td>7.24</td>
<td>7.87</td>
<td>92.0</td>
</tr>
<tr>
<td>1.75</td>
<td>8.15</td>
<td>25.5</td>
<td>762.0</td>
<td>7.23</td>
<td>7.87</td>
<td>91.8</td>
</tr>
<tr>
<td>2.08</td>
<td>8.13</td>
<td>25.5</td>
<td>762.0</td>
<td>7.21</td>
<td>8.06</td>
<td>89.4</td>
</tr>
</tbody>
</table>

H. Changes in Bath Characteristics with Use.

The following section is a description of the changes which were observed to occur in four of the bath characteristics with use. The changes observed were in the usable current density at which shiny plates with no brown discoloration could be obtained, the color of the bath, the volume of the solution, and
the appearance of a sweet smell. The observations on the color change will be discussed first as that seems to have an important bearing on the reason for the current density change.

1. **Color Changes**

   It was observed that during the course of the use of both toluene and benzene baths, the color changed from a light yellowish-green to a dark red or red-brown. The possible factors which might cause such a color change were considered to be: The passage of the current, reaction of the solution with metallic aluminum, air oxidation of the solution, or a slow reaction between components of the solution, or combinations of these variables.

   The passage of the current was quickly eliminated as the cause. Solutions which were placed in similar electrolysis cells with dry air passing through, as usual, were found to undergo the same color change as found during the use of the bath.

   The reaction of the solution with metallic aluminum and the possibility of a slow reaction between components of the solution to produce a color change were excluded as single causes since tightly sealed solutions containing strips of aluminum gave only small changes in color to a slightly orange appearance.

   The lone remaining factor was air oxidation. To show this the cause, the proof was two-fold: The absence of air prevented the color change, and the passage of pure oxygen through a
portion of the solution speeded up the color change.

A sample of fresh electrolyte was placed in an electrolysis cell (aluminum present as anode) and the current passed for five days. During this period only a slight change from yellowish-green to pale orange occurred. This could easily have resulted from the presence of a small amount of air inside the cell above the electrolyte. During this period, a bath with air passing through would have become dark red.

The other part of the proof of air oxidation consisted of saturating fresh samples of electrolyte in test tubes with dry oxygen and allowing to stand. There was no aluminum present and no current was passed. The color change to deep red was not immediate, but was practically complete in a few hours. Normally several days would have been required.

It may thus be concluded that the color change to red is the result of air oxidation of one or more of the components of the solution. The presence of metallic aluminum or the passage of a current are not necessary to the reaction.

Some additional information was obtained as to which of the components was being oxidized. The question arose whether this same color might be observed on oxidation of a eutectic mixture containing no benzene or toluene. Four samples of freshly prepared eutectic were placed in test tubes flushed with dry nitrogen. Dry nitrogen was bubbled through two of the samples and dry oxygen through the other two. The nitrogen produced a very slight change in color to a very
light orange. The oxygen produced a darker orange color. But neither even approached the dark red color obtained when oxygen was passed through solutions of eutectic saturated with bensene. The bensene thus seems to play an important part.

Friedel and Crafts (12) studied the action of dry or moist oxygen and air on bensene and toluene in the presence of aluminum chloride. The results of their experiments showed that phenol and cresol are produced with the bensene and toluene, respectively, under these circumstances.

They explained the reaction by supposing that the aluminum chloride first adds on the bensene, for example, to form hydrochloric acid and an organometallic compound, $C_6H_5Al_2Cl_5$, which contains the residues of both molecules. The oxygen combines with this compound to produce a phenolate of aluminum pentachloride, which is decomposed by water to form the phenol according to the reactions:

$$C_6H_5Al_2Cl_5 + O \rightarrow C_6H_5O.Al_2Cl_5$$

$$C_6H_5O.Al_2Cl_5 + H_2O \rightarrow C_6H_5OH + OHAl_2Cl_5$$

They have explained reactions with alkyl halides in the same manner.

The reaction was fairly slow unless oxygen instead of air was used and the temperature close to the boiling point. After the reaction had ceased, the products were placed in water to decompose the organo-metallic compound and the oily
layer on the surface distilled. Benzene came over first, leaving a non-distillable residue which was red colored bordering on orange. The red material was soluble in benzene, ether and carbon disulfide but not in alcohol, acetic acid or water. The nature of this material is not stated.

This would account for the red color produced by the air oxidation of the electrolyte solution.

A large bath which had been used and which was dark red was analyzed to determine the classes of organic compounds present. The type of compound causing the color was partially identified. About 57 gms. of the electrolyte layer of the bath were extracted several times with water. The color remained full strength in the benzene layer so the water soluble substances were disregarded. The insolubility of the red material in water should be sufficient to indicate that the substance is not an aluminum compound and probably is not a simple pyridine derivative. The benzene layer was extracted with dilute hydrochloric acid and the acid solution neutralized with potassium hydroxide. The amount of acid soluble substance was very small. The benzene solution was then extracted with potassium hydroxide and the basic solution neutralized with hydrochloric acid. A film of liquid formed over the water layer, suggesting that some organic acid or phenol was present. The odor was strong and characteristic of
phenol or one of its derivatives. The addition of bromine water produced a yellow solid, but the amount was too small to separate and identify. This serves as a partial confirmation of the production of phenol by oxidation of benzene as described above.

The benzene layer was still dark red. Thus, the red color is not due to organic phenols, acids, or bases, but, of course, may be a neutral condensation product of any one of these.

A chromatographic adsorption separation (13) was performed on the resulting neutral benzene solution. The benzene solution was passed through a tube 20 cm long and 1 cm in diameter, and containing alumina. The colored material was adsorbed as a brown layer in the first one-fourth inch of the column. A pale yellow fluorescent liquid passed through the column without adsorption. No development or spreading of the adsorbed layer was obtained by elution procedures using benzene or carbon tetrachloride-benzene mixtures. The strong adsorption implies the presence of polar atoms such as oxygen or nitrogen in the molecule.

The yellow fluorescent benzene solution which had passed through the column without adsorption was examined in a spectrophotometer to determine the percent spectral transmission between 3000 Å and 10,000 Å. No definite absorption bands were found in this region. The absorption of the light
was greatest (90%) in the neighborhood of 3000 Å. and gradually decreased to no absorption at wave lengths greater than 7000 Å. Since bensene has no absorption in this region, there is some other substance (or substances) present. The fact that the material was not adsorbed on the activated alumina, which is a relatively strong agent in this type of work, indicates that it is very likely a hydrocarbon. The odor of the electrolyte solution after use had resembled diphenyl and if it is present, this would be the fraction of the analysis in which it would appear. Diphenyl has an absorption band beginning in the neighborhood of 3000 Å. More discussion about diphenyl will be given later.

2. Decrease in Usable Current Density

It was observed that the usable current density at which shiny plates could be obtained with no brown discoloration decreased with the use of the bath. This occurred if the bensene and toluene baths were used with air passing through the cell in the fashion described earlier in connection with Figure 2, or if they were used with a static air atmosphere in the cell.

The data taken during the period of use of one of the bensene baths are shown in Table IV. The total time in days, the amount of electrolysis in ampere-hours, the current density and the solution density are given. The density
<table>
<thead>
<tr>
<th>Total time (days)</th>
<th>Electrolysis (amp-hrs)</th>
<th>Density (g/cc)</th>
<th>Current Density (amps/dm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.0</td>
<td>1.124</td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>4.25</td>
<td></td>
<td>0.68</td>
</tr>
<tr>
<td>1.1</td>
<td>4.45</td>
<td>1.148</td>
<td></td>
</tr>
<tr>
<td>1.9</td>
<td>4.50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.1</td>
<td>5.10</td>
<td>1.157</td>
<td>0.66</td>
</tr>
<tr>
<td>2.8</td>
<td>5.10</td>
<td>1.160</td>
<td></td>
</tr>
<tr>
<td>2.9</td>
<td>5.28</td>
<td></td>
<td>0.57</td>
</tr>
<tr>
<td>3.0</td>
<td>5.44</td>
<td>1.161</td>
<td></td>
</tr>
<tr>
<td>4.9</td>
<td>5.44</td>
<td>1.168</td>
<td></td>
</tr>
<tr>
<td>5.0</td>
<td>5.60</td>
<td></td>
<td>0.31</td>
</tr>
<tr>
<td>5.1</td>
<td>5.60</td>
<td>1.169</td>
<td></td>
</tr>
<tr>
<td>5.8</td>
<td>5.60</td>
<td>1.170</td>
<td>0.29</td>
</tr>
<tr>
<td>6.1</td>
<td>5.63</td>
<td>1.174</td>
<td></td>
</tr>
<tr>
<td>6.8</td>
<td>5.63</td>
<td>1.177</td>
<td></td>
</tr>
<tr>
<td>6.9</td>
<td>5.69</td>
<td></td>
<td>0.25</td>
</tr>
<tr>
<td>7.8</td>
<td>5.69</td>
<td>1.188</td>
<td></td>
</tr>
<tr>
<td>7.85</td>
<td>5.71</td>
<td></td>
<td>0.22</td>
</tr>
</tbody>
</table>
data will be discussed in a subsequent section. These data for current density have been plotted in two ways in Figure 15. Curve A shows the observed variation of current density in amperes/dm² as a function of the total time in days. Curve B gives the variation of the current density in amperes/dm² with the amount of current passed in ampere-hours for this bath. The general variation can be seen to be a decrease from 0.68 amperes/dm² to 0.22 amperes/dm² in a period of slightly less than 8 days. This was more rapid deterioration than usually observed, and most baths were not carried to this state of deterioration. Neither curve A nor curve B gives any simple regular variation of the current density. Neither seems to be entirely independent of other factors.

There are two general ways in which the bath might deteriorate, namely, the depletion of one or more of the starting materials or the production of a substance whose presence interfered with the plating operation. This latter effect might be a trace effect in which case it would be very difficult to locate by analysis of a solution of this sort.

Attempts at rejuvenation of spent baths were conducted along the lines of the separate addition of small amounts of each of the original components. Additions of aluminum chloride, ethyl pyridinium bromide, ethyl bromide or pyridine to separate samples of a deteriorated bath failed to return the plating conditions to even approximately their original
Figure 13. Current Density as a function of Total Time and of the Amount of Current Passed.
state. By the addition of about 10% of fresh electrolyte, it was possible to raise the current density of a badly deteriorated bath about 20% but the effect was really that of a weighted mean of the operating conditions of the two. There seemed little to be gained by the continuous use of this procedure.

a. Standing Tests: Since the current density at which clean, shiny plates could be obtained was observed to decrease with time, the question of whether this might be the result of a reaction of the solution in the absence of electrolysis with itself or with the aluminum anode was first investigated.

A freshly prepared eutectic was saturated with benzene, divided into five 25 ml portions and placed in similar small cells containing the aluminum anodes. These were tightly corked and paraffined. One was electrolyzed on the day of preparation to determine the usable current density for shiny plates. The others were opened one at a time after various lengths of standing, and the shiny plate current density determined. They were opened successively after 4, 7, 10 and 15 days' standing. The data obtained are given in Table V.
Table V.  Behavior of Usable Current Density When Cell Allowed to Stand Closed.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Days' Standing</th>
<th>Current Density (amps/dm²)</th>
<th>Color of Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0</td>
<td>1.30</td>
<td>Light brownish-green. Gas evolved on electrolysis.</td>
</tr>
<tr>
<td>B</td>
<td>4</td>
<td>1.00</td>
<td>Orangish. Minute amount of gas on electrolysis.</td>
</tr>
<tr>
<td>C</td>
<td>7</td>
<td>1.08</td>
<td>Same as B.</td>
</tr>
<tr>
<td>D</td>
<td>10</td>
<td>1.00</td>
<td>Same as B.</td>
</tr>
<tr>
<td>E</td>
<td>15</td>
<td>1.00</td>
<td>Same as B.</td>
</tr>
</tbody>
</table>

The data indicate that under these conditions with the solution sealed and with no electrolysis that the usable current density does not decrease appreciably. Although the value of 1.30 amps/dm² obtained for the first day is somewhat higher than the other values, more gas was evolved in the electrolysis, which would mean less than the indicated amount of current was actually depositing aluminum. The results seem to be conclusive that the cause must be something else. Other possible causes might be the moisture introduced by opening the cell so often to insert the cathodes, the passage of the air, or the passage of the electric current.

It is important to note that there was only very slight change in color of the solutions during these tests.

b. Oxidation Tests: In view of the above-mentioned small amount of color change in the standing tests which showed no current density decrease and the fact that,
as mentioned in the previous section, the color change was the result of air oxidation, the effect of oxidation on current density was investigated. The following experiments were performed.

A fresh sample of eutectic was prepared and saturated with benzene, the whole of the process in a nitrogen atmosphere. This was transferred to a 25 cc. cell which had been flushed with dry nitrogen. After the transfer, the cell was again flushed with nitrogen as a precaution. The shiny plate current density was then determined using short runs. It was found to be at least 1.7 amps/dm² (no higher values were used). The bath was sealed and allowed to stand over night. Then one electrolysis was made at this current density and produced exactly the same type of plate. This was the shiny plate current density before oxidation. A fine stream of oxygen was then passed into the electrolyte layer for one hour through a capillary. This produced an intense red color immediately and confirmed the air oxidation experiments on color change. The shiny plate current density was immediately redetermined and found to be about 0.8 amps/dm². The oxidation had definitely caused a decrease in current density.

In support of this some data available for a toluene solution may be offered. The data are presented in Table VI, in which the total time in days, the current density in amps/dm²
for shiny plates with no brown coloration, and the color of the solution are given.

TABLE VI. Current Density and Color Change in a Toluene Solution.

<table>
<thead>
<tr>
<th>Total Time days</th>
<th>Usable Current Density, a/dm²</th>
<th>Color of the solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.85</td>
<td>Green</td>
</tr>
<tr>
<td>3</td>
<td>0.37</td>
<td>Red-brown</td>
</tr>
<tr>
<td>6</td>
<td>0.37</td>
<td>Red-brown</td>
</tr>
<tr>
<td>7</td>
<td>0.31</td>
<td>Red-brown</td>
</tr>
<tr>
<td>8</td>
<td>0.31</td>
<td>Redder</td>
</tr>
<tr>
<td>13</td>
<td>0.25</td>
<td>Redder</td>
</tr>
<tr>
<td>18</td>
<td>0.25</td>
<td>Redder</td>
</tr>
<tr>
<td>24</td>
<td>0.11</td>
<td>Redder</td>
</tr>
</tbody>
</table>

On the first day, the color was greenish and a current density of 0.85 amps/dm² was obtained. Between the first and third days, no electrolyses were conducted but the toluene layer evaporated because the toluene ran out of the saturator for the air being passed through. The color changes to reddish brown occurred during this period. When the toluene layer was replaced and the usable current density measured, the value for shiny plates was found to have decreased to 0.37 amps/dm². The value continued to decrease, although slowly, on further electrolysis.

In the case of one bath which was used, no color change occurred during a period of 26 days and the current density remained constant at approximately 0.65 amps/dm². During this period electrolyses were conducted on 16 of the 26 days. This serves as a confirmation of the color change effect in a negative way in contrast with the previous experiments.
It further demonstrated that the passage of the current alone was not sufficient to cause the current density decrease. Even further confirmation was obtained from this bath by the fact that after standing 5 more days the solution became red. The current density was tested then and it was found that clean, shiny plates could still be obtained from the bath, but they were cracked. After two more days, the solution was tested again and found to produce black plates at this current density. The shiny plate value had decreased when the bath was used after it turned red. This last bit of evidence seems to indicate that in cases where the oxidation is by atmospheric oxygen, it may be necessary to pass the current for a while to produce the decrease in current density.

This bath was used with a static air atmosphere inside, i.e. no air was passed through the cell, and in addition it was used during a period of prolonged cold, dry weather. The cell was kept carefully paraffined and was never opened more than a few seconds at a time. It is to be expected that the action of atmospheric oxygen on these solutions (with a benzene layer present) would be much slower than that of pure oxygen in intimate mixture with the solution. Also the action would not be as rapid in the absence of moisture in the solution in view of the reactions discussed for the color change. These facts may account for the fact that the color change of this bath did not occur very rapidly.
Some interesting observations were made on two baths which were prepared in a nitrogen atmosphere and which were used in a cell through which no air was passed. The air in the room was much more humid and red color appeared after only about two days. However, the important observation was in connection with the behavior of these baths when the red solutions were electrolyzed at low current densities. The shiny plate current density for both of these baths was about 1.2 amperes/dm², but the solutions were run at current densities of only about 0.4 amperes/dm². These low current densities produced uniform white plates with no brown cast. Each of the solutions was run for 10 days at the low current density and then tested for the shiny plate current density. It was found to still be 1.2 amperes/dm² in both cases. One of the baths was then run at the current density which produced shiny plates for several days and the brown stains began to appear on the plates, so that the current density had to be lowered to avoid this. With the other bath, the current density was intentionally further raised to values that produced black, non-adherent deposits. This was done by using a much smaller cathode so that only the cathode current density was increased over the value for shiny plate. Several black deposits were produced. The decrease in usable current density was more rapid under these circumstances.
These heavy, black deposits appeared to contain occluded aluminum chloride or electrolyte and sometimes organic matter, and may very well be an additional type of deterioration to that given above.

The conclusions that may be reached from all of these experiments on oxidation are as follows:

1) Solutions exposed to oxygen or air and moisture became red. The bath was then susceptible to deterioration on use, the deterioration being defined as a decrease in the current density at which clean, shiny plates can be obtained.

2) If the solution color did not change to red the bath did not seem to deteriorate.

3) Whether the bath deteriorated or not once it had turned red seemed to depend on the current density or probably more exactly on the type of plate obtained. If the current density was low enough for white plates, there was no deterioration, or, at least, it was very slow. If the current density was high enough for shiny plates to be produced, deterioration occurred, the speed probably depending on a number of factors. If the current density was high enough to produce black deposits, the deterioration was even more rapid.

3. **Change in Volume of Electrolyte**

During the use of the benzene bath for which the change in current density has been described, the volume decreased
with use. At the beginning, the depth of immersion of plates, which were always touching the bottom of the glass cell, was 4.8 cm. After 8 days the immersion was 3.8 cm. This represented a volume decrease of 21% during this period. Other baths which were not carried to this extent of deterioration did not show this large a volume decrease although the electrolyses were conducted over a longer period of time. This probably the maximum amount to be expected.

This decrease in volume could conceivably be accounted for in several ways. Evaporation of the electrolyte layer might take place, except that there is a relatively large layer of excess benzene covering the electrolyte. This would have to evaporate before the electrolyte layer would. This source is not important. A part of the volume decrease may be accounted for as "carry-out" of the electrolyte when the plates are removed. Tests showed this to be only very slight. This may also be excluded as a major effect because appreciable changes in volume occurred during periods in which there were no electrolyses being carried on.

b. Change in density: One would expect that the change in volume might be the result merely of a change in density with no loss in weight of electrolyte taking place. The density was determined during the
course of the use of one of the large baths. These data have been included in Table IV with other data for the bath. During the course of one week, the density changed from 1.124 to 1.177, an increase of 4.7%. The decrease in volume was of the order of magnitude of 21%. Therefore, the density alone is not sufficient to account for all of the volume change. This implies that there is a decrease in the weight of the electrolyte layer. In view of the elimination of evaporation and "carryout" as sources of the loss in weight of the electrolyte, it seems logical to consider that this loss is the result of a transfer of a portion of the benzene (or possibly other products) from the electrolyte layer to the benzene layer. This displacement would result in an increase in density of the electrolyte since the density of the benzene is less than that of the solution. The decrease in volume would be greater than the increase in density because of the weight loss involved. This is entirely in agreement with the observed facts.

A number of experiments were performed to ascertain whether certain types of reactions which the electrolyte might undergo were effective in causing a change in density. These experiments may be briefly summarized as follows:

1) Reaction with itself: No change in density was observed for a solution which was tightly corked and allowed
to stand for 6 days.

2) Reaction with aluminum: A similar sample containing strips of aluminum which was also tightly corked showed a density decrease of 0.2% over a period of 10 days. The slight observed decrease was within the limit of experimental error but a similar effect was noticed with a toluene bath.

3) Reaction with air: When air dried in the regular way was passed over the solution and its excess layer for four days there was no change in the density or volume, although perhaps a slight reddening of the color.

4) Reaction with aluminum in the presence of air: Dried air saturated with benzene was passed over a sample of the electrolyte with its benzene layer and containing metallic aluminum for 5 days. The density increased from 1.120 to 1.127 or about 0.6%. During this time interval, the plating bath had increased in density about 8 times as much. In the light of this, the increase observed here was not considered very significant. A toluene solution under the same conditions showed no increase.

5) Passage of current: A current of the usual strength for a white plate was passed through a sealed solution for five days and nights. No air was flowing through the cell. There was no density change. This was the effect for a low current density.

However, in one bath which was used for regular electrolysis,
the effect of both high and low current density were determined. The bath was used for electrolysis at low current densities (white plates) for 10 days, during which time the immersion only decreased from 2.40 cm to 2.35 cm. This amount easily could be attributed to "carry-out" because of the number of plates made. But on the tenth day, black plates were intentionally produced and the solution then allowed to stand closed for 2 days. The immersion dropped to 2.25 cm. Simultaneously the shiny plate current density dropped.

The results seem to imply that as long as the bath does not deteriorate the volume will not decrease appreciably except by "carry-out," which is usually small. But when the bath deteriorates, this volume change, which is evidently an equilibrium displacement, also occurs.

4. Appearance of a Sweet Smell

One characteristic property of the baths was a sweet odor on the cathodes and in the cell that appeared after they had been used. This seemed much more noticeable with benzene baths than with toluene baths. The odor was very similar to that of diphenyl ether, diphenyl methane, diphenyl and related compounds. This was compared with samples of these materials. Of these, diphenyl seems to be the logical one, and its presence is highly probable. According to Thomas (14), the action of
aluminum chloride on benzene obviously results in a loosening of the hydrogen. "It is uncertain whether biphenyl or phenylecyclohexane is the primary reaction product. Phenylecyclohexane has been shown to change probably into diphenylecyclohexane. This isomerizes to phenylmethylcyclopentane, which has been reported as in the main reaction product. If the reaction proceeds through primary formation of biphenyl,

\[
2 \text{ } \begin{tikzpicture}[baseline=-0.5ex]
  \node (c1) at (0,0) {\text{C}};
  \node (c2) at (0.5,0) {\text{C}};
  \node (c3) at (1,0) {\text{C}};
  \node (c4) at (1.5,0) {\text{C}};
  \node (c5) at (2,0) {\text{C}};
  \node (c6) at (2.5,0) {\text{C}};
  \draw (c1) -- (c2) -- (c3) -- (c4) -- (c5) -- (c6);
\end{tikzpicture} \rightarrow \begin{tikzpicture}[baseline=-0.5ex]
  \node (c1) at (0,0) {\text{C}};
  \node (c2) at (0.5,0) {\text{C}};
  \node (c3) at (1,0) {\text{C}};
  \node (c4) at (1.5,0) {\text{C}};
  \node (c5) at (2,0) {\text{C}};
  \node (c6) at (2.5,0) {\text{C}};
  \node (c7) at (3,0) {\text{C}};
  \draw (c1) -- (c2) -- (c3) -- (c4) -- (c5) -- (c6) -- (c7);
\end{tikzpicture} + \text{H}_2
\]

the presence of cyclohexane may be ascribed to hydrogenation of the benzene by the evolved hydrogen. Cracking of the cycloparaffin would result in fragments that give alkyl benzenes upon reaction with benzene. Phenols are obviously secured through oxidation by air during treatment with aluminum chloride."

He further states that "when polynuclear hydrocarbons are treated with lower alkyl halides and aluminum chloride, the dehydrogenating effect of aluminum chloride is stronger than its catalytic effect. The reaction

\[
\text{RH} + \text{AlCl}_3 \rightarrow \text{RR} + \text{H}_2
\]

is more rapid than

\[
\text{RH} + \text{AlCl}_3 \rightarrow \text{R-Alkyl} + \text{HX}
\]

It is not at all unlikely that some diphenyl is present."
This reaction would also account for some of the gas (as \( \text{H}_2 \)) which is evolved in the early stages of a benzene bath.

I. **Factors Affecting the Magnitude of the Usable Current Density.**

It was mentioned earlier that the current density at which shiny plates with no brown coloration could be produced varied from 0.5 amperes/cm\(^2\) to 2 amperes/cm\(^2\). This variation seemed to depend on several factors.

A number of the baths that were used were prepared in a nitrogen atmosphere and were used in cells with a higher anode/cathode area ratio than previously had been used. This ratio was sometimes as much as 10 or more. These baths were found to have usable current densities ranging from about 1.2 amperes/cm\(^2\) to 2.0 amperes/cm\(^2\) and in one case even 3.5 amperes/cm\(^2\).

Baths which were prepared in a flask through which no nitrogen was passed and which were used in cells with anode/cathode ratios of about 3 were found to give usable current densities ranging from 0.5 amperes/cm\(^2\) to 1.0 amperes/cm\(^2\).

There had been indications that this might be the result of the anode/cathode ratio. This lay in observations on at least 3 or 4 baths. In one bath, the usable current density was 1.2 amperes/cm\(^2\) when a cathode of 2.00 cm circumference was used. This corresponded to a certain anode current density.
Immediately thereafter, a cathode 1.34 cm in circumference was used at the same total current, which was the same anode current density, and produced a clean, shiny plate, as before. The cathode current density was then 1.8 amps/dm². This implied that the anode current density and therefore the anode/cathode ratio played an important part in the determination of the type of cathode deposit. This type of experiment was repeated many times on different baths and found to give the same general results. However, it was also observed that there still was a limit to the cathode current density as use of too small a cathode to produce high cathode current density produced black deposits. This summarizes the case for a constant anode area with varied cathode area and ratio.

But when the cathode area was held constant and the anode area and therefore the cell size was varied there was no effect. Using a solution prepared in a nitrogen atmosphere in a small cell with a 1.34 cm circumference cathode and an anode/cathode ratio of only 4 it was possible to use 2.0 amps/dm². The same value was obtained using the same size cathode in a larger cell containing the same solution. Thus the anode/cathode ratio is not the only important factor.
The preparation in a nitrogen atmosphere seems to be of considerable importance. The temperature of the solution during the preparation, which is related to the rate of addition of aluminum chloride in the method used, may play a very significant role. Unfortunately, no data are available for this.

J. Current-Total Voltage Curves for a Benzene Bath.

In connection with the theory of the effect of alternating current on the cell voltage, discussed in Part II, it was necessary to have a curve of the direct current density as a function of the total voltage for the cell. The total voltage represents the voltage drop across the anode film, the cathode film and the electrolyte. This was obtained by using a cathode of the same dimensions as used with the alternating current, namely, 1.34 cm. in circumference and immersed 3.60 cm. to give a total area of 4.82 cm$^2$. The equilibrium voltage reached at various current densities was determined using one continuous electrolysis in which the current density was increased in steps. This was found to give the same variation as individual electrolyses but much more reproducible results. After the 1.34 cm. circumference cathode curve was determined, the relation between anode
current density and cathode current density was altered by using a 2.00 cm circumference cathode immersed to the same depth to give a total cathode area of 7.20 cm².

The data for both of these cases are given in Table VII, part A being for the smaller cathode and part B for the larger cathode. The data are plotted in Figure 14 with cathode current density in amps/cm² as ordinates and equilibrium voltages as abscissae. Two curves are obtained. These are not coincident since the anode current density does not correspond in the two cases. There is one surprising feature about these curves, however. That is the change in slope of each of the curves, which seem to be divided into two parts although not sharply. No explanation will be given here, but it will be remembered that these are total voltage curves.

IV. The System: Aluminum Chloride-Ethylene Dipyridinium Dibromide-Benzene or Toluene

In an earlier portion of this research (1) it was shown that aluminum plates could be made using a fused electrolyte consisting of a eutectic 4:1 mol ratio of AlCl₃ to ethylene dipyridinium dibromide. The melting
TABLE VII  **Current Density-Total Voltage Relations for a Benzene Bath**

**Solution:** Aluminum Chloride-Ethyl Pyridinium Bromide Eutectic-Benzene  
**Cell:** Aluminum anode-brass cathode.

**Part A:** Cathode area 1.34 cm² (circumference) x 3.60 cm (immersion)  
4.82 cm².  
Anode/Cathode ratio 10.

**Part B:** Cathode area 2.00 cm² (circumference) x 3.60 (immersion)  
7.20 cm².  
Anode/Cathode area ratio 7.5

<table>
<thead>
<tr>
<th>Current Density -amps/dm²</th>
<th>Part A Equilibrium Voltage</th>
<th>Part B Equilibrium Voltage</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>0.118</td>
<td>0.160</td>
</tr>
<tr>
<td>0.20</td>
<td>0.200</td>
<td>0.270</td>
</tr>
<tr>
<td>0.30</td>
<td>0.283</td>
<td>0.363</td>
</tr>
<tr>
<td>0.40</td>
<td>0.368</td>
<td>0.468</td>
</tr>
<tr>
<td>0.50</td>
<td>0.455</td>
<td>0.570</td>
</tr>
<tr>
<td>0.60</td>
<td>0.533</td>
<td>0.652</td>
</tr>
<tr>
<td>0.70</td>
<td>0.600</td>
<td>0.719</td>
</tr>
<tr>
<td>0.80</td>
<td>0.640</td>
<td>0.785</td>
</tr>
<tr>
<td>0.90</td>
<td>0.698</td>
<td>0.850</td>
</tr>
<tr>
<td>1.00</td>
<td>0.750</td>
<td>0.912</td>
</tr>
<tr>
<td>1.10</td>
<td>0.801</td>
<td>0.970</td>
</tr>
<tr>
<td>1.20</td>
<td>0.843</td>
<td>1.030</td>
</tr>
<tr>
<td>1.30</td>
<td>0.900</td>
<td>1.095</td>
</tr>
<tr>
<td>1.40</td>
<td>0.948</td>
<td>1.152</td>
</tr>
<tr>
<td>1.50</td>
<td>1.000</td>
<td>1.220</td>
</tr>
<tr>
<td>1.60</td>
<td>1.040</td>
<td>1.270</td>
</tr>
<tr>
<td>1.70</td>
<td>1.090</td>
<td>1.320</td>
</tr>
</tbody>
</table>
Figure 14. Current Density-Total Voltage Relationships for a Benzene Bath.
point of the eutectic mixture was about 70° and the plating temperature was 115° to 145°. In an attempt to lower the plating temperature of this bath to room temperature, toluene or benzene was added to the bath, as was done in the case of ethyl pyridinium bromide. However, in this case the resulting mixture was not as satisfactory for plating purposes.

To 1 volume of eutectic were added two volumes of toluene which produced on mixing and gentle heating (above 75°) 2.5 volumes of a brown liquid of low viscosity and 1 volume of a clear layer which was principally toluene. On cooling this mixture to 55°, needle-like crystals started forming in the brown layer, and at 35° there were signs that the brown layer was becoming an emulsion. These data indicate that the toluene solution of the aluminum chloride-ethylene dipyridinium dibromide eutectic does not offer much in the way of a room temperature plating solution.

The solution was electrolyzed at a temperature slightly above 75°, where complete liquifaction occurred, but the deposit was a heavy, non-adherent and spongy aluminum deposit containing fine crystals. The spongy deposit is similar to the spongy deposits obtained with fused ethyl pyridinium bromide-aluminum chloride₃ baths at low temperatures. Benzene solutions showed the same general behavior.
V. The System: Aluminum Chloride-Ethylene Dipyridinium Dichloride-Benzene or Toluene

A. Preparation of the Eutectic: The reaction between ethylene dichloride and pyridine was shown in an earlier part of this research (1) to produce purified solid ethylene dipyridinium dichloride only in low yield. This is a serious difficulty confronting the use of such a bath. As a result, a direct preparation of the 4:1 mol ratio eutectic was tried by mixing aluminum chloride₃, ethylene dichloride and pyridine in the required proportions. This procedure was found to work only fairly well. The best procedure seemed to be to mix pyridine and ethylene chloride and only a part of the aluminum chloride₃ at the beginning. After this had reacted overnight at about 65⁰, the remaining part of the aluminum chloride₃ was found to go into solution readily. The mixture thus prepared was very dark and melted at about 30⁰. The direct preparation has the advantage of giving a higher yield of material although most probably lower purity.

B. Solubility of Eutectic in Toluene or Benzene: The addition of toluene to the eutectic produced a second clear layer when the solution was greater than about 55% toluene by weight. The density of the dark electrolyte layer was 1.04. The addition of benzene to the eutectic produced a second layer at a concentration of 2-3% by weight higher in benzene than that with toluene.
C. **Plating Properties:** The electrolysis of benzene or toluene solutions of the aluminum chloride₃-ethylene dipyridinium dichloride mixture produced white adherent plates at current densities as high as 0.9 amperes/dm², but the plates were best and most reproducible at about 0.5 amps./dm². Plates made from benzene or toluene solutions which were not saturated were better and easier to obtain than those from saturated solutions.

Nevertheless, reproduction of the plating properties of different baths was difficult because of the variations involved in the preparation of the eutectic.

Any excess ethylene chloride in the solution can react with aluminum in the presence of aluminum chloride₃ to dissolve the aluminum with evolution of gas and production of a red color. This reaction would lower the cathode efficiency and possibly affect the plating properties of the bath. It was probably present to a noticeable extent as evidenced by the change in color of this type bath from nearly black to dark red with simultaneous gas evolutions on standing in contact with the aluminum anode.

VI. **System:** *Aluminum Chloride-Ethyl Pyridinium Bromide Eutectic-Chlorobenzene* and *Mixtures of Benzene and Chlorobenzene.*

The solubility relations in this system and the effect of moisture have been discussed in a previous section. It was not practical to use very dilute solutions in chlorobenzene because of the deleterious effect of moisture. Since it was...
desired to compare chlorobenzene as a solvent with benzene, a chlorobenzene solution of about the same concentration as a saturated benzene solution was prepared and electrolyzed. The actual concentration was 50% eutectic and 50% chlorobenzene by volume.

A 25 cc. cell with about a 5:1 anode/cathode area ratio was used, the cathode being 1.00 cm wide. The anode was aluminum.

The following results were obtained from the use of this bath:

1. The plates were white and very adherent at current densities up to 1.1-1.2 a/dm². Under the same conditions, benzene baths gave clean, shiny plates at this current density.

2. The plates did not become uniformly shiny at higher current densities. As the current density was increased, they merely became shiny on the edges, then brown and shiny at the edges, then dark gray or black and non-adherent. Stirring the solution before an electrolysis seemed to have some beneficial effect in reducing the brown discoloration.

3. Gas was evolved at the anode without electrolysis and at both electrodes during electrolysis.

4. The use of a smaller cathode (0.6 cm wide) enabled the use of 1.6 a/dm², but above 2 a/dm² the deposit was black.

5. The alternating current and direct current conductivities were not quite so good for chlorobenzene solutions as they were for saturated benzene solutions.

6. There was some deterioration with use. Stirring
before electrolysis seemed to lessen the rate of deterioration.

VII. **Summary**

In an earlier portion of this research (1), the electrodeposition of aluminum from fused quaternary armonium salts was discussed. Several new processes have been developed in the present research. This has been accomplished by the addition of organic solvent reagents to the mixture of aluminum chloride and pyridinium salts described earlier (1). Among the reagents whose behavior was investigated were pyridine, benzene, toluene, xylene, petroleum ether, kerosene, gasoline, ethyl ether, carbon disulfide, chloroform, some alkyl halides and chlorobenzene. Of these the benzene and toluene solutions were the most satisfactory and the properties of these solutions for electrolysis have been investigated in considerable detail.

The phase equilibria have been determined for the aluminum chloride-ethyl pyridinium bromide-toluene system. The plating properties were investigated over a range of concentration and the optimum concentration was found to be that obtained by saturating the 66.7 mol percent aluminum chloride 33.3 mol percent ethyl pyridinium bromide eutectic with toluene. This was the concentration normally employed for electrolysis from benzene and toluene solutions.

A detailed description of the effect of current density, has been given with many pictures and photomicrographs to illustrate the effect. Some of the factors which seem to affect the magnitude of the usable current density have been discussed. A current density-total voltage curve is included.
The cathode efficiency has been determined by two methods and found to be about 92% for the shiny plates.

A study was made of some of the metals as well as excess reagents which might contaminate the bath. These are described.

The observed changes in bath characteristics have been described and investigations into their cause have been made. The changes were in the current density, color, volume, and appearance of a sweet odor.

Three other systems have been investigated but were not as satisfactory as the above-mentioned ones for various reasons. These systems were: aluminum chloride-ethyl pyridinium bromide-chlorobenzene; aluminum chloride-ethylene dipyridinium dichloride-toluene or benzene; and aluminum chloride-ethylene dipyridinium dibromide-toluene or benzene.
PART II.

THE ELECTRODEPOSITION OF ALUMINUM USING AN ALTERNATING CURRENT SUPERIMPOSED ON THE DIRECT CURRENT.
Part II. **The Electrodeposition of Aluminum Using an Alternating Current Superimposed on the Direct Current.**

I. **Introduction**

A. **The Effect Produced by Superimposing an Alternating Current on the Direct Current.**

It was mentioned in a previous section of this paper that frequently when the current density was near the upper limiting value for shiny plates there occurred a rise in voltage and a poor plate resulted. It was thought that stirring might have some beneficial effect. However, earlier mechanical stirring procedures had not given uniformity in the rate of flow on various parts of the cathode. It appeared that the effect of stirring might be obtained by use of an alternating current superimposed on the direct current. This procedure should give a more uniform effect than mechanical stirring.

B. **Literature**

As early as 1908 E. Wohlwill (15) had patented a process for the refining of gold from gold-silver alloys employing an alternating current superimposed on the direct current. Using direct current only, the cathode gold deposits made from a cold solution were dark brown or black even if a current density of less than 5 a/dm² were used. By using a pulsating current it was possible to obtain dense, coherent deposits from a cold
solution if the current density did not exceed 10 a/dm$^2$. The use of a hot solution increased the usable current density which was further increased by use of the superimposed alternating current. The alternating current was usually greater than the direct current. He also found that it was possible to use higher current densities and higher silver content in the anode when the alternating current was superimposed on the direct current.

Ghosh (16) studied the action of a high frequency alternating current on simple voltaic cells and on electrolytic cells for both reversible and irreversible processes. He summarizes his work as follows:

"1. When an alternating current of high frequency, about 30,000 per minute, passes through a cell consisting of two platinum electrodes dipped in any electrolyte, the electrode potentials change, thus indicating that some chemical action at the electrode surface takes place in that short amount of time.

"2. When an alternating current passes through a reversible voltaic cell, there is no change in the electrode potential. If, however, one of the electrodes consists of a metal covered with its insoluble salts, the alternating current has pronounced effect on that electrode.

"3. A greater amount of current could be supplied by a cell with one reversible and another irreversible electrode, when an alternating current plays in the circuit."
"4. In cells like Cd-ZnCl₂-Hg, Cd-ZnCl₂-Pt, etc., the E.M.F. of Hg or Pt electrode approaches the value of the zinc electrode on the passage of the alternating current.

"5. In perfectly reversible electrolytic cells the alternating current has no action when impressed on the cell along with a direct current.

"6. But if the electrolytic cell be irreversible, the alternating current greatly increases the current strength through the circuit.

"7. This increase in current strength is due to the diminution in the back electromotive force of polarization.

"8. This diminution in the discharge potential is also observed in electrolytic cells consisting of two cathodes and two anodes, the alternating current playing between the anodes or the cathodes, but not passing through the whole circuit."

No account was taken of the ratio of alternating to direct current in Ghosh's experiments.

Goodwin and Knobel (17) superimposed alternating current (AC) on direct current (DC) and studied the effect of three factors on the hydrogen overvoltage on platinum, lead, and copper cathodes. They found that the effect of the frequency was small and that the effect of the alternating current was independent of the kind of electrodes and of the current density. The ratio of the AC/DC was found to be the most important factor.
They claimed that the lowering of the overvoltage was the result of the formation of oxygen by the reverse current. This was based on the observation that no appreciable lowering was observed until the AD/DC ratio large enough to produce an actual reversal of the current.

W. R. Cooper (18) gives a detailed description of the effect that a superimposed alternating current has on the DC of an electrolysis cell. The three possible cases are discussed, namely, where the AC amplitude is 1) less than, 2) greater than, and 3) equal to the DC amplitude. He says there is always an increase in the DC for each of the three cases. No definite explanation of the effect was suggested.

However, Glasstone (19) has also investigated the effect of small AC (with no reversal of current) on cathodic and anodic overvoltages for a number of different metals in N-H₂SO₄ and N-NaOH solutions. The results indicate that lowering of the voltage takes place only in a limited number of cases. Glasstone claims that previous literature values of lowering of overvoltage by AC are of doubtful value because the electrical circuits were so arranged that the voltmeter read only the average value.

Later, Glasstone and Reynolds (20) studied the effect of high frequency currents on polarized electrodes. They accounted for the decrease in polarization of an electrode
resulting from the application of high frequency on the assumption that the high frequency caused an increase in the rate of diffusion of active material from, and depolarizer to, the electrode. The magnitude and mechanism of the high frequency effect appeared to be the same at both anode and cathode. In a subsequent publication, Glasstone and Reynolds (21) stated that:

"A study of the effect of high frequency oscillations on the limiting current density for 100 percent electrode efficiency shows that the high frequency effect cannot be due to its influence on the chemical reaction at the electrode, but is related to an increase in the rate of diffusion of the depolarizer.

"The high frequency effect is probably brought about by a mechanical disturbance in the electrolyte; this cannot be due to local heating at the electrode, but may be caused by the oscillatory rotation of the molecular dipoles constituting the water used as solvent."

The effect is also increased by an increase in viscosity, and decreased by stirring the solution or raising its temperature. Kameyama and collaborators (22) electroplated aluminum from a fused bath of aluminum bromide in potassium bromide using aluminum anodes and aluminum or other metal cathodes. The vapor pressure of the solution was high and the bath was
easily decomposed by moisture. Studies of the effect of alternating current superimposed on direct current were made. The electrode system consisted of one central cathode, two anodes and two auxiliary wire electrodes between the anodes and the cathode. The DC was applied between the cathode and the anodes and the AC was applied between the auxiliary electrodes and the cathode. Using direct current only and at a current density of 0.5 a/cm², the plates obtained were needle-like, especially at the edge. When a 10% RMS (root mean square) AC was applied in addition to this DC, the plates became smooth, very clean, silvery-white and lustrous and the projections had apparently been smoothed out by the AC. The efficiency of the DC process alone was 81.4% at this current density. With the AC it was 92%. It is important to note the very small amount of AC used here. Yet they said that "the cathode becomes only slightly positive." A 10% AC would not produce any reversal of the sign of the cathode. This is discussed further in the following section on AC/DC ratio in connection with Figure 17.

II. Effect of the Ratio of Alternating Current to Direct Current.

A. Apparatus

In designing an electrical circuit to measure the effect of alternating current on direct current, there were two features
which it was desired to incorporate. It should be possible to vary the AC and DC independently and to read them separately and directly. In order to do this, the circuit shown in Figure 15 was first used. Two variable rheostats were connected in parallel with the cell as shown. One of the rheostats was connected to a 7 volt battery supply. The other rheostat was connected through a variable transformer to the AC supply, which was a 110 volt, 60 cycle main. In order to prevent the DC from entering the AC part of the circuit, a 28 mf condenser was placed in the line between the cell and the AC rheostat. An iron core inductance was placed in the DC line between the cell and the DC rheostat and meters. AC and DC meters were placed in the appropriate positions as shown.

However, it was found that the inductance was not sufficient to prevent the AC from entering the DC circuit. Since an inductance of the proper magnitude was not available, the percentage of the total AC passing through the cell was determined by a calibration procedure. The tests on the cell were first made and the direct current, the voltage and the total AC determined. A carbon rheostat in series with an AC milliammeter was then connected in place of the cell. The AC and DC currents and the voltage were adjusted to the same values to get the same rheostat positions. The direct current was then shut off and the amount of alternating current through the rheostat representing
Figure 15. First Apparatus for Superimposing Alternating Current on Direct Current.
the cell was read.

This apparatus was later replaced by the one shown in Figure 15. The same AC arrangement was used but the DC was supplied by a power pack capable of delivering 100 ma at 290 volts. This was connected in series with a 13,900 ohm rheostat and the two connected across the cell. The DC voltammeter was inserted as shown.

In considering the ratio of AC to DC, there are three general cases. Using the symbols

\[ I_{AC\text{-max}} = \text{maximum value of the alternating current during a cycle, and} \]

\[ I_{DC} = \text{value of the direct current,} \]

these cases are 1) \( I_{AC\text{-max}} \) is less than \( I_{DC} \), i.e., the minimum current is always positive; 2) \( I_{AC\text{-max}} \) is equal to \( I_{DC} \), i.e., the current falls to zero periodically, which amounts to an interrupted DC; and 3) \( I_{AC\text{-max}} \) is greater than \( I_{DC} \), i.e., the current reverses its direction periodically. The extremes represented by cases 1 and 2 are shown in Figures 2-a and 2-b, respectively. In Figure 17-a, the \( I_{AC\text{-max}} = 0.5 I_{DC} \) and in Figure 2-b, \( I_{AC\text{-max}} = 3.0 I_{DC} \). The effect observed by Kameyama and collaborators with fused baths for aluminum deposition was obtained using conditions represented by Figure 2-a. The fluctuation shown is actually greater than that employed by them.
Figure 17-b. shows the general condition found to be useful for the plating process developed in the present research. The contrast between the conditions used by Kaneyama and those used in this research is easily seen.

B. **Studies With the Systems: Aluminum Chloride-Ethyl Pyridinium Bromide-Toluene or Benzene**

The effect of the ratio of AC/DC was first determined using toluene baths and was later confirmed for benzene baths. It was mentioned in an earlier section that the baths had been found to deteriorate with use. The effect of AC was determined for different stages of deterioration.

1. **Change in Appearance and Adherence of Plates with AC/DC Ratio:** Tables VIII, IX and X summarize the data obtained at different periods in the life of a toluene bath using the apparatus described in Figure 15. Table XI is for another toluene bath. The following list is that of the data given and the symbols used in these tables:

   DC: direct current strength

   AC(RMS): root mean square value of the alternating current.

   AC/DC (RMS): ratio of the root mean square alternating current to the direct current

   \( \frac{AC_{\text{max}}}{DC} \): ratio of the maximum value of the alternating current during a cycle to the direct current. (This ratio minus one indicates the extent of the reversal of the current.

   Equilibrium voltage: The constant value which the voltage reached after a few minutes, and

   A description of the plates.
Figure 16. Revised apparatus for superimposing alternating current on direct current.
Figure 17. Two Cases with Alternating Current Superimposed on Direct Current.
In each table, the DC current density is fixed at the value for shiny plates at that stage of deterioration. It is different for each of the four tables. Plates were made with superimposed AC at different AC/DC ratios varying from less than 1 to greater than 3.

The tables show that the superposition of AC on DC changes the plates from shiny to satiny and even to white. The extent of the effect varies with the AC/DC ratio. There is some effect with even a 1:1 ratio but about 2:1 seems best. The plates are very uniform. Along with the change in appearance there is an improvement in the adherence of the aluminum plate. Ratios of 1:1 had only slight effect on adherence but 2:1 is sufficient to give excellent adherence to bending. This was an extremely important result of the AC.

The effect of the AC on the appearance and adherence of the plates was tested for copper, brass, iron and steel electrodes and found to be the same. It was also found that a copper wire could be plated with aluminum using superimposed AC and that the wire could be coiled and bent at will without producing breaks.

Using the apparatus shown in Figure 16 with a benzene solution, more reliable data were obtained. The description of the type of plate at several AC/DC ratios is given in Table XII. Several exact checks were obtained for each of the ratios.

From these results it is seen that a 1:0 ratio has practically no effect; that a 1.5 ratio has a slight effect,
### TABLE VIII  Effect of AC/DC Ratio on the Type of Plate

DC current density \[ 0.54 \text{ a/dm}^2 \]
Time: 30 minutes
Electrolyte: \( \text{AlCl}_3 \)-Ethyl Pyridinium Bromide Eutectic-Toluene
Voltage set at 1.00 volts before every electrolysis.
Anode/cathode area ratio 3

<table>
<thead>
<tr>
<th>DC (ma)</th>
<th>AC (ma) (RMS)</th>
<th>AC/DC</th>
<th>( \frac{AC_{max}}{DC} )</th>
<th>Equil. Voltage</th>
<th>Description of Plate</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.98</td>
<td>Clean, shiny (faint brown cast), uniform.</td>
</tr>
<tr>
<td>100</td>
<td>43</td>
<td>0.43</td>
<td>0.61</td>
<td>1.00</td>
<td>Shiny plate; almost exactly same as DC only, except extreme bottom edges burned.</td>
</tr>
<tr>
<td>100</td>
<td>72</td>
<td>0.72</td>
<td>1.02</td>
<td>1.10</td>
<td>Same as DC, except upper half seemed thinner, lower half burned</td>
</tr>
<tr>
<td>100</td>
<td>75</td>
<td>0.75</td>
<td>1.06</td>
<td>0.90</td>
<td>Clean, white, with mixed shiny and dull patches—mostly shiny; adherent in bend test.</td>
</tr>
<tr>
<td>100</td>
<td>152</td>
<td>1.52</td>
<td>2.15</td>
<td>0.80</td>
<td>Clean, white plate, mostly dull, but some shiny areas.</td>
</tr>
<tr>
<td>100</td>
<td>220</td>
<td>2.20</td>
<td>3.11</td>
<td>0.80</td>
<td>Clean, white, very uniform and satiny. Adherent in bend test.</td>
</tr>
<tr>
<td>100</td>
<td>285</td>
<td>2.85</td>
<td>4.03</td>
<td>0.75</td>
<td>Very uniform, satiny plate. Almost exactly same as previous plate.</td>
</tr>
<tr>
<td>100</td>
<td>380</td>
<td>3.80</td>
<td>5.37</td>
<td>0.70</td>
<td>Same as 2.85 except burnt along extreme edges.</td>
</tr>
</tbody>
</table>
TABLE IX  **Effect of AC/DC Ratio on the Type of Plate**

DC current density: 0.37 a/dm²  
Time: 30 minutes  
Electrolyte: AlCl₃-Ethyl Pyridinium Bromide-Eutectic-Toluene  
Voltage set at 0.60 volts before every electrolysis.  
Anode/cathode area ratio 3

<table>
<thead>
<tr>
<th>DC/ma (RMS)</th>
<th>AC/ma (RMS)</th>
<th>AC/m max DC</th>
<th>Equilibrium Voltage</th>
<th>Description of Plate</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>0</td>
<td>0</td>
<td>0.85</td>
<td>Shiny (brown cast), faint brown streaks, bottom corners burned.</td>
</tr>
<tr>
<td>60</td>
<td>36</td>
<td>0.60</td>
<td>0.85</td>
<td>0.90</td>
</tr>
<tr>
<td>60</td>
<td>75</td>
<td>1.25</td>
<td>1.77</td>
<td>0.70</td>
</tr>
<tr>
<td>60</td>
<td>115</td>
<td>1.93</td>
<td>2.73</td>
<td>0.70</td>
</tr>
<tr>
<td>60</td>
<td>160</td>
<td>2.68</td>
<td>3.79</td>
<td>0.62</td>
</tr>
<tr>
<td>60</td>
<td>198</td>
<td>3.30</td>
<td>4.67</td>
<td>0.61</td>
</tr>
</tbody>
</table>

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### TABLE X  Effect of AC/DC Ratio on the Type of Plate

DC current density: 0.26 a/dm²  
Time: 30 minutes  
Electrolyte: AlCl₃-Ethyl Pyridinium Bromide Eutectic-Toluene  
Voltage set at 0.40 volts before every electrolysis  
Anode/cathode area ratio 3

<table>
<thead>
<tr>
<th>DC-current (mA)</th>
<th>AC-current (mA RMS)</th>
<th>AC/DC (RMS)</th>
<th>AC/DC max</th>
<th>Equilib. Voltage</th>
<th>Description of Plate</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.60</td>
<td>Very clean, shiny plate. No brown streaks. This plate easily cracked off on bending.</td>
</tr>
<tr>
<td>40</td>
<td>15</td>
<td>0.38</td>
<td>0.54</td>
<td>0.57</td>
<td>Clean and shiny like DC only, but with white patches visible only by diffuse light. Cracked off much less readily than DC only, but did crack.</td>
</tr>
<tr>
<td>40</td>
<td>15</td>
<td>0.38</td>
<td>0.54</td>
<td>0.58</td>
<td>Clean, shiny plate. Few dull streaks, brittle.</td>
</tr>
<tr>
<td>40</td>
<td>15</td>
<td>0.38</td>
<td>0.54</td>
<td>0.55</td>
<td>Excellent plate like other 0.54 plates; somewhat whiter. Very smooth.</td>
</tr>
<tr>
<td>40</td>
<td>50</td>
<td>1.25</td>
<td>1.77</td>
<td>0.52</td>
<td>Satiny, uniform finish. Cracked in bend test.</td>
</tr>
<tr>
<td>40</td>
<td>72</td>
<td>1.80</td>
<td>2.55</td>
<td>0.50</td>
<td>Satiny, white plate which cracked only under severe bending.</td>
</tr>
<tr>
<td>40</td>
<td>70</td>
<td>1.75</td>
<td>2.48</td>
<td>0.52</td>
<td>Uniform, satiny; did not crack on bending.</td>
</tr>
<tr>
<td>40</td>
<td>69</td>
<td>1.73</td>
<td>2.45</td>
<td>0.55</td>
<td>Clean, white, somewhat dull.</td>
</tr>
<tr>
<td>40</td>
<td>143</td>
<td>3.56</td>
<td>5.04</td>
<td>0.50</td>
<td>Clean, white.</td>
</tr>
</tbody>
</table>
**TABLE XI**  
**Effect of AC/DC Ratio on the Type of Plate**

DC current density: 0.25 a/dm²  
Time: 15 minutes  
Electrolyte: AlCl₃-Ethyl Pyridinium Bromide Eutectic-Toluene  
Voltage set at 0.763-0.80 volts before every electrolysis.  
Anode/cathode area ratio 3

<table>
<thead>
<tr>
<th>DC- ma (RMS)</th>
<th>AC- ma (RMS)</th>
<th>AC/DC</th>
<th>AC max DC</th>
<th>Equilib. Voltage</th>
<th>Description of Plate</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.78</td>
<td>Shiny (brown cast), brown streaks.</td>
</tr>
<tr>
<td>40</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.77</td>
<td>Shiny (brown cast), faint brown streaks, edges slightly burned.</td>
</tr>
<tr>
<td>40</td>
<td>20</td>
<td>0.50</td>
<td>0.71</td>
<td>0.65</td>
<td>Partly shiny with brownish cast; partly white, both shiny and dull.</td>
</tr>
<tr>
<td>40</td>
<td>20</td>
<td>0.50</td>
<td>0.71</td>
<td>0.72</td>
<td>Same as second DC only plate.</td>
</tr>
<tr>
<td>40</td>
<td>53</td>
<td>1.33</td>
<td>1.88</td>
<td>0.61</td>
<td>Clean, shiny and no brown.</td>
</tr>
<tr>
<td>40</td>
<td>117</td>
<td>2.92</td>
<td>4.13</td>
<td>0.52</td>
<td>Clean, less shiny and more white than 1.33</td>
</tr>
<tr>
<td>40</td>
<td>176</td>
<td>4.41</td>
<td>6.24</td>
<td>0.50</td>
<td>Slightly whiter than 2.92.</td>
</tr>
<tr>
<td>40</td>
<td>208</td>
<td>5.20</td>
<td>7.37</td>
<td>0.52</td>
<td>White; burnt along bottom edge. Seemed thin.</td>
</tr>
</tbody>
</table>
but is still shiny on parts of the cathode; while a 2.0 ratio gives a uniform white plate. Further increase in ratio does not produce much change in the appearance of the plates. These are substantially the results obtained with the other apparatus.

Photographs and photomicrographs of the plates were taken and some of them are presented on the following pages. These should be considered in the light of the previous discussion concerning the procedure for making them (see Part I.)

Figures 18-a and 18-b are the normal and 100 power photographs, respectively, of a shiny plate on brass. The high specular reflection and vertical marking may be noted. The change in appearance of the plates when AC is superimposed may be realized by comparing these pictures with those for AC-DC. Figures 19 and 20 are AC-DC plates made on brass at the same DC current density but using a 2:1 and a 1.5:1 AC/DC ratio, respectively. Both the normal and 100 power photographs are displayed here also. The specular reflection has been reduced and the diffuse reflection increased by the use of AC. The reason can be discerned in the increased coarseness of the surface shown by the photomicrographs. There is also no vertical marking. This was also true in the case of low current density DC only plates.

It was pointed out that if the AC current density became too high, the edges of the plate became burnt. This effect is demonstrated in Figure 21.
Figure 18. Shiny Direct Current Plate on Brass  
(a) Normal, (b) 100 X.

Figure 19. Alternating Current Superimposed on Direct Current.  
AC/DC: 2  (a) Normal, (b) 100 X.
Figure 20. Alternating Current Superimposed on Direct Current. AC/DC: 1.5. (a) Normal. (b) 100 X.

Figure 21. Effect of Too High Alternating Current
Table XII  Effect of AC/DC Ratio on the Type of Plate.

Direct current c.d.: 1.20 a/dm²  
Time: 10 minutes  
Electrolyte: AlCl₃-EtPyBr eutectic-Benzene  
Anode/Cathode ratio: 10

<table>
<thead>
<tr>
<th>DC ma</th>
<th>AC ma</th>
<th>AC/DC (RMS)</th>
<th>Type of Plate</th>
</tr>
</thead>
<tbody>
<tr>
<td>58</td>
<td>0</td>
<td>0</td>
<td>Uniform, shiny plate with small brown patches.</td>
</tr>
<tr>
<td>58</td>
<td>58</td>
<td>1.0</td>
<td>Exactly the same as DC only plate.</td>
</tr>
<tr>
<td>58</td>
<td>87</td>
<td>1.5</td>
<td>Principally shiny, partly white. Not much change—but no brown.</td>
</tr>
<tr>
<td>58</td>
<td>116</td>
<td>2.0</td>
<td>Uniform white, somewhat satiny finish.</td>
</tr>
<tr>
<td>58</td>
<td>174</td>
<td>3.0</td>
<td>Uniform white deposit, not much change from 2.0 type.</td>
</tr>
</tbody>
</table>
2. **Increase in Usable Current Density by Alternating Current:** The experiment summarized in Table XIII was conducted by fixing the AC at a high value, 350 ma, and increasing the DC gradually above the usable value for DC only. As the current density was raised, shiny areas began appearing at the extreme edges, but otherwise the plates were uniform and satiny. By the application of 350 ma AC, the DC was raised from 100 to 200 ma, or from 0.54 a/dm² to 1.08 a/dm², a 100% increase over the usable value for DC only. The voltage at this increased current density was higher than at the DC shiny plate current density. Therefore, this does not represent the amount of current increase obtained by keeping the voltage at the DC only value. It represents the extent to which the bath might be pushed by superimposing AC.

When the bath is forced to a 100% increase in current density by the 350 ma AC, the plates are not quite as uniform or as reproducible as might be desired. By further increasing the AC, the plate became uniform and satiny except at the extreme edges where it was burned. There is probably a limit to the AC that can be passed.

In one experiment at 200 ma DC and 350 ma AC, a bright green organic deposit was obtained. This was very unusual for an electrolyte of this high AlCl₃ concentration.

Of the plates made with AC in which DC current density was
<table>
<thead>
<tr>
<th>DC- ma</th>
<th>DC- c.d. a/dm²</th>
<th>AC- ma (RMS)</th>
<th>AC/DC Voltage</th>
<th>Equilibr.</th>
<th>Description of Plates</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0.54</td>
<td>350</td>
<td>3.5</td>
<td>0.98</td>
<td>Clean, shiny (faint brown cast), uniform.</td>
</tr>
<tr>
<td>100</td>
<td>0.54</td>
<td>350</td>
<td>3.5</td>
<td>0.70</td>
<td>Very uniform, satiny plate; except burnt along extreme edges.</td>
</tr>
<tr>
<td>140</td>
<td>0.78</td>
<td>350</td>
<td>2.5</td>
<td>0.93</td>
<td>Clean, very uniform, satiny deposit.</td>
</tr>
<tr>
<td>170</td>
<td>0.96</td>
<td>350</td>
<td>2.0</td>
<td>1.10</td>
<td>Very uniform satiny plate. Extreme edges shiny. Excellent.</td>
</tr>
<tr>
<td>185</td>
<td>1.00</td>
<td>350</td>
<td>1.9</td>
<td>1.14</td>
<td>Dull and white by diffuse light but brown and shiny by reflected light.</td>
</tr>
<tr>
<td>200</td>
<td>1.08</td>
<td>350</td>
<td>1.75</td>
<td>None-(rose continues)</td>
<td>Bright green organic product over shiny plate with some black streak</td>
</tr>
<tr>
<td>200</td>
<td>1.08</td>
<td>350</td>
<td>1.75</td>
<td>1.25</td>
<td>Same as 1.00 a/dm² but edges shinier.</td>
</tr>
<tr>
<td>200</td>
<td>1.08</td>
<td>350</td>
<td>1.75 (1.34)</td>
<td>White, satiny, with burned edges and shiny strip between the two areas.</td>
<td></td>
</tr>
</tbody>
</table>

TABLE XIII  Increase in Usable Current Density by Alternating Current.

AC equal 350 ma; DC varied.
Time: Equivalent to 30 minutes at 0.54 a/dm².
Electrolyte: AlCl₃-Ethyl Pyridinium Bromide Eutectic-Toluene
Voltage set at 1.00 volts before every electrolysis.
increased over the maximum for DC alone, the plate at 170 ma DC (0.96 a/dm$^2$) and 350 ma AC was the best in both appearance and adherence. This is a 2:1 ratio of AC/DC with a 70% increase of DC current density.

3. Increase in Thickness of Plates by Use of Alternating Current: It was pointed out earlier that increasing the thickness of plates using DC only caused them to be less uniform. Very thick plates tended to crack. By superimposing an AC it was found that the thickness of the plates could be increased manyfold without producing any non-uniformity of the plate. This is shown by the data of Table XIV. These thick plates have absolutely no pinholes and therefore should offer complete protection to iron or other metal undersurfaces. The data also indicate that a higher AC/DC ratio is required as the desired thickness of the plate is increased. The reason is that the brittleness of the plates increases with thickness.

4. Polishing of Plates Made with Alternating Current: The plates using an alternating current were not shiny like the direct current plates. However, if brilliance is desired, it may be obtained by polishing the plate in the manner previously described for DC plates.

A plate produced on brass using an AC/DC ratio of 2:1 and which has been polished is presented in Figure 22. The increase in specular reflection and decrease in diffuse reflection is
Figure 22. Effect of Polishing Aluminum Plates on Brass Made with Alternating Current. (a) Normal. (b) 100 X.
<table>
<thead>
<tr>
<th>DC-amp ma</th>
<th>AC-amp ma</th>
<th>AC/DC (RMS)</th>
<th>Time-Min</th>
<th>Equilib-Voltage</th>
<th>Description of Plates</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>0</td>
<td>0</td>
<td>30</td>
<td>0.60</td>
<td>Clean, shiny plate (no brown). Plate readily cracked off on bending.</td>
</tr>
<tr>
<td>40</td>
<td>15</td>
<td>0.4</td>
<td>30</td>
<td>0.57</td>
<td>Clean and shiny like DC only. Cracked off much less readily than DC only.</td>
</tr>
<tr>
<td>40</td>
<td>15</td>
<td>0.4</td>
<td>118</td>
<td>0.58</td>
<td>Excellent, clean, shiny plate. Few dull streaks. It was very brittle.</td>
</tr>
<tr>
<td>40</td>
<td>72</td>
<td>1.80</td>
<td>30</td>
<td>0.50</td>
<td>Satiny, white plate. Cracked only under severe bending.</td>
</tr>
<tr>
<td>40</td>
<td>70</td>
<td>1.75</td>
<td>115</td>
<td>0.52</td>
<td>Very uniform, thick, satiny plate, which did not crack off on bending, but which did show a minute amount of buckling.</td>
</tr>
<tr>
<td>40</td>
<td>89</td>
<td>1.73</td>
<td>235</td>
<td>0.55</td>
<td>Clean, white, and dull plate. Very thick, but cracked off on bending. Did not flake, however.</td>
</tr>
<tr>
<td>40</td>
<td>143</td>
<td>3.56</td>
<td>535</td>
<td>0.50</td>
<td>Clean, white. Complete coverage, without question. No pinholes. Plate did not crack off readily except at end of plated area.</td>
</tr>
</tbody>
</table>
easily demonstrated by a comparison of Figures 22-a (polished) and 19-a (unpolished). The photomicrograph of Figure 22-b shows that the low spots cannot be polished by this procedure. The polishing of the AC plates usually does not produce as high a luster as obtained for a shiny plate or produced by polishing a low current density DC only plate, but the brilliance can be increased considerably.

5. **Lowering of the Voltage by Alternating Current**

It will be observed from Tables VIII, IX, X and XI that the superposition of alternating current on direct current lowers the voltage required to produce the same current density. Furthermore, the higher the AC/DC ratio, the greater the lowering of the voltage. A plot of voltage against AC/DC ratio shows the values of the voltage to be somewhat inaccurate. This is partly the result of the fact that the data are taken from separate electrolyses at these values. Much better data were obtained by using one continuous electrolysis in which the AC/DC ratio was increased at intervals. The electrolysis was started at a current density which gave shiny plates for DC only and the voltage was allowed to come to equilibrium. Then a small amount of AC was applied and the equilibrium voltage obtained. The AC was increased in steps, with 3-5 minutes between changes. This was sufficient for equilibrium to be reached since the changes were not very large.
The data thus obtained are given in Table XV. The AC/DC (RMS) ratio and the corresponding equilibrium voltage are shown. Parts A and B represent data taken under the same conditions at 1.20 a/dm² on consecutive days. Part A was taken first. Part C was made at 1.60 a/dm² under the same conditions. These data are plotted in Figure 23. The voltages are ordinates and the AC/DC (RMS) ratios are abscissae. Curves A and B are for 1.20 a/dm² and curve C is for 1.60 a/dm². Curve D is a theoretical curve which will be discussed later.

The first three curves are seen to have almost the same shape, except for one feature. In the high current density curve (C), there is a very small decrease even at very low ratios. This is not present in the two low current density curves. The decrease becomes greater as the ratio is increased until it becomes almost constant when the AC/DC (RMS) ratio becomes greater than 2. The decrease in voltage is very gradual for ratios higher than 2.

It is interesting to note that although the voltage has decreased considerably by AC/DC = 1.0, there is no change in the character of the plate. At AC/DC = 1.5, the voltage decreases somewhat more and the plates are somewhat white, but principally shiny. Between AC/DC = 1.5 and 2.0, the change in voltage is only very slight yet the change in type of plate is complete to a uniform white deposit. Further increase did not change the voltage or the type of plate appreciably.
**TABLE XV  Lowering of the Voltage by Alternating Current.**

Solution: Aluminum Chloride-Ethyl Pyridinium Bromide

Eutectic-Benzene

Cell: Aluminum anode; brass cathode

Anode/cathode area ratio 10

Cathode area 7.10 cm$^2$

**Part A:** Cathode current density (DC) 1.20 amps/cm$^2$

<table>
<thead>
<tr>
<th>AC/DC (RMS)</th>
<th>Equilibrium Voltage</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>0.915</td>
</tr>
<tr>
<td>0.20</td>
<td>0.915</td>
</tr>
<tr>
<td>0.40</td>
<td>0.900</td>
</tr>
<tr>
<td>0.60</td>
<td>0.895</td>
</tr>
<tr>
<td>0.80</td>
<td>0.868</td>
</tr>
<tr>
<td>1.00</td>
<td>0.820</td>
</tr>
<tr>
<td>1.20</td>
<td>0.796</td>
</tr>
<tr>
<td>1.40</td>
<td>0.780</td>
</tr>
<tr>
<td>1.60</td>
<td>0.770</td>
</tr>
<tr>
<td>1.80</td>
<td>0.760</td>
</tr>
<tr>
<td>2.00</td>
<td>0.755</td>
</tr>
<tr>
<td>2.50</td>
<td>0.745</td>
</tr>
<tr>
<td>3.00</td>
<td>0.745</td>
</tr>
<tr>
<td>3.50</td>
<td>0.735</td>
</tr>
<tr>
<td>4.00</td>
<td>0.730</td>
</tr>
<tr>
<td>5.00</td>
<td>0.720</td>
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</tbody>
</table>
### TABLE XV (Continued)

**Part B:** Cathode current density 1.20 amps/dm\(^2\) (DC)

<table>
<thead>
<tr>
<th>AC/DC (RMS)</th>
<th>Equilibrium Voltage</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>0.900</td>
</tr>
<tr>
<td>0.30</td>
<td>0.900</td>
</tr>
<tr>
<td>0.50</td>
<td>0.885</td>
</tr>
<tr>
<td>0.70</td>
<td>0.860</td>
</tr>
<tr>
<td>0.90</td>
<td>0.832</td>
</tr>
<tr>
<td>1.00</td>
<td>0.820</td>
</tr>
<tr>
<td>1.20</td>
<td>0.800</td>
</tr>
<tr>
<td>1.40</td>
<td>0.780</td>
</tr>
<tr>
<td>1.60</td>
<td>0.765</td>
</tr>
<tr>
<td>1.80</td>
<td>0.760</td>
</tr>
<tr>
<td>2.00</td>
<td>0.750</td>
</tr>
</tbody>
</table>

**Part C:** Cathode current density 1.60 amps/dm\(^2\) (DC)

<table>
<thead>
<tr>
<th>AC/DC (RMS)</th>
<th>Equilibrium Voltage</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>1.150</td>
</tr>
<tr>
<td>0.20</td>
<td>1.140</td>
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<tr>
<td>0.40</td>
<td>1.125</td>
</tr>
<tr>
<td>0.60</td>
<td>1.115</td>
</tr>
<tr>
<td>0.70</td>
<td>1.105</td>
</tr>
<tr>
<td>0.80</td>
<td>1.090</td>
</tr>
<tr>
<td>0.90</td>
<td>1.070</td>
</tr>
<tr>
<td>1.00</td>
<td>1.050</td>
</tr>
<tr>
<td>1.20</td>
<td>1.020</td>
</tr>
</tbody>
</table>

(Table continued)
### Table XV (Continued)

**Part C: (Continued)**

<table>
<thead>
<tr>
<th>AC/DC (RMS)</th>
<th>Equilibrium Voltage</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.40</td>
<td>0.997</td>
</tr>
<tr>
<td>1.60</td>
<td>0.990</td>
</tr>
<tr>
<td>1.80</td>
<td>0.985</td>
</tr>
<tr>
<td>2.00</td>
<td>0.960</td>
</tr>
<tr>
<td>2.50</td>
<td>0.930</td>
</tr>
<tr>
<td>3.00</td>
<td>0.920</td>
</tr>
<tr>
<td>3.50</td>
<td>0.900</td>
</tr>
<tr>
<td>4.00</td>
<td>0.895</td>
</tr>
</tbody>
</table>

The explanation of the voltage lowering seems to lie in several effects. In the first place, the voltage was measured directly and is, in reality, a measure of the varying voltage required to produce equal increments of current above and below the basic DC current density. A detailed explanation is given in the Appendix showing, for a general case, how the voltage lowering in the absence of other effects could be predicted from the direct current polarization curve.

However, other effects also may exist which would cause an additional lowering. A logical mechanism which would account for at least part of the lowering of the polarization and change in character of the plates is that there is an increase in the rate of diffusion of the depolarizer to the electrodes.
Figure 23. Voltage Lowering Produced by a Superimposed Alternating Current.

- C: 1.60 amps/dm²
- D: 1.20 amps/dm²

AC/DC (RMS)
when an AC is superimposed. As was mentioned earlier, this mechanism was stated by Glasstone (19) to account for the lowering of hydrogen overvoltage when AC is superimposed. According to Glasstone, "when a circuit containing a large self-inductance is suddenly broken, the potential of the electrode falls more rapidly than it does when the circuit is broken under normal conditions. It thus appears that electrical discharges aid those processes that tend to remove electrochemically active material from the electrode, and alternating current may act in the same way."

The amount of lowering to be expected on the basis of the polarization curve only has been calculated for AC/DC (RMS) ratios between 0 and 0.707 (ACmax/DC between 0 and 1). These values are given in Table XVI. To obtain the theoretical curve for ratios above 0.30 it was necessary to assume an extension of the polarization curve above 1.7 a/dm² to be a straight line of the same slope. The theoretical curve is not plotted for values greater than 0.707 because the reverse polarization is not known.

These values have been plotted in curve D of Figure 23. The shape of the curve is more important than the fact that the initial value is not the same as that for DC at the same current density. There is no lowering indicated for ratios less than about 0.30. The break then becomes linear. The observed curves A and B for the same current density are both horizontal for this same interval. This suggests that there
<table>
<thead>
<tr>
<th>AC/DC (RMS)</th>
<th>Average Voltage</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>0.850</td>
</tr>
<tr>
<td>0.059</td>
<td>0.851</td>
</tr>
<tr>
<td>0.118</td>
<td>0.849</td>
</tr>
<tr>
<td>0.177</td>
<td>0.850</td>
</tr>
<tr>
<td>0.246</td>
<td>0.848</td>
</tr>
<tr>
<td>0.294</td>
<td>0.844</td>
</tr>
<tr>
<td>0.353</td>
<td>0.834</td>
</tr>
<tr>
<td>0.412</td>
<td>0.820</td>
</tr>
<tr>
<td>0.471</td>
<td>0.801</td>
</tr>
<tr>
<td>0.589</td>
<td>0.768</td>
</tr>
<tr>
<td>0.707</td>
<td>0.729</td>
</tr>
</tbody>
</table>

Basic Direct Current Density 1.20 amps/dm².
1.34 cm cathode.
is probably no other effect in operation at these ratios. Curve C for the higher current density, however, shows a decrease at the low values. The fact that the observed curves A and B do not fall as rapidly as curve D for ratios greater than 0.30 suggests that linear extension of the polarization curve, at least at the same slope, is not valid. Any other effect of the AC could be expected to further decrease the voltage observed. The only explanation which it seems possible to make at this time is that the polarization curve for higher current densities actually gives higher voltages than the extension would indicate.

In order to show the effect of deterioration on the general character and position of the curves, the rather inaccurate data of Tables VIII, IX and X have been plotted in Figure 24. The voltages are ordinates and the AC/DC ratios (RMS-corrected) are abscissae. The amount of decrease possible is seen to be less as the maximum current density for shiny plates decreases.

6. **Cathode Efficiencies with Superimposed Alternating Current:** The cathode efficiencies were determined for various amounts of alternating current superimposed on the direct current. The determinations were made by the method described in Part I in which the volume of gas evolved by dissolving the cathode deposit in acid is measured. An aluminum chloride-ethyl pyridinium bromide eutectic-benzene
Figure 24. Voltage as a Function of AC/DC (RMS) Corrected. Effect of Deterioration.
bath was used. The efficiency for a direct current plate at 1.2 amps/cm² was first measured. Then the efficiencies were determined at AC/DC (RMS) ratios of 1.0, 2.0, and 3.0. The results are shown in Table XVII.

**TABLE XVII**  
**Cathode Efficiencies with Superimposed Alternating Current**

<table>
<thead>
<tr>
<th>AC/DC (RMS)</th>
<th>Cathode Efficiency %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>90.9</td>
</tr>
<tr>
<td>1</td>
<td>90.6</td>
</tr>
<tr>
<td>2</td>
<td>92.8</td>
</tr>
<tr>
<td>3</td>
<td>91.8</td>
</tr>
</tbody>
</table>

From these data it may be concluded that the plates made with superimposed alternating current show efficiencies as good as those for direct current only. The values seem to indicate a rise in efficiency with increase in AC/DC ratio. But this increase is only slight and the efficiency of alternating current-direct current and direct current only processes may be considered to be about the same.

**III. X-Ray Analysis of the Effect of Alternating Current on the Type of Plate.**

A. **General Method and Apparatus:**

The superimposition of an AC on the DC has been shown to change the character of the plate from very shiny, but brittle to satiny or white and very adherent. It was desired to find
out the exact nature of the change. Therefore, transmission x-ray pictures were taken of both DC and AC-DC plates. For this purpose, a Phillips x-ray machine with copper radiation was employed. The camera was a flat type which allowed transmission pictures to be taken with the sample set at various angles or rotated.

B. Preparation of Samples:

In the first x-ray examinations the plates were made on iron and back reflection pictures were taken. However, the general radiation produced by the iron caused too much fogging of the picture. To get a better picture, the plates of both types were made on flat copper sheets. The DC plates were shiny and brittle. The AC-DC plates were made with 3:1 AC/DC ratio and were satiny and adherent. The plates were made from several different baths and at different stages of deterioration.

After the plates were made, the deposit on one side was carefully sanded off to expose the copper base. The electrode was then dissolved in concentrated nitric acid, which reacted with the copper but did not attack the aluminum on the other side of the electrode. This produced a thin foil of electrodeposited aluminum which was mounted on a gummed label. A thin slice about 2 mm wide was taken of each sample and x-rayed.

C. X-Ray Pictures and Discussion

By adjustment of the distance between the sample and the
film it was possible to obtain three of the aluminum lines on the film. It will be noted that in some of the following pictures the rings seem shifted toward the center. The reason is that these pictures were taken early in the work when the size of the sample holder permitted a distance of 15 mm to be used. With the rotating platform, the minimum distance which would be attained was 16 mm. It did not seem necessary to repeat earlier pictures at a distance of 16 mm. In each picture there is a narrow line inside the first aluminum line (heavy) which is due to the paper used in mounting the samples. This was proven by an x-ray picture of the paper which is not included here.

1. Direct Current Only: Some of the results obtained for shiny aluminum plates made using DC only are shown in Figures 25 and 26. Several more plates were examined and in every case the results were the same as indicated here. In both figures a is taken with the beam perpendicular to the electroplated surface; b is taken with the beam parallel to the electroplated surface; and c is taken with the sample rotated.

The small particle size of the shiny DC plates is shown by Figures 25-a and 26-a. There are no spots which indicate large crystals. There is no orientation detectable with the beam perpendicular to the plated surface. However, by placing the sample parallel to the beam, a marked degree of orientation
Figure 25. X-Ray Pictures of Aluminum Plates made with Direct Current Only.
Figure 26. X-Ray Pictures of Aluminum Plates made with Direct Current Only.
is found. The banding of the rings is shown in Figures 25-b and 26-b. In order to show that this effect was produced by orientation in the sample, the effect was eliminated by rotating the sample while the picture was being taken. The results of this are shown in Figure 26-c. The banding has disappeared.

The conclusion is definite. Shiny aluminum plates made with DC only have small particle size and they are oriented.

2. **Alternating Current Superimposed on Direct Current**

Some of the results obtained for aluminum plates made with AC superimposed on the DC are shown in Figures 27 and 28. Other plates showed the same effect. The large particle size of the AC-DC plates is shown in Figures 27-a and 28-a. The great contrast in particle size between AC-DC plates and DC only plates is seen by comparison of these figures with Figures 25-a and 26-a.

Figures 27-b and 28-b were made with the beam parallel to the plated surface. There is no orientation shown here. This is evidenced by the lack of banding in the first two rings. Although the third ring is very weak, it would be difficult to consider this the result of orientation since the width of sample exposed to the x-rays is very much smaller when the beam is parallel to the surface. The relative intensity is probably about the same.

Figures 27-c and 28-c show the pattern obtained by rotating
Figure 27. X-Ray Pictures of Aluminum Plates made with Alternating Current Superimposed on Direct Current.
Figure 28. X-Ray Pictures of Aluminum Plates made with Alternating Current Superimposed on Direct Current.
the sample. The effect of particle size has been removed. The conclusions are that the AC-DC plates have much larger particle size than DC plates and are not oriented like the DC plates. The increase in adherence must be accounted for on this basis.

IV. Summary

The effect of superposing an alternating current on the direct current was investigated in this research. The principal results of this superposition are the change in appearance of the plates from shiny to satiny or white and particularly the greatly increased adherence and ductility. The effect varies with the AC/DC ratio and seems to be best at about 2:1 (R:S). By this procedure, an increase in the usable current density may also be accomplished. The increase may be as much as 70% at a 2:1 AC/DC ratio. It is also possible to increase the thickness of the aluminum plates many times without producing non-uniformity or brittleness if AC is superimposed on the DC. The white or satiny plates produced by the use of AC may be polished to a good luster.

A lowering of the voltage was observed when AC was superimposed on DC and the voltage measured directly. The amount of the decrease varied with the AC/DC ratio. The curves for this variation are given. The shape of these curves has been taken into account by a consideration of the shape of a current-polarization curve for DC only.

The cathode efficiency is the same for AC-DC plates as for DC only plates.
The use of AC with DC produces a much more useful and adaptable plate than obtained when using DC alone.
PART III

SOME EXPERIMENTS ON THE NATURE OF THE ELECTROLYTE:
ALUMINUM CHLORIDE-ETHYL PYRIDINIUM BROMIDE-BENZENE

I. Introduction

In an electrodeposition it is frequently of considerable importance to know the kinds of ions that exist in the solution. This information was desired for the system: aluminum chloride-ethyl pyridinium bromide-benzene. A number of experiments have been performed which seem to shed some light on this.

A. Phase Diagrams

The phase diagram for the two-component system aluminum chloride-ethyl pyridinium bromide has been discussed (1). For that system, a compound was indicated having the empirical formula $\text{AlCl}_3 \cdot \text{EtPyBr}$. On further addition of aluminum chloride, a eutectic occurred at a stoichiometric composition of two mols of aluminum chloride to one mol of ethyl pyridinium bromide. In the eutectic, there is thus a mixture of about equimolar proportions of aluminum chloride and the compound $\text{AlCl}_3 \cdot \text{EtPyBr}$. This was the solution to which benzene was added to produce the electrolyte from which aluminum may be deposited. The phase diagram for the three-component system described in Part I shows that the addition of benzene does not destroy the compound $\text{AlCl}_3 \cdot \text{EtPyBr}$ other than by the possibility of ionization. Therefore equimolar proportions of aluminum chloride and the compound or the ions produced from these materials should be present in the electrolyte.
B. Possibilities of Ionization

The ionization of these components could produce a miscellany of ions. For aluminum chloride, the ionization would be expected to proceed in the following steps:

\[ \text{AlCl}_3 \rightarrow \text{AlCl}_2^+ + \text{Cl}^- \rightarrow \text{AlCl}^+ + 2\text{Cl}^- \rightarrow \text{Al}^{3+} + 3\text{Cl}^- \]

These materials would exist in some equilibrium distribution if the ionization was not complete. The aluminum would always be in a cation in the above ions.

For the compound \( \text{AlCl}_3 \cdot \text{LEtPyBr} \), two possibilities for ionization exist:

a) \( \text{AlCl}_3 \cdot \text{LEtPyBr} \rightleftharpoons \text{AlCl}_3 + \text{EtPyBr} \)

\[ \text{(as indicated above)} \]

\[ [\text{EtPy}]^+ + \text{Br}^- \]

b) \( \text{AlCl}_3 \cdot \text{LEtPyBr} \rightleftharpoons [\text{AlCl}_3 \text{Br}^-] + [\text{EtPy}]^+ \)

The possibility of ionization in which \( [\text{EtPy}]^+ \) is coordinated on the aluminum atom was excluded since metals do not coordinate cations in the formation of complex ions. If the compound ionizes according to pattern a above, the aluminum will be in the cations in this case also. However, if the ionization follows pattern b above, the aluminum will be present in a single anion. In this case it would be possible for aluminum to move toward both the anode and cathode during electrolysis. It will be noted that in either case, the \( [\text{EtPy}]^+ \) ion can exist in the solution.

The first part of the investigation was directed toward the determination of whether the compound ionized according to pattern a or b shown above.
II. **Migration Experiment**

It was pointed out that if the ionization of the compound occurs according to pattern a, migration of aluminum on electrolysis would be toward the cathode, whereas for pattern b the migration of aluminum in an anion would be toward the anode. In the eutectic mixture there would also be migration toward the cathode of the aluminum from the aluminum chloride. It would be impossible to determine the mode of ionization of the compound by migration procedures using a solution of the eutectic unless there was a knowledge of the relative transference numbers which each of the ions would show if they were present.

Since, for this portion of the work, it was desired to determine only the mode of ionization of the compound AlCl$_3$:EtPyBr, this was studied on a benzene solution containing only this compound. On such a solution it would only be necessary to determine the direction of migration of the aluminum.

B. **Apparatus**

The migration was determined with an apparatus of the Hittorf type. This is shown in Figure 29, which is a full-scale drawing. The anode was copper and the cathode iron. The change in concentration was determined in the anode compartment only, as electrolysis of the compound produces blue organic material at the cathode due to the reduction of the [EtPy]$^+$ ion. The copper anode was used so that the change in aluminum concentration would be only the result of migration into or out of the anode compartment.
Figure 29. Migration Apparatus
No excess benzene layer was used since the change in composition of the anode compartment on electrolysis might have produced a displacement in the equilibrium between the benzene and the electrolyte layer.

The solution to be used for electrolysis was prepared in a nitrogen atmosphere and a 1% excess of aluminum chloride over the theoretical amount for the compound AlCl₃·1EtPyBr was added. The reason for this may be seen by inspection of the three-component phase diagram for the toluene system. It was desired to avoid the possibility of the formation of the meta-stable lower complex in the solution. The composition of the solution used as determined by analysis was:

\[
\begin{align*}
\text{AlCl}_3 & = 21.92 \text{ weight } \% \text{ (based on aluminum)} \\
\text{EtPyBr} & = 39.60 \text{ weight } \% \text{ (based on bromide)} \\
\text{Benzene} & = 48.48 \text{ weight } \% \text{ (by difference)}
\end{align*}
\]

(Saturated with benzene at 30°C)

The procedure for the determination was as follows: The cell was filled with solution to the levels shown in Figure 29. The current was then passed through the solution at 0.04–0.05 amps for 35 minutes. During this time a blue organic material was produced in the cathode compartment, and a white solid (copper salt) in the anode compartment. Both of these diffused through their respective compartments and then toward the side-arm. The electrolysis was stopped before either reached the point of
division. Immediately after the current was stopped, the compartments were separated by increasing the air pressure in the center tube. The anode and cathode lead wires were removed and the tubes closed off with short lengths of rubber tubing and pinch clamps. The whole of the solution in the anode compartment was then withdrawn into a weighed bottle for analysis by opening the stopcock. The closing of the anode and cathode lead tubes was necessary to prevent a drop in pressure when the anode compartment solution level was lowered below the side-arm during withdrawal for analysis. A drop in pressure would have caused some of the cathode compartment solution to spill over into the anode compartment.

C. Analysis Procedure

The accurate determination of the amount of migration in a solution of this sort is attended with many more difficulties than normally found in migration experiments. The main difficulty is that the solution is very concentrated whereas the changes in concentration must be small to avoid diffusion and deleterious side-reactions. This makes the relative change in concentration very much smaller than normally possible, since dilute solutions can be used in most other work. Thus, the analyses must be very accurate in order to obtain even fair values for the migration.

The analysis work for the determination was performed by Mr. Henry Baumgarten (23) to whom due acknowledgement and appreciation is expressed.

Analyses were made for the changes in concentration of
aluminum, chloride, and bromide in the anode compartment. A sample of the solution before electrolysis was analyzed and the mols per gram of the solution were determined for each of the above elements. The solution after electrolysis was analyzed similarly. The number of mols of each material which migrated due to the current was determined by multiplying the change in the number of mols per gram by the total number of grams of solution withdrawn from the anode compartment.

For the analysis, the benzene solution was first dissolved in water and the benzene removed by filtration through a previously wetted filter paper, then washed thoroughly. A solution of the materials in water was thus prepared for analysis.

The aluminum was determined by the 8-hydroxy quinoline method of Berg (24) as modified by Goren (25). The total halide was determined by the Volhard method. The bromide was determined in the presence of chloride by the differential oxidation method of Koltchoff and Yutzy (26) with modifications by H. Baumgarten (23).

D. Results:

The concentrations of aluminum, bromide, and chloride in the solution before and after analysis, and the total change in mols of each in the anode compartment are shown in Table XVIII. The signs of all of the changes are positive, therefore, the aluminum is in the anion. According to the previous discussion this means the ionization follows pattern b, namely the production of $[\text{AlCl}_3\text{Br}]^-$ and $[\text{EtPy}]^+$. As further evidence for this, the changes
in concentration of bromide and chloride may be compared with that for aluminum. This is done in Table XIX by calculation of the ratio of the changes of Cl/Al, Br/Al, and Cl/Br. For comparison, the theoretical ratios for the complex anion \([\text{AlCl}_2\text{Br}]^-\) are shown. The agreement serves to confirm pattern b as the mode of ionization.

**TABLE XVIII**  
**Migration Analysis Results.**

<table>
<thead>
<tr>
<th></th>
<th>Before Electrolysis mols/gm</th>
<th>After Electrolysis mols/gm</th>
<th>Total Change mols</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>$1.645 \times 10^{-3}$</td>
<td>$1.681 \times 10^{-3}$</td>
<td>$+ 0.71 \times 10^{-3}$</td>
</tr>
<tr>
<td>Chloride</td>
<td>$4.761 \times 10^{-3}$</td>
<td>$4.363 \times 10^{-3}$</td>
<td>$+ 2.02 \times 10^{-3}$</td>
</tr>
<tr>
<td>Bromide</td>
<td>$1.563 \times 10^{-3}$</td>
<td>$1.596 \times 10^{-3}$</td>
<td>$+ 0.65 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

**TABLE XIX**  
**Comparison of Observed and Theoretical Changes**

<table>
<thead>
<tr>
<th></th>
<th>Experimental</th>
<th>Theoretical</th>
</tr>
</thead>
<tbody>
<tr>
<td>Change in Cl</td>
<td>2.85</td>
<td>3</td>
</tr>
<tr>
<td>Change in Al</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Change in Br</td>
<td>0.92</td>
<td>1</td>
</tr>
<tr>
<td>Change in Al</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Change in Cl</td>
<td>3.10</td>
<td>3</td>
</tr>
<tr>
<td>Change in Br</td>
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<td></td>
</tr>
</tbody>
</table>

The signs of all ratios are positive.
III. Alternating Current Conductivities

It was thought that if the equivalent conductivity at infinite dilution could be determined for solutions of the compound and of the eutectic, it might be possible to estimate fairly well the percent dissociation of the material present. However, the experimental determination of this quantity for these solutions is attended with numerous experimental difficulties. One major difficulty with the benzene or toluene solutions of these materials is the large two-liquid region encountered when one attempts to dilute the solutions. The second liquid produced has far too low a conductivity to be measurable with the apparatus available. Although chlorobenzene solutions seemed to show complete miscibility, these could not be used because of the high sensitivity to moisture. Ethyl chloride formed dilute solutions but these had a boiling point of about $12^\circ$. All of the solutions had too high a resistance to be measured by the normal Wheatstone bridge method.

For approximate purposes, however, it may be useful to assume the conductivity at infinite dilution, of the benzene solution of the compound $A_1C_l_3.1B_tP_yBr$ to be of the same order of magnitude as other mono-monovalent compounds. This has been done and the results are described below.

A. Apparatus

1. Cell: The conductivity cell consisted of two similar cylindrical compartments about one inch in diameter connected
by a tube about 3/16 inch in diameter and one inch long. Each compartment contained a large platinized platinum electrode with a platinum lead sealed into a side-arm. The cell constant was determined using 0.1 N potassium chloride and found to be 9.55 cm⁻¹.

2. **Conductivity Bridge:** An ordinary laboratory Wheatstone bridge was used to measure the conductivity of the solutions in the cell.

3. **Conductivity of the Compound AlCl₃·Et₂Br in Benzene.**

   1. **Composition of Solution:** The solution was part of the same one that was used in the migration experiment. The density was 1.121 at 27°.

   2. **Conductivity and Approximate Percent Dissociation:** The specific conductivity of the solution was found to be 0.02408 mho/cm³. Using the data for the composition given in the section on the migration experiment, and the density given above, the molecular conductivity, \( \Lambda \), was calculated to be 13.4 mho/mol.

   To estimate the percentage ionization, a value of the conductivity at infinite dilution, \( \Lambda_\infty \), must be assumed. In water, uni-univalent compounds have a \( \Lambda_\infty \) about 120. In solvents of low dielectric constant, \( \Lambda_\infty \) appears to be less, for example, values of 60-75 have been obtained with some quaternary ammonium compounds. These values are all much above the observed value of 13.4. Thus, the percent dissociation must be fairly low.
compound acetate, tablets are prepared.

1. Procedure: Preparation of absolute alcohol and anhydrous ethanol.

Experiment.

The following statements seem to summarize the conclusions.

I. CONCLUSION

The assumption of the absolute alcohol is not very great.

As to the conductivities of the alcohol, it seems correct to consider the absolute alcohol:

Since the compound inion does not give a very high value for the conductance assumed that the entire of the conductance is due to anion of the alcohol:

Hence, it can be seen that the molal concentration of the compound.

The concentration was found to be 0.078 molar of acetate.

When the solution was found to be 0.081 molar.

2. Conductivity: the specific conductance and 55 percent of benzene. The density was 1.48 at 20°C. The composition was about 45 percent of 66.7 mol percent absolute alcohol saturated with solution.

3. Composition of the solution: The solution was

4. Conductivity of the relative mixture in benzene.
2. Ionization of the compound occurs according to the reaction

\[ \text{AlCl}_3.1\text{EtPyBr} \xrightleftharpoons{} [\text{AlCl}_3\text{Br}]^- + [\text{EtPy}]^+ \]

3. The compound seems to be only slightly ionized in a benzene solution of the compound only and may be only slightly ionized in the eutectic-benzene solution also.

4. The aluminum chloride present also seems to be only partially ionized. In this event the following ions would probably be present in some equilibrium distribution:

\[ \text{AlCl}_3 \xrightarrow{} \text{AlCl}_2^+ + \text{Cl}^- \xrightleftharpoons{} \text{AlCl}^{++} + 2\text{Cl}^- \xrightleftharpoons{} \text{Al}^{+++} + 3\text{Cl}^- \]
APPENDIX
APPENDIX

Theoretical Lowering of Voltage by Alternating Current

If an alternating current is superimposed on a direct current and the voltage drop across a cell through which this current is flowing is measured directly, the voltage read will be the average of a varying voltage.

It was Glasstone (19) who first recognized this fact and took it into account when he used a direct method for measuring the voltage. He investigated "the action of small alternating currents on an electrode polarized by direct current under such conditions that no reverse current ever flowed through the electrolysis cell during the course of a whole cycle. The average potential of a polarized electrode could be measured by the direct method with simultaneous direct and alternating current; further, the potentials corresponding to the maximum and minimum current in the circuit could be determined with direct current alone. The arithmetical mean of these two latter values should give an approximate measure of the average potential that would be expected with superimposed alternating and direct current if the former exerted no specific effect on the electrode. A comparison of this calculated value with that experimentally determined would give a rough idea of the actual influence of alternating current on the polarized electrode."

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By expansion of this idea it may be stated that, if there is no specific effect of the alternating current, the mean voltage will depend on the shape of the polarization (current-voltage) curve for the direct current only. Any specific effect would be in addition to the change in voltage derived on the basis of the polarization curve.

A general case will be considered and the variation of average voltage with AC/DC ratio to be expected in the absence of other effects will be explained. For the discussion, certain conditions will be assumed, namely:

1. The shape of the direct current-voltage curve is of the common form shown in Figure 1, curve 1.

2. There may be a family of curves which represents different conditions of electrolysis or even different stages of deterioration. This assumption is not altogether necessary but it seems to add to the completeness of the presentation. The explanation would work equally well if curves 1, 2, and 3 of Figure 1 were coincident.

In order to deduce the shape of the voltage - AC/DC ratio curves, the appropriate one of the family of curves of Figure 1 is chosen. Suppose that curve 1 is chosen here. Then point $P_1$ will give the operating conditions of direct current and voltage. For this case, $P_1$ will be assumed to be on the flat portion of the curve. The results obtained by choosing another starting point will be discussed later.
Figure 1. Family of Theoretical Polarization Curves for the electrolyte
If, now, a small sinusoidal AC is superimposed on the DC, the resultant current will be greater than the DC part of the time and less than the DC part of the time, as shown in Figure 17. The amount of increase will be equal to the amount of decrease. In other words, the operating conditions are continuously varying between $P_2$ and $P_3$ as shown in Figure 2. Since this is a straight line portion of the curve, the equal increments of current subtend similar equal increments of voltage, i.e., $\Delta E_{1-2} = \Delta E_{1-3}$. Under these conditions, $M$, the mean of the upper and lower operating conditions corresponds to the DC voltage, given by $P_1$. However, as soon as the increments of current produced by the AC become large enough so that the minimum current is on the curved portion of the curve, then $\Delta E_{1-2}$ is no longer equal to $\Delta E_{1-3}$. In fact, $\Delta E_{1-2}$ is less than $\Delta E_{1-3}$ and, as a result, the mean operating voltage is less than that given by $P_1$. This is depicted in Figure 3. The mean is represented by $M$ on the diagram.

It should be noted that for both of these cases, the ratio of $I_{AC\text{-max}}$ to $I_{DC}$ is still less than 1, which means the RMS ratio $AC/DC$ is still less than 0.70. A slight further increase in $AC/DC$ ratio would produce a considerable lowering of the mean voltage. This is seen from Figure 4. At this point it is necessary to make some additional statements about the shape of the polarization curve since the current will now actually be negative part of the time. There probably exists a polarization curve for the current going in the reverse direction, and the shape may be roughly symmetrical to that for positive current. It will be assumed to be
Figure 2. Mean Voltage Read when Both End Conditions are on the Straight Portion of the Polarization Curve.
Figure 3. Mean Voltage Read when One End Condition is on Curved Portion of Polarization Curve.
Figure 4. Mean Voltage head when Alternating Current Exceeds the Direct Current.
symmetrical here. The effect of lack of symmetry will be
discussed later. It will be seen from Figure 4 that a large
change in voltage occurs near AC/DC (RMS) 0.7 for this case

As the ratio is increased to 3, 4, 5, etc., the mean
voltage would be determined by the shape of the reverse current
polarization curve as compared to the positive current polariza-
tion curve. If these were symmetrical with each other, there
would be no further lowering after passing over the curved
portions. If the reverse current curve has a smaller slope
than the symmetrical one as shown in Figure 4, a further
decrease in voltage would be expected for higher ratios.
However, if the reverse current curve had a greater slope than
the symmetrical curve, the voltage would begin to rise again
for higher ratios.

Thus, to summarize, for this starting condition, in the
curve for voltage vs AC/DC ratio there would be an initial
flat period followed by a short gradual break, then a sudden
break, followed by a long flat period. This is demonstrated
by Curve A of Figure 5. It would be unwise to state that
this is the only factor operating to lower the voltage. The
problem becomes a question of the relative magnitude of the
effects produced by the various factors. During the period
of the break it seems likely that the effect produced according
to the above theory is of the first order of magnitude. On either
side it would not be appreciable. Now suppose that the effect
Figure 5. Curves Derived from Theoretical Polarization Curve.
of the stirring produced by the AC is an approximately linear function of the AC/DC ratio, which is not too unlikely. This would be the condition represented by curve B of Figure 5. The sum of the two effects would be that of curve C. The other factors could operate in a similar manner to alter the shape or position of the curve. For example, if the electrodes possess a capacity, which may be the result of film formation and therefore probably a function of the DC, the amount of AC actually passing through the solution would be reduced. This would mean that the true AC values would be less than those plotted and would result in a shift of the curve from its theoretical position in the direction of higher apparent AC/DC ratios. This factor could be very complex but may be only of second degree importance.

By repeating the whole process using as a starting point a point, such as $P_2$, curve 3 in Figure , which is on the curved portion, it can be shown that no initial flat period would be expected. Thus practically any shape of the curve for voltage as a function of AC/DC ratio might be possible depending on the shape of the polarization curve and the part of the curve on which the basic current density lies.
ACKNOWLEDGEMENT

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